684. *Steric Hindrance in Analytical Chemistry. Part II.* The Interaction of Ferrous Salts with 2-Substituted* 1 : 10-*Phenanthrolines.*

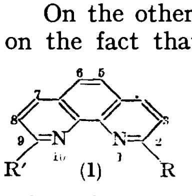
By H. Irving, M. J. Cabell, and D. H. Mellor.

Although 2-methyl-1 : 10-phenanthroline (pK = 5·42) is a stronger base than 1 : 10-phenanthroline (pK = 4·96) it forms weaker complexes with ferrous ions (log K_1 = 4·2, log K_2 = 3·7, and log K_3 = 2·9). This difference in behaviour is due to steric hindrance to co-ordination which increases with further substitution to such an extent that 2 : 9-dimethyl-1 : 10-phenanthroline will not form complexes with Fe^{II} although it does so with Cu^{I}.

Tris-complexes predominate in the strongly red solutions formed by equivalent amounts of Fe^{++} and 1 : 10-phenanthroline. Corresponding solutions of Fe^{++} and 2-methylphenanthroline are feebly yellow and contain principally the bis-complex. That perchlorate ions precipitate tris-complexes from either solution can be explained quantitatively from considerations of the stability constants of the respective complex ions and the measured solubility products of their perchlorates.

1 : 10-Phenanthroline (" phenan "; I; R = R′ = H) with ferrous salts gives a series of compounds containing the stable red ion $Fe(phenan)_3^{++}$ which is of great analytical importance. The diamagnetism of its salts indicates that the organic components are held by octahedral d^2sp^3 hybrid orbitals. The coplanar resonating system formed by the three aromatic rings of each phenanthroline molecule and the five-membered ring which it forms with the central iron atom is thus repeated in three atomic planes at right angles, and the asymmetry of the resulting structure has recently been confirmed by a successful resolution (Dwyer and Gyarfas, *J. Proc. Roy. Soc. N.S.W.*, 1949, **83**, 263). The considerable optical stability of the enantiomorphous tris-1 : 10-phenanthroline ferrous ions ($t_{\frac{1}{2}}$ = 121 min. at 15°; Dwyer, personal communication) is in keeping with the slow rate of exchange with the radio-nuclide ^{59}Fe ($t_{\frac{1}{2}}$ = 100 min.; Ruben, Kamen, Allen, and Nahinsky, *J. Amer. Chem. Soc.*, 1942, **64**, 2297) and the high over-all stability constant, since $K_3 = [Fe\ phenan_3^{++}]/[Fe^{++}][phenan]^3 = 2 \times 10^{21}$ (Kolthoff, Lee, and Leussing, *ibid.*, 1948, **70**, 2348).

On the other hand, Pfeiffer and Christeleit (*J. pr. Chem.* 1938, **151**, 127) commented on the fact that 2-methyl-1 : 10-phenanthroline (" mephenan "; I; R = Me, R′ = H) forms sparingly soluble complex salts $[Fe(mephenan)_3](ClO_4)_2$ and $[Fe(mephenan)_3]SO_4,12H_2O$, which are only orange-coloured in contrast to the deep red of the corresponding 1 : 10-phenanthroline complexes, and in agreement with McCurdy and Smith (*Analyst*, 1952, **77**, 846) we have found that the introduction of a second methyl group adjacent to the other nitrogen atom produces a compound, 2 : 9-dimethyl-1 : 10-phenanthroline (I; R = R′ = Me), which shows no tendency to form complexes with ferrous ions (cf. Case, *J. Amer.*


(I)

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* Part I, Irving, Ring, and Butler, *J.*, 1949, 1489.

Chem. Soc., 1948, **70**, 3994). Indeed, while as little as 2 p.p.m. of ferrous iron give a strongly red solution with $2{\cdot}5 \times 10^{-4}$M-1 : 10-phenanthroline at pH 3—9 (absorbancy = 0·40 in a 1-cm. cell at $\lambda_{\max.}$ 510 mμ; cf. Moss and Mellon, *Ind. Eng. Chem. Anal.*, 1942, **14**, 931), we find that replacement of 1 : 10-phenanthroline by 2-methyl-1 : 10-phenanthroline gave a solution with effectively 100% transmittancy over the range 290—600 mμ when measured against a blank containing no iron, and the ferrous concentration had to be increased twenty-fold before a visible yellow colour was produced. Similar weak yellow colours were observed when 1 : 10-phenanthroline was replaced by an equivalent amount of the 2-chloro-compound (cf. Halcrow and Kermack, *J.*, 1946, 155).

This decrease in absorbancy produced when there are substituents α to the nitrogen atoms of 1 : 10-phenanthroline might be due (i) to lower molecular extinction coefficients of the tris-complexes, (ii) to their presence in lower concentration as a consequence of smaller overall stability, or (iii) to a combination of both factors. We have examined these various possibilities.

The synthesis of 2-methylphenanthroline (I; R = Me, R′ = H) by a Doebner–Miller reaction between 8-aminoquinoline and crotonaldehyde gave poorer yields than a Skraup reaction on 8-aminoquinaldine. The intermediate 8-nitroquinaldine, previously prepared by nitrating quinaldine and separating the 5- and the 8-nitroquinaldine (Gerdeisen, *Ber.*, 1889, **22**, 245), was more conveniently made by condensing *o*-nitroaniline with paraldehyde or, better, crotonaldehyde. 2 : 9-Dimethylphenanthroline was prepared by essentially the method described by Case (*loc. cit.*), and 2-chlorophenanthroline following Halcrow and Kermack (*loc. cit.*).

