1003. *The Stability of Metal Complexes of* 1,10-*Phenanthroline and its Analogues. Part II.** 2-*Methyl- and* 2,9-*Dimethyl-phenanthroline.*

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The dissociation constant of the acid conjugate to 2,9-dimethyl-1,10-phenanthroline is found to be $10^{5\cdot85}$ in 0·1M-potassium chloride at 25°. The distribution coefficients for 2-methyl- and 2,9-dimethyl-1,10-phenanthroline between aqueous buffers and n-hexane, chloroform, or carbon tetrachloride have been measured, both alone and in the presence of known quantities of certain bivalent cations; thence the step-stability constants have been computed for the metal complexes formed in the aqueous solutions. All complexes formed by 2-methyl-1,10-phenanthroline are appreciably less stable than those with 1,10-phenanthroline, but the stability order Mn $<$ Fe $<$ Co $<$ Ni $<$ Cu $>$ Zn and Cd is obeyed for both the 1 : 1 and the 2 : 1 complexes. There is no anomaly for K_3 with iron(II); and copper(II) does not form a 3 : 1 complex.

Complexes with 2,9-dimethyl-1,10-phenanthroline are still less stable, owing to the increased steric hindrance, and there is reasonable evidence that for the 2 : 1 copper complex $K_1 < K_2$. The implications of these measurements when designing a specific reagent for copper are discussed.

MANY results published since 1953 have confirmed the validity of the generalisation that the stability of complexes formed by the bivalent transition metals follows the order Mn $<$ Fe $<$ Co $<$ Ni $<$ Cu $>$ Zn and Cd, irrespectively of the nature of the ligand. In the paper in which the evidence then available was summarised[1] Irving and Williams pointed to two possible factors that might operate to alter the stability sequence from its normal order. The first of these, " orbital stabilisation " (*i.e.*, a change from the normal ground state of the ion to a spin-paired state), was shown to be likely to occur with compounds of ferrous iron with certain ligands and should lead to complexes of unusual stability, so that the normal order Mn $<$ Fe $<$ Co would be replaced by Mn $<$ Co $<$ Fe. The

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* Part I, preceding paper.

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

TABLE 1.

Measurement of stability constants.

2-*Methylphenanthroline*

Manganese: $10^{4}C_{L}$ 17·74—39·0; $10^{3}C_{M}$ 3·0—0·6.

$\bar{n}$	0·20^{1}	0·37^{1}	0·385^{2}	0·47^{2}	0·54^{2}	0·55^{1}	0·63^{2}	0·78^{2}	0·85^{2}	0·97^{4}	1·06^{4}	1·07^{3}
pL	3·65	3·40	3·29	3·16	3·10	3·24	3·03	2·995	2·955	2·90	2·81	2·84
$\bar{n}$	1·30^{3}	1·32^{3}	1·35^{4}	1·47^{3}	1·85^{3}	1·97^{3}						
pL	2·745	2·675	2·71	2·63	2·61	2·595						

Iron: $10^{4}C_{L}$ 8·16: $10^{3}C_{M}$ 1·50—0·30.

$\bar{n}$	0·36^{2}	0·45^{2}	0·48^{1}	0·67^{1}	0·98$_{1}$	1·08^{1}	1·19^{2}	1·25^{1}	1·34^{2}	1·37^{1}	1·38^{1}	1·42^{1}
pL	4·35	4·21	4·35	4·17	3·97	3·90	3·825	3·85	3·50	3·585	3·74	3·56
$\bar{n}$	1·50^{1}	1·53^{2}	1·82^{1}	1·86^{3}	2·05^{3}	2·10^{3}	2·30^{3}	2·55^{3}	2·59^{3}	2·65^{3}		
pL	3·70	3·53	3·68	3·30	3·29	3·38	3·32	3·28	3·30	3·26		

Cobalt: $10^{4}C_{L}$ 8·75; $10^{3}C_{M}$ 1·80—0·15.

$\bar{n}$	0·48^{3}	0·54^{3}	0·575^{3}	0·66^{3}	0·72^{2}	0·86^{2}	0·87^{1}	1·07^{2}	1·22^{2}	1·42^{2}	1·67^{1}	1·69^{2}
pL	5·33	5·40	5·305	5·27	5·06	4·89	5·03	4·89	4·785	4·745	4·56	4·65
$\bar{n}$	2·03^{2}	2·43^{2}	2·43^{2}	2·55^{1}	2·60^{2}	2·72^{1}						
pL	4·31	3·91	3·91	3·74	3·55	3·43						

Nickel: $10^{4}C_{L}$ 4·36—2·16; $10^{3}C_{M}$ 0·5—0·04.

