553. *Oxidation–Reduction Potentials of Metal Complexes in Water. Part II.*[1] *Copper Complexes with* 2,9-*Dimethyl- and* 2-*Chloro*-1,10-*phenanthroline.*

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Standard oxidation–reduction potentials for the copper complexes of 2,9-dimethyl- and 2-chloro-1,10-phenanthroline have been determined, and the relative contributions of enthalpy and entropy to these potentials have been assessed. Thermodynamic stability constants for the 1 : 1 and 1 : 2 copper(II) and zinc complexes, and the 1 : 1 iron(II) complex, with 2,9-dimethyl-1,10-phenanthroline suggest that in 1 : 1 complexes the 2- and the 9-methyl groups interfere sterically with water molecules occupying any co-ordination sites lying in the same plane around the metal ion.

The highest oxidation–reduction potential so far recorded for corresponding pairs of copper(I) and copper(II) complexes is that for the 1 : 2 complexes of 2,9-dimethyl-1,10-phenanthroline: the formal potential[2] at $I = 0{\cdot}3$ is 0·594 v. That this value is elevated above the potentials of copper complexes with other substituted 1,10-phenanthrolines (representing enhanced relative stability of the cuprous state) has been attributed[2] to steric interaction of the 2- and the 9-methyl group in different ligand molecules, which prevents the 1 : 2 cupric complex from adopting an energetically preferred square-planar or a vertically distorted octahedral structure.

In view of the importance of 2,9-dimethyl-1,10-phenanthroline and related compounds as analytical reagents for the determination of copper as copper(I),[3] we have examined the system in more detail. We also determined the relative contributions of enthalpy and entropy to the oxidation–reduction potentials of 2,9-dimethyl- and 2-chloro-1,10-phenanthroline; such information has not previously been available for a copper(II)–copper(I) complex couple.

Experimental

2-Chloro-1,10-phenanthroline[4] recrystallised from benzene as pale fawn needles, m. p. 130° (lit.,[4] 130°) (Found: C, 67·2; H, 3·3; N, 13·0. Calc. for $C_{12}H_7ClN_2$: C, 67·1; H, 3·3; N, 13·05%). 2,9-Dimethyl-1,10-phenanthroline (Fluka, "Puriss.") and the remaining reagents ("AnalaR" grade) were used without purification.

Bis-(2,9-*dimethyl*-1,10-*phenanthroline*)*copper*(I) *Sulphate Pentahydrate*.—Copper(II) sulphate pentahydrate (0·862 g.), dissolved in water (5 ml.), was added to a suspension of 2,9-dimethyl-1,10-phenanthroline hemihydrate (1·5 g.) in water (100 ml.). The mixture was stirred until dissolution was complete. Sodium sulphite (0·9 g. of heptahydrate in 5 ml. of water) was added dropwise, with stirring, to the solution, from which orange-red needles of the *copper*(I) *complex*

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[1] Part I, Hawkins and Perrin, *J.*, 1962, 1351.

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

[3] Smith and McCurdy, *Analyt. Chem.*, 1952, **24**. 371.

[4] Halcrow and Kermack, *J.*, 1946, 155.

were then precipitated. Recrystallisation from 10% aqueous ethanol gave 1·37 g. of product (Found: C, 58·85; H, 5·15; N, 9·7. $C_{56}H_{48}Cu_2N_8O_4S,5H_2O$ requires C, 58·7; H, 5·1; N, 9·8%).

Bis-(2-*chloro*-1,10-*phenanthroline*)*copper*(I) *Sulphate Pentahydrate*.—A solution of copper sulphate (0·87 g.) and 2-chloro-1,10-phenanthroline, treated with sodium sulphite solution as described above, yielded dark red plates of the corresponding 2-*chloro-complex* (1·4 g.) which recrystallised from 50% aqueous ethanol (Found: C, 49·3; H, 3·3; N, 9·6. $C_{48}H_{28}Cl_4Cu_2N_8O_4S,5H_2O$ requires C, 49·2; H, 3·3; N, 9·6%).

Apparatus and Methods.—The cell used for the potential measurements was a cylindrical, glass, flanged beaker of about 200-ml. capacity, closed by a rigid Polythene top which was sealed to the beaker with soft petroleum jelly and clipped in position to make the vessel air-tight. Through the top passed " Quickfit " ground-glass sockets carrying two gold electrodes (cleaned with concentrated nitric acid to which had been added a drop of concentrated hydrochloric acid), an adjustable glass rod from which hung a platinum cage, a thermometer, an " Agla " micrometer syringe, a gas-inlet tube, and a gas-outlet tube passing through a water-trap. The cell was connected to an external saturated calomel electrode by an 0·1M-potassium chloride bridge, the ends of which were plugged with tightly rolled Whatman 542 filter-paper. The potentiometer was a Tinsley type 4046B instrument, easily readable to 0·1 mv, and was used with a Cambridge " spot " galvanometer.