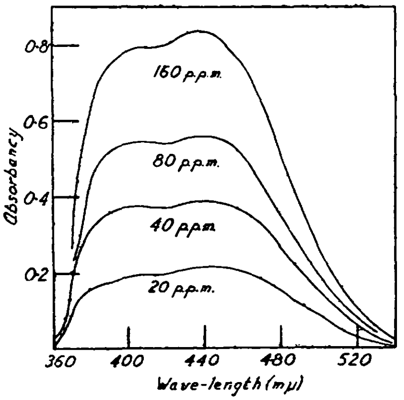

FIG. 1. *The absorbancy of mixtures of* $5{\cdot}9 \times 10^{-3}$M-*2-methylphenanthroline in an acetate buffer of* pH 4·7 *containing respectively* 20, 40, 80, *and* 160 *p.p.m. of ferrous iron.*

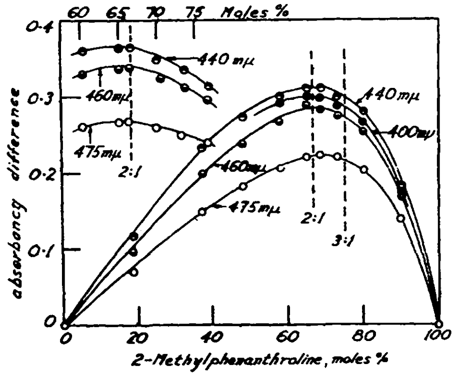

FIG. 2. *The formula of the complex formed by ferrous ions and* 2-*methyl*-1 : 10-*phenanthroline—Job's method of continuous variations.*

Fig. 1 shows the absorption spectra of solutions containing varying amounts of ferrous iron and a constant excess of 2-methylphenanthroline in buffers of pH 4·7 containing hydroxylamine; over the spectral range shown the absorbancy of the reagent is negligible. Although the molecular ratio [reagent] : [iron] was varied from 2 : 1 to 16 : 1, the form of the spectra did not change and there was no evidence of the co-existence of more than one absorbing species; for although the broad band in the visible is resolvable into two component bands which almost coalesce, their maxima remain at 400 and 440 mμ respectively, and the relative absorbancies ($\varepsilon_{440}/\varepsilon_{400} = 1{\cdot}05 \pm 0{\cdot}04$) do not vary systematically with composition. The weakness of the complex is shown by the marked deviation from Beer's law.

Since protons compete with ferrous ions for molecules of the basic ligand, complex formation should be favoured by decreasing acidity. Absorbancy data for buffers containing 80 p.p.m. of ferrous iron and a constant 8-fold excess of reagent showed that complex formation was negligible below pH 2·13 and increased linearly with pH over the range 3—4·2.

Solutions of still higher pH could not be studied accurately, for even at pH 4·18 the yellow solution was supersaturated with respect to the very insoluble salt $[\mathrm{Fe(mephenan)_3}](\mathrm{ClO_4})_2$ and deposited golden crystals after some hours. At pH 5·14 an immediate yellow turbidity appeared on mixing of the components and, though the solid dissolved readily on warming, crystallization took place during the absorbancy measurements. The composition of the iron complex present in these yellow solutions was next examined spectrophotometrically by the method of continuous variations (Job, *Ann. Chim.*, 1928, **9**, 113; Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437).

Fig. 2 shows how the difference between the measured absorbancy, and that calculated on the assumption that no complex formation has taken place, varies with the mole-fraction of reagent, the sum of the molar concentrations of iron and 2-methylphenanthroline being kept constant throughout at $5·73 \times 10^{-3}$M. The maximum does not occur at 75 mols.% of reagent as expected for a tris-complex, but between 66 and 68 mols.%, suggesting a 2 : 1 complex for which the theoretical value would be 66·67%. In these measurements the buffering proved to have been inadequate, for the pH of various solutions increased over the range 3·7—4·3 with the proportion of base present. Since the extent of complex formation had been shown to increase with pH (see above), this introduced some uncertainty, although the variation of acidity over the crucial composition range 60—80 mols.% was insufficient to account for the observed deviation from the expected maximum at 75 mols.%. A second series of measurements was carried out with slightly less concentrated solutions and at acidities which never fell outside the pH range 4·09—4·11. As shown in Fig. 2 (top left-hand corner), the formation of a bis-complex is confirmed as the predominant species present under the conditions of measurement. The low stability of the complex is the immediate cause of the marked curvature of the Job plots (Fig. 2) which clearly do not lend themselves to the calculation of stability constants, even by the method discussed by Schwarzenbach and Willi (*Helv. Chim. Acta*, 1951, **34**, 528). However, it proved possible to obtain them by the potentiometric titration technique first used by Calvin and Wilson (*J. Amer. Chem. Soc.*, 1945, **67**, 2003) and fully described by Irving and Griffiths (unpublished work).

The absorption spectrum of 2-methylphenanthroline in alkali shows two well-defined bands at $\lambda_{\max.}$ 228 and 267 mμ. On acidification they separate slightly and the former suffers a marked decrease in intensity. The absorption of both acid and basic species is negligible in the visible region. The close similarity between the spectrum of 1 : 10-phenanthroline and that of its 2-methyl and 2 : 9-dimethyl derivatives is shown in Table 1. The substances are all monoacid bases and show no tendency to take up a second proton even in strongly acid solutions (cf. Lee, Kolthoff, and Leussing, *loc. cit.*).