$\bar{n}$	0·43^{3}	0·43^{1}	0·48^{3}	0·62^{2}	0·86^{2}	1·06^{1}	1·08^{2}	1·40^{2}	1·66^{2}	1·98^{1}	2·01^{2}	2·18^{3}
pL	6·40	6·425	6·30	6·17	6·01	5·87	5·89	5·69	5·55	5·26	5·36	5·15
$\bar{n}$	2·32^{2}	2·56^{1}	2·57^{3}	2·65^{3}	2·72^{3}	2·75^{3}	2·78^{1}	2·73^{3}				
pL	4·95	4·62	4·815	4·43	4·40	4·53	4·36	4·36				

Copper: $10^{4}C_{L}$ 4·36—8·72; $10^{3}C_{M}$ 1·2—0·30.

$\bar{n}$	0·30^{7}	0·33^{6}	0·44^{1}	0·455^{7}	0·53^{6}	0·595^{7}	0·75^{6}	0·90^{1}	1·10^{1}	1·17^{4}	1·20^{1}	1·27^{3}
pL	7·63	7·44	7·66	7·56	7·41	7·40	7·36	7·13	7·15	6·81	6·71	6·47
$\bar{n}$	1·31^{3}	1·39^{3}	1·45^{2}	1·52^{8}	1·54^{2}	1·55^{4}	1·62^{4}	1·64^{4}	1·65^{3}	1·75^{5}	1·75^{8}	1·77^{2}
pL	6·44	6·38	6·41	6·17	6·24	6·09	6·20	6·34	6·20	6·11	6·00	5·92
$\bar{n}$	1·85^{2}	1·90^{2}	1·90^{3}	1·90^{8}	1·92^{8}	1·93^{2}	1·96^{2}	2·06^{5}	2·10^{5}	2·13^{5}		
pL	5·59	5·67	5·73	5·87	5·57	5·29	4·90	4·43	3·71	3·45		

Zinc: $10^{4}C_{L}$ 8·72; $10^{3}C_{M}$ 0·07—2·50.

$\bar{n}$	0·345^{1}	0·43^{4}	0·57^{1}	0·57^{4}	0·83^{1}	0·85^{4}	1·20^{3}	1·32^{1}	1·59^{3}	1·66^{1}	1·80^{3}	1·82^{1}
pL	5·36	5·17	5·16	5·02	4·87	4·86	4·69	4·50	4·22	4·13	3·93	3·82
$\bar{n}$	1·84^{3}	1·90^{3}	1·94^{3}	2·00^{3}	2·04^{3}	2·07^{3}	2·24^{2}	2·30^{2}	2·40^{2}	2·52^{2}	2·80^{4}	
pL	3·75	3·63	3·58	3·44	3·53	3·56	3·38	3·31	3·22	3·27	3·25	

Cadmium: $10^{4}C_{L}$ 8·73; $10^{3}C_{M}$ 2·0—0·10.

$\bar{n}$	0·43^{3}	0·48^{5}	0·50^{3}	0·575^{2}	0·575^{3}	0·615^{5}	0·69^{3}	0·85^{5}	0·86^{3}	0·86^{3}	1·07^{2}	1·20^{1}
pL	5·52	5·19	5·383	5·35	5·14	5·02	4·94	4·83	4·86	5·00	4·84	4·665
$\bar{n}$	1·20^{3}	1·39^{2}	1·62^{1}	1·65^{5}	1·75^{2}	1·93^{1}	1·94^{1}	2·10^{2}	2·13^{1}	2·35^{2}	2·56^{2}	2·60^{4}
pL	4·68	4·55	4·34	4·38	4·26	4·13	4·10	3·98	3·87	3·66	3·42	3·38
$\bar{n}$	2·67$_{4}$	2·72^{3}	2·78^{4}									
pL	3·305	3·35	3·46									

2,9-*Dimethyl*-1,10-*phenanthroline*

Manganese: $10^{3}C_{L}$ 1·4—7·8; $10^{3}C_{M}$ 1·90.

$\bar{n}$	0·02	0·09
pL	3·05	3·04
pH	7·27	7·45

At higher alkalinities the absorbancies became irreproducible, doubtless owing to the incipient precipitation of manganese hydroxide.

Iron: $10^{4}C_{L}$ 9·2; $10^{3}C_{M}$ 3·0.

$\bar{n}$	0·03	0·04
pL	3·90	3·80

Incipient precipitation at higher alkalinities made measurements of ligand concentrations impossible.

Cobalt: $10^{4}C_{L}$ 4·61—23·0; $10^{3}C_{M}$ 4·61—23·0.