TABLE 1. *Absorption spectra of* 1 : 10-*phenanthroline and its methyl derivatives.*

		In acid solution :			In alkaline solution :		
1 : 10-Phenanthroline [a, b]			pH 1·5			pH 10·6	
λ (mμ)	—	221	243	272	229	242	264
10^{-4} ε	—	3·09	0·68	2·99	4·3	0·93	2·94
2-Methylphenanthroline [a]			pH 1·05			pH 10·0	
ε (mμ)	—	221	243	277	228	244	267
10^{-4} ε	—	3·35	0·51	2·85	4·5	1·06	2·95
2 : 9-Dimethylphenanthroline [c]			pH 1·0			pH 5·1	
λ (mμ)	201	222	—	282	224	—	272
10^{-4} ε	4·02	3·84	—	2·99	4·28	—	2·70

[a] Present authors. [b] Compare Kruse and Brandt, *Anal. Chem.*, 1952, **24**, 1307; Fielding and Le Fèvre, *J.*, 1951, 1811, report 10^{-4} ε = 4·07, 0·40, and 2·69 at λ 230, 242, and 264 mμ, respectively, in ethyl alcohol. [c] McCurdy and Smith, *loc. cit.*; solutions in aqueous alcohol.

Despite the relatively small influence of pH upon the absorption spectrum of 2-methylphenanthroline, the value $K_a = [\text{mephenan}]\{\mathrm{H}^+\}/[\text{mephenanH}^+] = 5·3 \pm 0·1$ at 17° was obtained for its acid dissociation constant from measurements of the absorbancy of solutions of constant concentration in a series of buffers (cf. Irving, Ewart, and Wilson, *J.*, 1949, 2672; Phillips and Merritt, *J. Amer. Chem. Soc.*, 1948, **70**, 410). The more accurate value of $\mathrm{p}K_a = 5·42$ was obtained from a potentiometric titration of a 0·01M-solution in

0·1M-potassium chloride at 25°. Under the same conditions the dissociation constant of 1 : 10-phenanthroline itself was found to be $1{\cdot}1 \times 10^{-5}$, confirming the values $1{\cdot}2 \times 10^{-5}$ (potentiometric) and $1{\cdot}1 \times 10^{-5}$ (conductimetric) given by Lee, Kolthoff, and Leussing (*loc. cit.*) rather than those of Albert and Goldacre ($5{\cdot}4 \times 10^{-5}$ at 20°; *J.*, 1946, 706; 1948, 2240) or Dwyer and Nyholm ($0{\cdot}63 \times 10^{-5}$; *Proc. Roy. Soc. N.S.W.*, 1946, **60**, 28).

The formation of a tris-complex, ML_3, will proceed through a series of step-reactions

$$Fe^{++} + L \rightleftharpoons FeL^{++};\quad FeL^{++} + L \rightleftharpoons FeL_2^{++};\quad FeL_2^{++} + L \rightleftharpoons FeL_3^{++}$$

where L represents a molecule of the uncharged ligand base phenanthroline or methylphenanthroline. The complex equilibria existing in solution can be treated in terms of three formation or stability constants, K_1, K_2, and K_3* defined by $K_n = \{FeL_n\}/\{FeL_{n-1}\}\{L\}$, where $n = 1$, 2, or 3; in practice, classical constants can be used with sufficient accuracy if, as in the present experiments, the ionic strength is not high, and is held reasonably constant. The measurement of formation constants in such systems is often carried out by titrating an acidified solution of metal salt with a concentrated solution of the basic ligand (Irving and Griffiths, *loc. cit.*); but in the present instance, owing to the sparing solubility of the heterocyclic base in water, it was necessary titrate with alkali an acidified mixture of a ferrous salt with an equivalent amount of 2-methylphenanthroline. From measurements of the pH in solutions of which the total concentrations C_M of metal, C_H of acid, and C_L of chelating base are known, it is possible to calculate the degree of formation or ligand number, $\bar{n}$, $= (C_L - [L])/C_M$ at corresponding values of [L], the concentration of "free" ligand, *i.e.*, of heterocyclic base bound neither to protons nor to ferrous ions. From the experimental data a formation curve, *i.e.*, a plot of $\bar{n}$ against pL($= -\log_{10}[L]$), can be drawn. Its course (not reproduced) shows clearly that, in addition to mono- and bis-complexes, the tris-complex must participate in the equilibrium when the ligand concentration is high enough; but the formation curve could not be traced much above $\bar{n} = 2{\cdot}3$ owing to the precipitation of basic material above pH ~5·5. However, the equation to the formation curve is known to be (Bjerrum, "Metal Ammine Formation in Solution," Copenhagen, 1941)

$$n + (n - 1)K_1[L] + (n - 2)K_1K_2[L]^2 + (n - 3)K_1K_2K_3[L]^3 = 0$$

and by successive approximations we arrive at the values $\log K_1 = 4{\cdot}2$, $\log K_2 = 3{\cdot}7$, and $\log K_3 = 2{\cdot}9$, of which the last value is the least reliable. The overall stability constant β_3 for the reaction

$$Fe^{++} + 3(\text{mephenan}) \rightleftharpoons Fe(\text{mephenan})_3^{++}$$

is thus given by $\log \beta_3 = \log K_1K_2K_3 = 10{\cdot}8$, which should be compared with the value $\log \beta_3 = 21{\cdot}3$ for phenanthroline itself (Lee, Kolthoff, and Leussing, *loc. cit.*). The lower value supports the second hypothesis proposed on p. 3418, *viz.*, that 2-methyl substitution reduces the strength of the ferrous complexes. 2-Methylphenanthroline ($pK_a = 4{\cdot}96$) is a stronger base than phenanthroline ($pK_a = 5{\cdot}42$), the strength of the proton-complex having increased as expected from the known effect of the methyl group in similar systems. However, the strength of the corresponding metal complexes follows the reverse order, an effect which has been noted in complexes with *N*-substituted ethylenediamines (Irving and Griffiths, *loc. cit.*), and is apparent in other systems where there is marked steric hindrance to complex formation.

There are, however, still more significant differences between the reactions with ferrous iron of phenanthroline and its 2-methyl derivative. For the parent base, $\log K_1$ is only 5·9 (Kolthoff, Leussing, and Lee, *J. Amer. Chem. Soc.*, 1950, **72**, 2173), so the product $\log K_2K_3 = 15{\cdot}4$. Now, in general, there is a progressive decrease in the ease with which successive ligand molecules are co-ordinated to a central ion, *i.e.*, $K_n > K_{n+1}$. But even if we put $\log K_2 = \log K_3 = 7{\cdot}7$ in this case, the value of K_2 so obtained is still appreciably greater than that of K_1; should $\log K_2$ be greater than $\log K_3$, the anomalous inequality $\log K_1 < \log K_2$ will be still greater. 2-Methylphenanthroline, however, follows the normal pattern in its ferrous complexes, with $K_1 > K_2 > K_3$. Indeed, phenanthroline

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* For symbolism see *J.*, 1953, 3192, 3397.

itself behaves normally in its complexes with zinc, for which log $K_1 = 6{\cdot}43$, log $K_2 = 5{\cdot}72$, and log $K_3 = 4{\cdot}89$ (*idem, ibid.*, 1951, **73**, 390). The anomalous behaviour of ferrous ions with those phenanthroline derivatives which are *not* sterically hindered will be discussed in a later paper of this series in relation to the accompanying loss of paramagnetism and change in adsorption spectrum. It is believed to be due to orbital stabilisation (Irving and Williams, *Analyst*, 1952, **77**, 813; *J.*, 1953, 3192).

We have yet to explain why perchlorates of a tris-complex can crystallise out from ferrous solutions containing 1 : 10-phenanthroline or its 2-methyl derivative although the evidence of absorption spectrophotometry (see above) points to a bis-complex as the predominant species in solutions of the latter. The composition of any equilibrium mixture of step-complexes is uniquely determined by the concentration of free ligand and the relevant stability constants (Bjerrum, *op. cit.*). Explicitly

$$[\mathrm{ML}_n] = C_{\mathrm{M}}\beta_n[\mathrm{L}]^n / \sum_{0}^{n}\beta_n[\mathrm{L}]^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\beta_n = K_1K_2 \ldots . K_n$, and $\beta_0 = 1$. Since the iron–phenanthroline system greatly resembles the system iron–2 : 2′-dipyridyl, for which the values log $K_1 = 4{\cdot}2$,

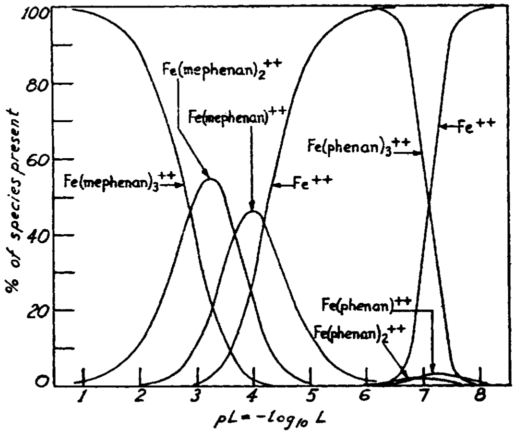


FIG. 3. (L *is* 1 : 10-*phenanthroline or* 2-*methylphenanthroline.*)

log $K_2 < 5$, and log $K_3 > 7{\cdot}3$ have been reported (Baxendale and George, *Trans. Faraday Soc.*, 1950, **46**, 55), we may reasonably assume that the relative values of stability constants in the iron–phenanthroline system follow the same pattern. Taking log $K_1 = 5{\cdot}9$, log $K_2 = 6{\cdot}9$, and log $K_3 = 8{\cdot}5$, we have calculated the relative concentrations of the various species co-existing in solution at various values of pL. It is immediately obvious (Fig. 3) that the complexes $\mathrm{Fe(phenan)^{++}}$ and $\mathrm{Fe(phenan)_2{}^{++}}$ have only a very limited range of existence and that they make an almost negligible contribution to the composition of the solution even under optimum conditions. With 2-methylphenanthroline, however, each complex is capable of playing a dominant rôle at an appropriate value of the concentration of free ligand.

Fig. 3 merely shows the *relative proportions* of the various complexes as a function of free ligand concentration. The *absolute* amounts of each in solution will increase with the total concentration of iron, C_{Fe}, and the solution will become saturated and precipitation take place when the solubility of the least soluble salt formed from any of the anions and cations (simple or complex) present in solution is exceeded. In the cases under consideration it is the perchlorates of the tris-complexes which are precipitated in this way; but we emphasise that such behaviour is not a prerogative of the highest complex present, for precipitation of lower complexes, or even of the cation itself, might take place preferentially if, from reasons of lattice energy, their salts with appropriate anions were less soluble than those of higher or lower complexes with the same partner.

The solubility of pure tris-1 : 10-phenanthrolineferrous perchlorate, $[\mathrm{Fe(phenan)_3}](\mathrm{ClO_4})_2$, in a number of aqueous buffers was readily obtained by withdrawing aliquots of the saturated solution, adding excess of phenanthroline, and making up to a known volume with buffer of pH 4. The absorbancy of the red tris-complex was then measured at 510 mμ, and the iron content calculated from the absorbancy of similar solutions containing the same concentration of reagent and known amounts of ferrous iron. From the experimental value of C_{Fe}, the total concentration of iron in equilibrium with the solid perchlorate, we are able to calculate [L] from the following equations

$$C_{\mathrm{L}} = 3C_{\mathrm{Fe}} \tag{2}$$

$$C_{\mathrm{L}} = [\mathrm{FeL}^{++}] + 2[\mathrm{FeL}_2{}^{++}] + 3[\mathrm{FeL}_3{}^{++}] + [\mathrm{HL}^+] + [\mathrm{L}] \tag{3}$$

$$C_{\mathrm{Fe}} = [\mathrm{Fe}^{++}] + [\mathrm{FeL}^{++}] + [\mathrm{FeL}_2{}^{++}] + [\mathrm{FeL}_3{}^{++}] \tag{4}$$