$\bar{n}$	0·39^{1}	0·59^{2}	0·64^{1}	0·77^{1}	0·78^{2}	0·86^{1}	0·91^{2}	1·21^{2}
pL	4·54	3·99	4·25	3·91	3·73	3·82	3·575	3·22

Nickel: $10^{4}C_{L}$ 4·61—22·8; $10^{3}C_{M}$ 1·0—0·6.

$\bar{n}$	0·45^{1}	0·49^{4}	0·54^{3}	0·59^{4}	0·69^{3}	0·81^{1}	0·98^{3}	1·04^{6}	1·10^{4}	1·27^{3}	1·23^{6}	1·32^{6}
pL	5·29	4·90	4·84	4·78	4·62	4·64	4·30	4·00	4·07	3·84	3·66	3·455
$\bar{n}$	1·32^{5}	1·38^{1}	1·40^{1}	1·43^{3}	1·48^{6}	1·50^{2}	1·51^{5}	1·55^{6}	1·65^{3}	1·76		
pL	3·78	3·88	3·35	3·66	3·25	3·38	3·39	3·21	3·49	3·17		

Copper: $10^{4}C_{L}$ 9·22; $10^{3}C_{M}$ 2·0—0·2.

$\bar{n}$	0·46	0·48	0·60	0·90	1·30	1·33	1·70	1·71	1·90	1·95	2·01	2·00
pL	5·815	5·81	5·72	5·605	5·42	5·30	4·94	4·87	4·48	4·24	3·25	3·15

Zinc: $10^{3}C_{L}$ 3·6—1·5; $10^{4}C_{M}$ 17·8.

$\bar{n}$	0·47^{2}	0·61^{1}	0·66^{2}	0·78^{2}	0·86^{2}	1·00^{2}	1·04^{1}	1·20^{3}	1·30^{1}	1·52^{3}	1·66^{3}	1·72^{3}
pL	4·26	4·22	4·115	3·96	4·08	3·79	3·92	3·58	3·74	3·40	3·21	2·925

TABLE 1. (*Continued.*)

Cadmium (with Miss Batstone): 10^3C_L 1·88; 10^3C_M 5·6—0·3.

$\bar{n}$	0·33	0·345	0·365	0·39	0·415	0·445	0·48	0·49	0·57	0·63	0·69	0·78
pL	4·51	4·485	4·44	4·41	4·38	4·34	4·29	4·23	4·25	4·22	4·08	4·01
$\bar{n}$	0·88	1·00	1·17	1·35	1·54	1·75	1·80	1·75	1·89	1·99	1·90	2·.1
pL	3·91	3·78	3·66	3·49	3·33	3·31	3·27	3·25	3·20	3·185	3·16	3·11
$\bar{n}$	2·80 *	2·60 *	2·39 *									
pL	2·85	2·93	2·99									

$^{1-8}$ Superscript numerals denote related series of experiments. * See text.

realisation of this effect, which nowadays receives a more sophisticated explanation in ligand-field theory,[2] is discussed and demonstrated experimentally in Part I of this series.[3] The second factor arose from repulsions between the atoms of the ligand and the central metal. Under the heading of " steric factors " examples were given of ligands adapted to, *e.g.*, tetrahedral rather than octahedral (or square-planar) co-ordination, and of their behaviour towards cations, *e.g.*, those of zinc, nickel, or copper, which favour one arrangement more than another. In the present paper we present measurements on the stabilities of metal complexes of 1,10-phenanthroline derivatives containing methyl groups adjacent to one of both of the nitrogen atoms, a feature which has been shown for iron [4] to hinder packing of the three bulky organic molecules round the central ion.

The procedure involved measurements of partition coefficients of the two organic bases between aqueous buffers and organic solvents, both in the presence and in the absence of known quantities of metal ions, essentially as described in Part I.[3]

EXPERIMENTAL

Reagents.—The preparation of 2-methyl-1,10-phenanthroline has been described.[4] 2,9-Dimethyl-1,10-phenanthroline was prepared similarly, by heating 8-aminoquinaldine (30 g., 1 mol.), crotonaldehyde diacetate (56 g. 1·6 mol.), and arsenic pentoxide (28·3 g.) in water (15 ml.) and 96·8% sulphuric acid (45·5 ml.) under reflux for 2 hr. After basification the base was isolated by extraction with benzene and on recrystallisation from water (charcoal) formed colourless needles, m. p. 159·5°, of the hemihydrate (Case [5] reports m. p. 159—160°) (Found: C, 77·5; H, 5·8; N, 13·0. Calc. for $C_{14}H_{12}N_2,0{\cdot}5H_2O$: C, 77·4; H, 6·0; N, 12·9%). The material was purified by sublimation *in vacuo*.