From the known composition of the solid perchlorate taken, we have $[\mathrm{ClO}_4{}^-] = 2C_{\mathrm{Fe}}$, so it is possible to evaluate the solubility product defined as $\beta_s = [\mathrm{ML}_3{}^{++}][\mathrm{ClO}_4{}^-]^2$. Results given in Table 2 show that values of β_s obtained from measurements in different buffers are in satisfactory agreement, and that the average value of $\mathrm{p}\beta_s = 8{\cdot}56$ for trisphenanthrolineferrous perchlorate is not greatly dependent upon the somewhat arbitrarily chosen values of log K_2 and log K_3.

TABLE 2. *Solubility measurements on the perchlorates of the tris-complexes.*

(*a*) Tris-1 : 10-phenanthrolineferrous perchlorate.

pH	10^4C_{Fe}	pL	$\mathrm{p}\beta_s$	pL	$\mathrm{p}\beta_s$	pL	$\mathrm{p}\beta_s$
3·22	9·35	6·374	8·492	6·994	8·633	6·347	8·490
4·12	8·84	6·149	8·561	6·155	8·530	6·076	8·554
5·02	8·18	5·975	8·665	6·374	8·456	6·854	8·661
		Average values :	8·57 [a]		8·54 [b]		8·57 [c]

[a] By assuming log K_1 = 5·89, log K_2 = 6·18, and log K_3 = 9·24. [b] By assuming log K_1 = 5·87, log K_2 = 5·00, and log K_3 = 10·40. [c] By assuming log K_1 = 5·90, log K_2 = 6·90, and log K_3 = 8·50.

(*b*) Tris-2-methylphenanthrolineferrous perchlorate.

pH	10^3C_{Fe}	pL	$10^4\mathrm{Fe}^{++}$	$\mathrm{p}\beta_s$
4·00	2·23	3·836	4·255	9·786
4·50	1·59	3·604	1·452	9·840
4·66	1·57	3·511	1·021	9·726
5·32	1·12	3·287	0·285	9·903
5·66	0·87	3·276	0·210	9·807

By assuming log K_1 = 4·2
log K_2 = 3·7
log K_3 = 2·9
Average value : $\mathrm{p}\beta_s$ = 9·81

Saturated solutions of pure ferrous tri-2-methyl-1 : 10-phenanthroline were prepared in a number of buffers and analysed for iron by adding excess of 1 : 10-phenanthroline and making up to a standard volume with a buffer of pH 4 containing hydroxylamine. Under these conditions all the iron is displaced from its weak complexes with 2-methylphenanthroline and transformed into the red tris-1 : 10-phenanthroline complex (ferroin) which was determined absorptiometrically at 510 mμ as before. A direct determination of C_{L}, and hence an independent check on the validity of equation (2), were also possible in this system, for when aliquots of the saturated perchlorate solutions were diluted 100-fold with 0·1N-hydrochloric acid, the weak complexes were completely resolved into ferrous ions and 2-methylphenanthrolinium ions so that the total amount of base, C_{L}, could be determined absorptiometrically at wave-lengths where interference from the ferrous ion was negligible.

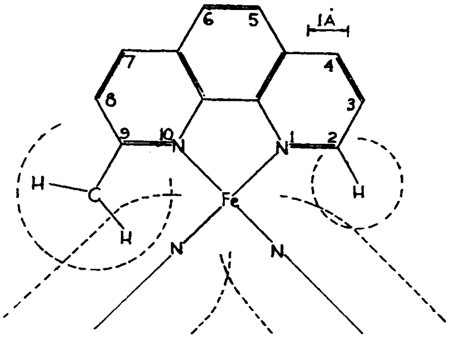
The remarkably low solubility of trisphenanthrolineferrous perchlorate ($8{\cdot}83 \times 10^{-4}$M; ~0·70 g./l.) has led to its use for the gravimetric determination of perchlorate ions (Brandt and Smith, *Analyt. Chem.*, 1949, **21**, 1313). The solubility of the corresponding tris-2-methylphenanthrolineferrous perchlorate is appreciably lower ($3{\cdot}38 \times 10^{-4}$M; ~0·28 g./l.).

At pH 5·0, the values of pL in saturated solutions of trisphenanthrolineferrous and trismethylphenanthrolineferrous perchlorates are 6·0 and 3·3 respectively. Reference to Fig. 3 and equation (1) shows that in the former case $\bar{n} \sim 3$ and the solution consists essentially of the tris-complex. However, in the case of the methyl derivative, when pL = 3·3 the solution contains at most 22% of the tris-complex with 54% of $\mathrm{Fe(mephenan)}_2{}^{++}$, 21·5% of $\mathrm{Fe(mephenan)}^{++}$, and about 2·5% of uncomplexed Fe^{++}. The degree of formation, $\bar{n}$, is only 1·95. In short, owing to a combination of circumstances—the very sparing solubility of the perchlorate of the tris-complex, the regular progression of the stability constants $K_1 > K_2 > K_3$, and their low absolute value—precipitation takes place when the total concentration of iron in solution is low, and when the principal species is the 1 : 2 complex.

Although Fe(phenan)$_3^{++}$ has the very high molecular extinction coefficient of $\varepsilon = 11{,}100$ at $\lambda_{max.}$ 510 mμ, the 1 : 1 complex Fe(phenan)$^{++}$ has a broad absorption band with $\varepsilon \sim 330$ at $\lambda_{max.}$ 400—450 (Kolthoff, Leussing, and Lee, *J. Amer. Chem. Soc.*, 1950, **72**, 2173). The absorption band of Fe(mephenan)$_2^{++}$ is also broad (cf. Fig. 1) and an upper limit for its molecular extinction coefficient is found to be $\varepsilon = 900$—1000 at 435 mμ, if contributions from 1 : 1 and 1 : 3 complexes are ignored.

Owing to its sparing solubility in water it was impossible to study the reactions of 2-chlorophenanthroline with ferrous iron under conditions exactly equivalent to those employed with 2-methylphenanthroline. The chloro-compound certainly forms a weak, pale yellow complex with ferrous iron, and the absorption spectrum resembles that of the 2-methyl analogue in having a very broad band with $\lambda_{max.}$ 510. The intensity of absorption is considerably below that given by equivalent amounts of ferrous iron and 2-methylphenanthroline, as would be expected from the similar degree of steric hindrance and the expected lower basicity of the reagent.

Fig. 4.



The effect of steric hindrance in preventing the formation of certain octahedral complexes has already been discussed in connection with the non-formation of the aluminium tris-8-hydroxy-2-methylquinoline complex (Irving, Ring, and Butler, *J.*, 1949, 1489). A similar "packing effect" with 2-substituted 1 : 10-phenanthrolines is readily demonstrated with the aid of models. Fig. 4 represents a section through the plane of one chelate ligand molecule based on conventional van der Waals radii and interatomic distances: the "interference envelope" of the atomic planes formed by the two other ligand molecules at right angles to the first are shown by broken lines. Interference by a single methyl (or halogen) group will clearly lead to distortion of bond lengths and angles with a consequent decrease in stability. With substituents adjacent to only one nitrogen in each ligand, distortion can be minimised if the methyl groups lie in positions as far removed from one another as possible. With substituents adjacent to each nitrogen atom steric hindrance is very greatly increased and complex formation between iron and, *e.g.*, 2 : 9-dimethylphenanthroline appears to be completely inhibited. Annelation in positions 2 : 3 and/or 8 : 9 will, of course, produce the same effect.

Despite their reluctance to co-ordinate to ferrous iron, 2-methyl-, 2-chloro-, and 2 : 9-bis-dimethyl-1 : 10-phenanthroline give strongly coloured complexes with cuprous copper which will be described in a later paper.

EXPERIMENTAL

Preparation of Reagents.—*2-Methyl-*1 : 10*-phenanthroline* (I; R = Me, R′ = H).—(*a*) Paraldehyde (40 g.) was added during ½ hr. to *o*-nitroaniline (50 g.), concentrated hydrochloric acid (50 g.), and water (15 ml.) with constant stirring. After the reaction had subsided the mixture was heated for 1 hr. on the water-bath, then cooled, poured into water (2 l.), and made strongly alkaline. After being kept overnight the precipitate was collected and dried. Recrystallization from alcohol (charcoal) gave yellow needles of 8-nitroquinaldine, m. p. 136°. Somewhat better yields were obtained by adding freshly distilled crotonaldehyde (50 g.) to a mechanically stirred mixture of *o*-nitroaniline (190 g.), arsenic pentoxide (82 g.), concentrated sulphuric acid (90 ml.), and water (30 ml.) at such a rate that the initial temperature of 80—90° was maintained without external heating. After a further ½ hour's heating on the water-bath the mixture was rapidly cooled and strongly basified. The tar which was formed was collected and taken up in hot concentrated hydrochloric acid (charcoal), and the filtrate basified. The product after drying was extracted (Soxhlet) with ethyl alcohol, giving 8-nitroquinaldine (34·8 g., 26%), m. p. 136° after recrystallization from aqueous alcohol (Doebner and Miller, *Ber.*, 1884, **17**, 1700, give 137°).

(*b*) 8-Aminoquinaldine (29 g.), obtained in 84% yield by reduction of 8-nitroquinaldine with stannous chloride following Gerdeisen (*Ber.*, 1889, **22**, 245), was mixed with arsenic pentoxide (27·2 g.), water (13·6 ml.), and concentrated sulphuric acid (71 g.) and stirred mechanically under reflux while the temperature was raised to 100° (oil-bath). Anhydrous glycerol (60·5 g.) was added during 15 min., and the temperature raised to 140° and kept there for 2 hr. After being cooled, the mixture was basified at 0° by adding 250 ml. of 40% sodium hydroxide solution. After being kept overnight the viscous brown product which separated was extracted several times with hot benzene, and the combined extracts were dried over pellets of sodium hydroxide. After 12 hr. the dried benzene extracts were decanted, and the solvent removed under reduced pressure. On fractionation *in vacuo* unchanged 8-aminoquinaldine distilled first (b. p. 110°/2 mm.), followed by 2-methylphenanthroline, as a viscous orange liquid, b. p. 180—185°/2 mm., which would not solidify. The latter was taken up in the minimum amount of pure benzene and, after the addition of light petroleum (b. p. 80—100°), moist air was drawn slowly through the solution, whereupon the dihydrate separated as white flocks which, after being collected, washed with light petroleum, and air-dried, had m. p. 53° (Gerdeisen, *loc. cit.*, p. 253, gives 53°) (Found: C, 67·5; H, 6·1; N, 12·1. Calc. for $C_{13}H_{10}N_2,2H_2O$: C, 67·75; H, 6·15; N, 12·2%).