Acid Dissociation Constants of the Reagents.—(*a*) 2-*Methyl*-1,10-*phenanthroline*. Potentiometric titrations with a glass electrode in 0·1M-potassium chloride at 25° gave pK_a 5·45 (3 determinations). The absorbancy of eighteen solutions, each containing the ligand at a total concentration of $4{\cdot}36 \times 10^{-4}$M, in buffers of pH ranging from 1·8 to 10·4 and adjusted to $\mu = 0{\cdot}1$ with potassium chloride, were measured over a range of wavelengths. From plots of the absorbancy against pH at selected wavelengths (not reproduced) the value p$K_a = 5{\cdot}39$ was obtained where $K_a = \{H^+\}[L]/[HL^+]$ and L = 2-methylphenanthroline in this case. The average value adopted for the (Brønsted) dissociation constant was p$K_a = 5{\cdot}42$ (25° and $\mu = 0{\cdot}1$M-KCl) which agrees well with the earlier value [4] of 5·45.

(*b*) 2,9-*Dimethylphenanthroline*. By the same potentiometric technique a solution ($1{\cdot}9 \times 10^{-3}$M) of the base in hydrochloric acid (8×10^{-3}M) gave p$K_a = 5{\cdot}85$ (25° and $\mu = 0{\cdot}1$M-KCl).

Partition Coefficients.—Solvents were purified as described in Part I.

(*a*) *Methylphenanthroline*. Eight independent measurements were made of the concentrations of both the aqueous and the organic phase (by spectrophotometry) after buffers of pH 7 each of ionic strength adjusted to 0·1M with potassium chloride and each containing 5—10 ml. of 0·01% 2-methylphenanthroline in a total volume of 25 ml. had been equilibrated with 10 ml. of carbon tetrachloride in a thermostat-bath at 25°. The average value for the distribution coefficient was $p_L = 5{\cdot}30 \pm 0{\cdot}18$. The results of similar measurements with chloroform (10 determinations) and n-hexane (12 determinations) are summarised in Table 2.

(*b*) 2,9-*Dimethylphenanthroline*. Ten determinations of the partition coefficient of this ligand between n-hexane and buffers of pH 5 or 10 gave $p_L = 0{\cdot}95 \pm 0{\cdot}05$. A second series

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[2] Orgel, " Introduction to Transition Metal Chemistry," Methuen, London, 1960.

[3] Irving and Mellor, preceding paper.

[4] Irving, Cabell, and Mellor, *J.*, 1953, 3417.

[5] Case, *J. Amer. Chem. Soc.*, 1948, **70**, 3994.

in which the concentration of reagent in each layer was determined spectrophotometrically after equilibration between n-hexane and seven different buffers covering the range pH 3·67—8·84 gave $p_L = 0{\cdot}90 \pm 0{\cdot}05$ and $K_a = 10^{5{\cdot}8}$. This value was adopted. Similar measurements (28 determinations) with carbon tetrachloride gave $p_L = 3{\cdot}6 \pm 1{\cdot}1$. No explanation was found for the low reproducibility and this solvent was not used in subsequent work with dimethylphenanthroline.

Measurements of Stability Constants.—The procedures described in Part I were adopted and the results are recorded in Table 1. The superscripts designate different series of experiments with different initial total concentrations of ligand (C_L) and metal (C_M). Equal phase volumes (10 ml.) were used except in the last three determinations (distinguished by an asterisk) where the volume of the aqueous phase was increased fivefold.

RESULTS

Table 2 summarises the features of the absorption spectra of the reagents (supplementing the data of Table 1 in ref. 4) and gives values for the acid dissociation constants and partition coefficients of the two ligands. As expected, the introduction of methyl groups into the phenanthroline ring (pK_a 4·95) has a base-strengthening effect. Although the wide range of values for the distribution coefficient of 2-methylphenanthroline (3820—0·22) implies that

TABLE 2.

Partition coefficients and spectral data for ligand bases.

Medium	$\lambda_{max.}$	$10^4\varepsilon$	p_L (pH 7 and μ in 0·1M-KCl or -KNO$_3$)
2-Methylphenanthroline.			p*K* 5·42.
Water, pH 9·0	268	2·94	
Water, pH 1·5	276	2·88	
Chloroform ...	268	3·01	3820 ± 130
CCl_4	268	3·09	5·30 ± 0·18
n-Hexane	266	3·19	0·22 ± 0·01

Medium	$\lambda_{max.}$	$10^4\varepsilon$	p_L (pH 7 and μ in 0·1M-KCl or -KNO$_3$)
2,9-Dimethylphenanthroline.			p*K* 5·85.
Water, pH 10·0	270·5	3·04	
Water, pH 2·01	283	2·94	
CCl_4	271	2·90	3·6 ± 1·1
n-Hexane	268·5	2·96	0·90 ± 0·03

TABLE 3.