The formation of the sparingly soluble mercuric chloride complex of the base, followed by its decomposition in dilute acid suspension with hydrogen sulphide and isolation of the base as previously described, did not bring about any further purification as judged from the constancy of the absorption spectrum. The *picrate* formed bright yellow crystals, m. p. 216° (Found: N, 16·5. $C_{19}H_{13}O_7N_5$ requires N, 16·6%), from ethyl alcohol. These could only be separated with difficulty from the *picrate* of 8-aminoquinaldine, which formed somewhat deeper orange needles, m. p. 188—189°, from ethyl alcohol (Found: N, 17·9. $C_{16}H_{13}O_7N_5$ requires N, 18·0%). 2-Methylphenanthroline perchlorate formed needles, m. p. 207° (decomp.), on recrystallization from hot dilute perchloric acid (Pfeiffer and Christeleit, *J. pr. Chem.*, 1938, **151**, 127, give m. p. 205—207°).

Formation and Composition of the Yellow Iron–2-Methylphenanthroline Complex.—(a) *Effect of changing the proportions of reagents.* Solutions of pH ~ 4·7 containing respectively 20, 40, 80, and 160 p.p.m. of ferrous iron and with 2-methylphenanthroline : iron concentration ratios of 16 : 1, 8 : 1, 4 : 1, and 2 : 1 were prepared by mixing 5 ml. of 0·36% 2-methylphenanthroline perchlorate, 0·2*x* ml. of stock ferrous solution (1·7553 g. of "AnalaR" ferrous ammonium sulphate in 250 ml. of metal-free water), and 0·25*x* ml. of 2·5% hydroxylamine hydrochloride solution (x = 1—4) and making up to 10 ml. with an acetate buffer. Absorption spectra were measured with a Beckman Model DU Spectrophotometer, the smallest slit-widths compatible with reasonable sensitivity being used. The results appear in Fig. 1.

(b) *Effect of changing the acidity.* 3-Ml. portions of a solution containing 0·28 g. of 2-methylphenanthroline perchlorate, 8 ml. of 10% hydroxylamine hydrochloride, and 6·67 ml. of standard iron solution (1000 p.p.m.) in 25 ml. of water were diluted to 10 ml. with a series of buffer solutions. The absorption spectra of these solutions (each containing 80 p.p.m. of ferrous iron, with a concentration ratio of metal : reagent = 1 : 8) were measured against blanks of the same composition save that 6·67 ml. of distilled water had replaced the standard iron solution. Typical values for the absorbancy, *A*, at λ 430 mμ were:

pH	1·79	2·13	2·54	3·00	3·10	3·64	3·82	4·18	4·43
A (1 cm.)	0·0	0·020	0·058	0·119	0·162	0·385	0·476	0·671	0·672

(c) *Application of the method of continuous variations.* The absorption spectra of mixtures of *x* ml. of a solution A (0·1227 g. of 2-methylphenanthroline dihydrate in 100 ml. of 0·05M-potassium hydrogen phthalate buffer of pH 3·97) with (10 − x) ml. of an iron solution B (0·2247 g. of ferrous ammonium sulphate and 1 g. of hydroxylamine hydrochloride in 100 ml. of the same buffer) were measured in 1-cm. Corex cells against a blank containing buffer solution alone. The differences between the experimentally determined absorbancies and those calculated on the basis of simple admixture are given below.

Mol.-fraction of reagent	pH	Absorbancy differences at λ (mμ) :				
		400	425	440	460	475
1·000	4·27	0·048	0·031	0·024	0·017	0·013
0·894	4·15	0·169	0·176	0·183	0·172	0·141
0·796	4·06	0·258	0·266	0·276	0·254	0·204
0·735	4·03	0·286	0·293	0·299	0·274	0·219
0·685	4·00	0·298	0·305	0·312	0·282	0·223
0·651	4·00	0·303	0·304	0·310	0·289	0·219
0·583	3·98	0·291	0·296	0·300	0·265	0·204
0·482	3·86	0·271	0·270	0·272	0·237	0·181
0·376	3·86	0·233	0·233	0·232	0·199	0·151
0·190	3·80	0·116	0·117	0·114	0·096	0·068
0·000	3·72	0·005	0·003	0·002	0·002	0·002

A similar set of measurements with mixtures prepared from solutions A and B after dilution with 3·4 ml. of distilled water and 3·4 ml. of diluted ammonia respectively gave the following results :

Mol.-fraction of reagent	pH	Absorbancy differences at λ (mμ) :				
		400	425	440	460	475
0·000	4·27	0·047	0·031	0·025	0·018	0·017
0·603	4·09	0·352	0·362	0·362	0·329	0·260
0·651	4·09	0·350	0·360	0·365	0·337	0·268
0·664	4·09	0·349	0·357	0·367	0·339	0·269
0·705	4·10	0·333	0·344	0·350	0·325	0·260
0·737	4·10	0·318	0·329	0·337	0·313	0·252
0·767	4·11	0·296	0·396	0·315	0·298	0·240
1·000	4·24	0·016	0·008	0·006	0·004	0·003

Dissociation Constant of the 2-*Methylphenanthrolinium Ion*.—(a) *Spectrophotometric determination.* 5-Ml. aliquots of a $\sim$2·2 × 10^{-5}M-solution of the base in water were diluted with an equal volume of sodium acetate–hydrochloric acid or phosphate buffers. The absorbancies measured in a 1-cm. silica cell against the appropriate blanks are given below for four wavelengths :

pH	Absorbancy at λ (mμ):				pH	Absorbancy at λ (mμ) :			
	235	268	275	280		235	268	275	280
1·54	0·265	0·585	0·669	0·629	5·25	0·406	0·600	0·605	0·494
2·40	0·284	0·600	0·687	0·640	5·67	0·420	0·589	0·535	0·430
3·32	0·287	0·570	0·650	0·592	5·94	0·462	0·612	0·533	0·422
4·04	0·290	0·559	0·625	0·561	6·50	0·468	0·612	0·509	0·388
4·48	0·317	0·565	0·619	0·542	7·00	0·491	0·615	0·491	0·372
4·83	0·331	0·573	0·610	0·528	7·20	0·500	0·623	0·495	0·374
5·04	0·359	0·590	0·611	0·514	7·76	0·504	0·634	0·502	0·377

pK_a (calc.) 5·2 5·3 5·4 5·2

Average pK_a = 5·3 for 17° and an ionic strength of $\sim$0·1M.