Stability constants of complexes of bivalent cations with 2-methyl-1,10-phenanthroline.

Method *	*I*	*T*	p*K* of HL$^+$	log K_1	log K_2	log β_2	log K_3	log β_3	Ref.
Manganese									
dist.	0·1M-KCl	25°	5·42	3·0	2·5	5·5	2·4	7·9	†
Iron									
dist.	0·1M-KCl	25	5·42	4·2	3·6	7·8	3·0	10·8	4
Cobalt									
dist.	0·1M-KCl	25	5·42	5·1	4·9	10·0	3·9	13·9	†
Nickel									
dist.	0·1M-KCl	25	5·42	5·95	6·85	11·8	4·9	16·7	†
Copper									
redox.	0·1M-K_2SO_4	25	5·30	—	6·20	—	—	—	6
spect. comp. ‡	—	—	—	—	6·21	—	—	—	6
dist.	0·1M-KCl	25	5·42	7·40	6·45	13·85	—	—	†
Zinc									
dist.	0·1M-KCl	25	5·42	4·96	4·40	9·36	$3{\cdot}3_5$	12·7	†
Cadmium									
dist.	0·1M-KNO_3	25	5·42	5·15	4·50	9·65	3·65	13·3	†

* In this and Table 4, dist. refers to the present distribution method; redox to the method described in ref. 6; spect. to spectrophotometry; and spect. comp. to the method described in ref. 8 in a footnote (cf. ref. 7). † Present paper. ‡ It is not clear what method was used although reference is made to ref. 8.

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[6] James and Williams, *J.*, 1961, 2007.

[7] *Chem. Soc. Special Publ.*, No. 6, London, 1957.

[8] Irving and Mellor, *J.*, 1955, 3457.

values of pL can be measured over a very wide range (cf. Part I), the situation with 2,9-dimethylphenanthroline was less favourable. Since the complexes are so weak a high concentration of ligand is required in the aqueous phase in order to increase the degree of complex formation, $\bar{n}$. This involves the use of concentrated solutions of the ligand, a high pH, or an organic solvent for which the distribution is in favour of the aqueous phase. Although the value of p_L for n-hexane was reasonably low (0·9), we failed to find an organic solvent with an even lower partition coefficient but optically transparent in the region where the ligand absorbed strongly. Carbon tetrachloride had an appreciably higher distribution coefficient but, apart from this, the poor reproducibility of measurements (which had not been found in work with 2-methylphenanthroline) led us to reject it even for measurements at low $\bar{n}$ values.

TABLE 4.

Stability constants of complexes of bivalent cations with 2,9-dimethyl-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									
dist.	0·1M-KCl	25°	5·85	$\leqslant$3 ‡	—	—	—	—	†
Iron									
dist.	0·1M-KCl	25	5·85	$\leqslant$4 §	—	—	—	—	†
Cobalt									
dist.	0·1M-KCl	25	5·85	4·2	2·8	7·0			
Nickel									
spect.	(0·5M)	25 ± 2	—	2·6 to 2·8	—	—	—	—	9
dist.	0·1M-KCl	25	5·85	5·0	3·5	8·5	—	—	†
Copper									
redox.	0·1M-K_2SO_4	25	5·88	~6·1	~5·6	11·7	—	—	6
dist.	0·1M-KCl	25	5·85	5·2	5·8	11·0^5	—	—	†
Zinc									
gl.¶	0·1M-KNO_3	25	6·15	3·1	—	—	—	—	10
dist.	0·1M-KNO_3	25	5·85	4·1	3·6	7·7	—	—	†
Cadmium									
gl.	0·1M-KNO_3	25	6·15	2·8	—	—	—	—	10
dist.	0·1M-KNO_3	25	5·85	4·1	3·3	7·4	~3·0	~10·4	†

* See Table 3. † Present work. ‡ $\bar{n}$ had only reached 0·03 when pL = 3·07. § $\bar{n}$ had only reached 0·04 when pL = 3·9. ¶ Potentiometric determination with a glass electrode.

Unlike the measurements reported for bipyridyl and 1,10-phenanthroline in Part I, where comparison could be made with results obtained by other workers using the same or different techniques, few results are available to supplement those now reported in Tables 3 and 4. Indeed, for 2-methylphenanthroline, the only additional datum is that for the copper complex where the values log K_2 = 6·20 by a redox procedure and 6·21 for some form of spectrophotometric procedure have recently been reported.[6] The agreement with our value of 6·45 is satisfactory. Our value log β_2 = 11·05 for the system copper(II)–2,9-dimethylphenanthroline (Table 4) is somewhat lower than that (11·7) found by a redox method;[6] while the values there reported for log K_1 and log K_2 are similar to ours they imply that $K_1 > K_2$ in contrast to our findings (see below). It is not easy to assess the reliance to be placed on stability constants obtained by James and Williams's procedure[6] since the ligand reacts with both cupric and cuprous ions to produce a change in the redox potential which is the primary measured quantity. Perrin[11] has drawn attention to difficulties that may arise if $K_1 = K_2$ (and *a fortiori* if $K_2 > K_1$) and notes that " this method does not provide a very good internal check in the consistency of the results."

DISCUSSION

The introduction of first one and then a second methyl group adjacent to the nitrogen atoms of 1,10-phenanthroline (pK 4·98) increases the basic strength (to pK 5·42 and 5·85, respectively). Were no other factor involved we could reasonably predict a similar increase in the strength of the 1 : 1 metal complexes.[12] Under ideal circumstances plots

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[9] Sone and Kato, *Naturwiss.*, 1958, **45**, 10.

[10] Yasuda, Sone, and Yamasaki, *J. Phys. Chem.*, 1956, **60**, 1667.

[11] Perrin, *J.*, 1962, 1351.

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

of log $K_{\mathrm{M(phenan)}}$ against log $K_{\mathrm{M(mephen)}}$ or log $K_{\mathrm{M(dimephen)}}$ (where phenan, mephen, and dimephen stand for the three reagents, respectively) for any of the metals examined should take the form of straight lines of unit slope and intercepts $(5{\cdot}42 - 4{\cdot}98) = 0{\cdot}44$ and $(5{\cdot}85 - 4{\cdot}98) = 0{\cdot}87$, respectively. These " theoretical " straight lines are shown in Fig. 1 where the horizontal displacement of the experimentally determined stability constants is a measure of the destabilisation caused by steric hindrance to co-ordination. This destabilisation increases along the series Mn (1 log unit), Fe (1·7), Co (1·9), Ni (2·7), Cu (2·3) and is largest for nickel and copper and least for cadmium. With dimethylphenanthroline the steric hindrance is appreciably greater [Mn ($\geqslant$1 log unit), Fe ($\geqslant$1·9), Co(2·8), Ni (1·6), Cu (4·5), Zn (2·4), and Cd (1·9)] and again shows a minimum value for cadmium. It is reasonable to suppose that the lower steric hindrance in complexes of cadmium is associated with its appreciably greater ionic radius. However, what is most striking, and perhaps unexpected, is that the steric effect of the methyl groups is observable in values of K_1, *i.e.*, not when, as might be expected, two bulky organic molecules are mutually repelling each other in positions round the central ion but when only the first molecule of organic ligand is involved. The steric hindrance must occur between the organic molecule and the hydration shell of the aquated ion. Similar effects are to be found (though they have not hitherto been commented upon) when the first molecule of an N-alkylethylenediamine or 8-hydroxy-2-methylquinoline reacts with metals.[7,13]

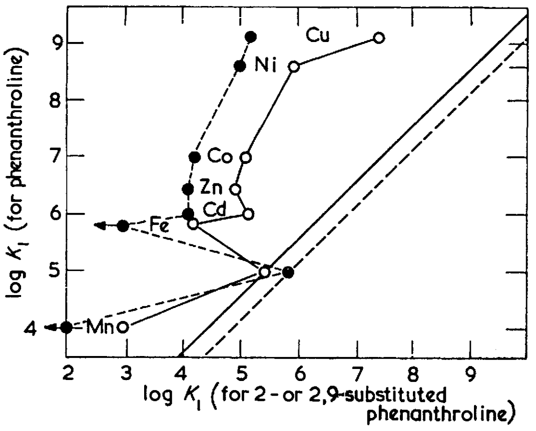

FIG. 1. Comparison of the stabilities of complexes of 1,10-phenanthroline with those of 2-methyl- (○) and 2,9-dimethyl-1,10-phenanthroline (●).