(b) *Potentiometric method.* A 0·01M-solution of 2-methylphenanthroline (0·1151 g. of the dihydrate in 50 ml. of 0·1M-potassium chloride containing 0·5 ml. of 0·168N-hydrochloric acid) was titrated potentiometrically in an apparatus (Irving and Griffiths, *loc. cit.*) kept in a thermostat at 25°. After correction for volume changes and buffering by the medium, the value pK_a = 5·42 at 25·0° ± 0·1° and μ = 0·1 was obtained.

Measurement of Stability Constants.—2-Methylphenanthroline dihydrate (0·0691 g.) and ferrous ammonium sulphate (0·0196 g.) were dissolved in 2·44 ml. of 0·164N-hydrochloric acid (which was 0·1M with respect to potassium chloride) and made up to 50 ml. with 0·1M-potassium chloride. All solutions were initially air-free. Exposure to air being avoided, 40 ml. of this solution were transferred to the titration vessel (Irving and Griffiths, *loc. cit.*) and titrated with 0·1016N-hydrochloric acid while being stirred with a stream of nitrogen equilibrated with water vapour by passage through 0·1M-potassium chloride solution at 25°. By using a Cambridge pH-meter with a saturated calomel–glass-electrode combination previously calibrated with standard buffers, the pH was measured after each addition of base. The solution remained quite colourless up to pH 3, whereat the yellow colour of the complex appeared and deepened with each addition of alkali. Incipient turbidity was noted at pH ~5·6 and precipitation was definite at pH 6·7, at which point small additions of alkali caused large increases in pH. Nevertheless, the solution gave no reaction for ferric iron on the addition of thiocyanate ions. Results of a typical titration are given below together with the corresponding calculated values of the degree of formation, $\bar{n}$, and the free ligand exponent, pL, *i.e.*, the decadic logarithm of the reciprocal of the concentration of 2-methylphenanthroline which is not bound to either proton or ferrous ion.

Vol. of alkali, ml.	pH	pL	$\bar{n}$	Vol. of alkali, ml.	pH	pL	$\bar{n}$	Vol. of alkali, ml.	pH	pL	$\bar{n}$
0·30	2·90	4·747	0·009	1·40	4·04	3·756	1·47	2·10	5·00	3·018	2·33
0·50	3·04	4·633	0·322	1·50	4·18	3·641	1·64	2·30	5·26	2·851	2·36
0·70	3·20	4·481	0·383	1·60	4·32	3·527	1·80	2·40	5·40	2·771	2·30
0·90	3·41	4·294	0·629	1·70	4·46	3·416	1·95	2·50	5·53	2·699	2·23*
1·10	3·64	4·095	0·943	1·80	4·59	3·400	2·14	2·60	5·68	2·628	2·09
1·30	3·91	3·869	1·29	1·90	4·73	3·211	2·20				

* Turbidity apparent.

Under comparable conditions, steady and reproducible potentials were obtained in the titration of ferrous iron in the absence of 2-methylphenanthroline up to pH 4·5. At this point addition of 0·04 ml. of alkali increased the pH abruptly to 6·70, and thereafter the acidity gradually increased and a fine reddish precipitate separated later.

*Solubility of Tris-2-methyl-*1 : 10*-phenanthrolineferrous Perchlorate.*—Saturated solutions at acidities between pH 3 and 6 were prepared by warming a suitable sodium acetate–hydrochloric acid buffer mixture to nearly 100° and adding solid complex (prepared according to Pfeiffer and Christeleit, *loc. cit.*, washed with 20% methanol, and dried in a vacuum desiccator to constant weight) until saturated. The solution was then cooled and kept at 25° with occasional shaking for 12 hr. to ensure equilibrium. Samples of the saturated solution were then separated from undissolved solid and analysed for total reagent and total iron as follows: (*a*) Total 2-methylphenanthroline: 0·25 Ml. of the saturated solution was diluted to 25 ml. with 0·1N-hydrochloric acid to decompose the ferrous complex, and the concentration of methylphenanthrolium ion was calculated from the absorbancies at 221, 277, and 310 mμ by comparison with the absorbancy of standard solutions of pure base in 0·1N-hydrochloric acid. It was established that ferrous ions at the concentration present in the analytical samples did not influence the absorbancy due to the 'onium ions. (*b*) Total iron: A measured excess of 1 : 10-phenanthroline was added to a suitable aliquot (0·25 or 0·50 ml.) of saturated solution together with hydroxylamine solution and an acetate buffer of pH 4 to give a total volume of 25 ml. Under these conditions all the iron is converted into the stable trisphenanthroline complex of ferrous iron (ferroin) which was determined absorptiometrically at 510 mμ by reference to absorbancy data obtained similarly from solutions of known iron content.

*Solubility of Tris-*1 : 10*-phenanthrolineferrous Perchlorate.*—The preparation of pure perchlorate and of its saturated solutions in aqueous buffers was carried out as above. Since this stable ferrous complex cannot be completely decomposed in 0·1N-acid a direct determination of the concentration of total phenanthroline was not feasible and it was assumed that this was exactly three times that of the ferrous ion. The latter was accurately determined by adding excess of 1 : 10-phenanthroline to 1 ml. of saturated solution and making up to 25 ml. with buffer of pH 4. The measured absorbancy at 510 mμ was then compared with that of solutions of known iron content prepared similarly.

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