The extent of the steric hindrance when a second organic ligand becomes attached can be estimated from values of the ratio K_1/K_2 shown in Table 5. It is unfortunate that these values necessarily involve differences between stability constants that are themselves subject to errors of uncertain magnitude (cf. Tables 4 and 5 of Part I,[3] and data in ref. 7). However, it can hardly be coincidental that those which are the most reliable suggest that there is *not* any sudden increase in steric hindrance when a second molecule of 2-methylphenanthroline is co-ordinated, at least as compared with the similar situation arising when a second molecule of phenanthroline is co-ordinated to a 1 : 1 complex. The situation seems more clear-cut for 2,9-dimethylphenanthroline with cobalt and nickel, but not with zinc or cadmium. The most interesting new feature is the behaviour of copper.

With both the sterically hindering reagents there is a definite stop in the formation curve when $\bar{n}$ approaches 2. With 1,10-phenanthroline itself a third molecule becomes attached at high ligand concentration. Our measurements with copper and dimethylphenanthroline were not as detailed as we should now wish, but the form of the rather steep formation curve can only be reproduced if $K_1 < K_2$. This behaviour is supported by

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[13] Irving, Feigl Anniversary Symposium, *Analyt. Chim. Acta*, in the press.

TABLE 5.

Values of log (K_1/K_2) for various metal–ligand systems.

	Mn	Fe	Co	Ni	Cu	Zn	Cd
Ethylenediamine	0·7	1·0	1·7	1·2	1·5	1·0	1·0
Phenanthroline	0·5	0·6	0·3	0·5	2·4	0·8	0·9
2-Methylphenanthroline	0·5	0·6	0·2	0·9	1·0	0·6	0·7
2,9-Dimethylphenanthroline ...	?	?	1·4	1·5	−0·6	0·5	0·8

the value for the mid-point slope [14] and, most convincingly, by the fact that a plot of $(\bar{n}/[L])$ against [L] is not monotonic and decreasing but passes through a maximum (Table 6). This is diagnostic of an "abnormal" relationship in the values of successive stability constants and can be shown to occur with data for the system silver–ammonia and iron(II)–1,10-phenanthroline.[15]

TABLE 6.

Proof of the abnormal order $K_1 < K_2$ for complexes of copper and dimethylphenanthroline.

$\bar{n}$	0·46	0·48	0·60	0·90	1·31	1·71	1·90
$10^{-5}(\bar{n}/[L])$	3·04	3·10	3·16	3·62	2·93	1·36	0·33

The new results certainly suggest that the co-ordination of the second molecule of ligand to copper(II) becomes progressively easier as methyl groups are introduced in positions where steric hindrance to the formation of a coplanar complex would be severe. Jørgensen has already produced evidence (cf. Part I) in favour of the hypothesis that the second molecule of phenanthroline itself becomes co-ordinated in the *cis*- rather than in the *trans*-position where the four nitrogen atoms would be coplanar. We may suppose that the effect of the methyl groups is to cause a progressive distortion towards tetrahedral bond orbitals. This is supported by studies of the absorption spectra of the relevant complexes.[16] James, Parris, and Williams [16] suggest that the change from octahedral to tetrahedral co-ordination occurs on the addition of the first ligand and state that this is consistent with the spectroscopic evidence and supported by the stability data. We agree with the conclusions but not with the evidence on which they are based. Qualitatively we may picture that repulsion between the first molecule of co-ordinated ligand and the water shell (which increases with increasing methyl substitution, as shown by the decreasing values of log K_1) facilitates entry of the second molecule in a plane at right angles to itself (*i.e.*, by use of sp^3-orbitals) to such an extent that the quotient K_1/K_2 decreases and eventually becomes less than one.

In contrast to the behaviour of iron(II) and 1,10-phenanthroline (Part I), where the co-ordination of the third molecule of ligand is accompanied by rearrangement of the atomic electrons to give a deep red, diamagnetic, spin-paired complex, tris-2-methylphenanthrolineiron(II) has now been found to be paramagnetic. If we consider the effect of an increasing ligand field upon the energy levels of the ferrous ion (Fig. 5 in ref. 17) it is clear that the value of $10Dq$ for 1,10-phenanthroline must be such as to force all six d-electrons to pair off in the three t_{2g}-orbitals. We have shown in Part I that this takes place only when the third molecule of base is co-ordinated to the 2 : 1 complex and that in consequence $K_1 > K_2 \ll K_3$. With 2-methyl-1,10-phenanthroline the sequence of stabilities is normal, with $K_1 > K_2 > K_3$, and all the values of log K_n are lower than corresponding values for phenanthroline. It must follow that the steric hindrance to co-ordination prevents close approach of the ligand to the central ion and that the ligand field only assumes some lower value where the smaller separation of t_{2g}- and e_g-energy levels may be represented by some situation well to the left of Fig. 5 of ref. 17. Here electron

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[14] Irving and Rossotti, *J.*, 1953, 3397.

[15] Irving, *J.*, 1962, 4056.

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

[17] Irving, Internat. Conf. on Co-ordination Compounds, London, 1959; *Chem. Soc. Special Publ.*, No. 13, 1960.

pairing is not favoured energetically and a paramagnetic complex results. The low value of 10*Dq* is consistent with the absorption spectrum of the feebly yellow complex.

The formation curves (Figs. 2 and 3) for the complexes studied in the present paper, and the values for stability constants given in Tables 3 and 4, confirm the Irving–Williams order for both ligands and for values of log K_1 and log K_2. We have not examined the possibility that zinc may form a 3 : 1 complex with 2,9-dimethylphenanthroline although preliminary experiments suggest that it behaves like cadmium. Further discussion of our results for copper and other transition metals, with special reference to ligand field stabilisation and the Jahn–Teller effect, has appeared elsewhere.[6,16]

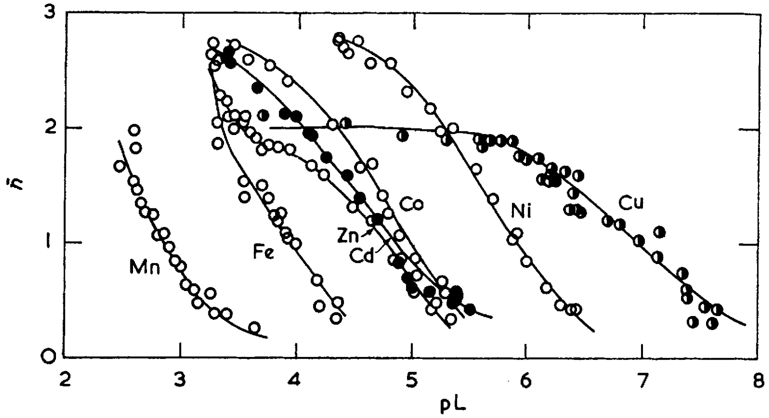

FIG. 2. Formation curves for complexes of bivalent ions with 2-methyl-1,10-, phenanthroline.

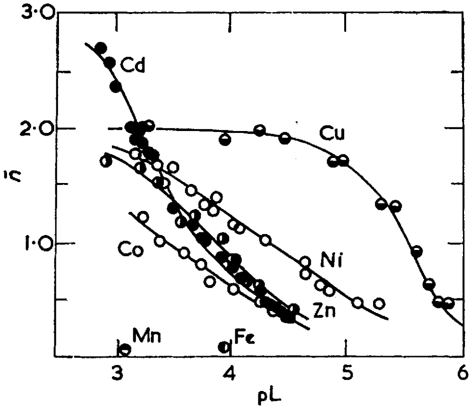

FIG. 3. Formation curves for complexes of bivalent ions with 2,9-dimethyl-1,10-phenanthroline.

It has now been demonstrated in Parts I and II that introducing one, and more especially two, substituents next to the nitrogen atoms of phenanthroline reduces the stability (relative to phenanthroline) of all the complexes formed with bivalent cations and also the chance of forming a 3 : 1 complex with octahedral co-ordination. Of all these bivalent elements, copper alone is readily reduced to a univalent state where it can form tetrahedral complexes with $4s4p^3$-orbitals. With a bidentate ligand such as phenanthroline or its analogues (*e.g.*, bipyridyl, biquinolyl, etc.) the two molecules of ligand become co-ordinated in planes at right angles, and models show that bulky α-substituents now have no adverse steric effects. It is thus clear why, in the presence of a mild reducing agent such as hydroxylamine, a reagent such as 2,9-dimethylphenanthroline, 6,6′-dimethyl-2,2′-bipyridyl, or biquinolyl is " specific " for copper and can be used for its absorptiometric determination even in the presence of large amounts of transition metals which, for steric reasons, are unable to form stable and coloured complexes. To obtain the most sensitive reagent (*i.e.*, one with the largest practicable molecular extinction coefficient) an increase in the number of aromatic rings in the chelated complex will be advantageous, but care must be taken not to introduce substituents in the bipyridyl skeleton which will interfere with the coplanarity of the resonating ring system.[6,18]

The only other bivalent metal of the first long Period that commonly forms tetrahedral bonds and might therefore interfere is zinc. Since its complexes with 2,9-dimethylphenanthroline and its analogues are colourless, the absorptiometric determination of copper will not be adversely affected provided a sufficient excess of reagent is present. The extent to which zinc can interfere in the " cuproin " reaction does not appear to have been adequately investigated.

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[*Received, May 8th,* 1962.]

[18] Irving and Hampton, *J.*, 1955, 430.