A solid bis(substituted phenanthroline)copper(I) complex was weighed in a small platinum boat which was placed in the platinum cage in the " up " position. After the solution of copper sulphate and the ligand in the cell had been deoxygenated by passing oxygen-free nitrogen through the solution for 1 hr. the platinum cage was lowered into the solution and the copper(I) complex was dissolved by stirring (magnetically) and gentle warming. The cell was brought to the desired temperature, and the electrodes were inserted. For ionic strengths greater than 0·01, sodium sulphate was incorporated in the original copper sulphate–ligand solution: otherwise the ionic strength of the solution was varied by adding oxygen-free 0·1M-sodium sulphate. After each addition, the solution was stirred by bubbling nitrogen through it. It was then allowed to come to equilibrium with the electrode for 10 min. Nitrogen was passed continuously over the surface of the solution. Readings were taken immediately after the insertion of the salt bridge; this was then withdrawn from the solution and its outside was thoroughly washed and dried. The process was repeated at 5-min. intervals until constancy was obtained (usually, two measurements were sufficient). The potentials for the two gold electrodes at each reading agreed to within 0·1 mv. To evaluate the experimental results, it was necessary to know the potential of the saturated calomel electrode, including the liquid-junction potential due to the 0·1M-potassium chloride bridge. This was measured against a 0·01M-hydrochloric acid–quinhydrone electrode, at least 40 hr. being allowed for electrode equilibration at each temperature. The potential, E_q, of this quinhydrone electrode was calculated from the equation,

$$E_q = E_q^\circ + (\boldsymbol{RT}/\boldsymbol{F}) \ln a_{H^+},$$

with published values for E_q°,[5] and $f_{\pm(HCl)}$.[6] Details are summarised in Table 1.

TABLE 1.

Potential of the saturated calomel electrode, $E_{s.c.}$, with an 0·1M-potassium chloride bridge.

Temperature	10°	20°	30°
E_q°, in volts *	0·71073	0·70343	0·69607
$f_\pm$ for 0·01M-HCl †	0·9055	0·9052	0·9034
$2·3026\boldsymbol{RT}/\boldsymbol{F}$	0·056182	0·058165	0·060149
E_q, in volts	0·5959	0·5846	0·5731
Measured E for sat. cal.//quin.	0·3312	0·3292	0·3240
$E_{s.c.}$ with 0·1M-KCl bridge	0·2647	0·2554	0·2491

* Ref. 5. † Ref. 6.

Because the copper(II) and copper(I) complexes of 2,9-dimethyl- and 2-chloro-1,10-phenanthroline have maximum co-ordination numbers of 4,[2] and the 1 : 2 complexes have high

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[5] Clark, " Oxidation–Reduction Potentials of Organic Systems," Williams and Wilkins Co., Baltimore, 1960, p. 363.

[6] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 2nd edn., 1950, p. 547.

stability constants, in aqueous solutions containing an excess of ligand the oxidation–reduction potential is that of the fully formed 1 : 2 complexes. Hence, the standard oxidation–reduction potential, $E^\circ_{\mathrm{CuL_2^{2+},CuL_2^+}}$, where L is the uncharged ligand, can be determined from the equation,

$$E_{\mathrm{obs}} + (\boldsymbol{RT/F})\ln([\mathrm{CuL_2^+}]/[\mathrm{CuL_2^{2+}}]) = E^\circ_{\mathrm{CuL_2^{2+},CuL_2^+}} - (6\cdot9078A\boldsymbol{RT/F})\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})\} - E_{\mathrm{s.c.}}, \qquad (1)$$

which is derived from the Nernst equation and the Güntelberg [7] expression,

$$-\log f_{\mathrm{i}} = Az_{\mathrm{i}}^2 I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}),$$

for the activity coefficient of an ion of charge z. In this equation, square brackets denote concentrations, A is a Debye–Hückel–Onsager parameter ($A = 0\cdot4989$, $0\cdot5070$, $0\cdot5161$, at 10°, 20°, and 30°, respectively [8]), and I is the ionic strength. The Güntelberg expression is a good approximation at ionic strengths less than 0·1,[9] so that by plotting the left-hand side of equation (1) against $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ the standard potential should be obtained from the intercept of a straight line with the potential axis.

Stability constants of metal complexes were obtained from pH titrations by graphical solution of the equation,

$$\frac{\bar{n}}{(1-\bar{n})[\mathrm{L}]} = K_1 + \frac{(2-\bar{n})[\mathrm{L}]}{(1-\bar{n})}\beta_2,$$

where $\bar{n}$ is Bjerrum's "formation function," and K_1 and β_2 are the stability constants of the 1 : 1 and 1 : 2 complexes. The pH-meter was an Electrometer model 33B (Electronic Instruments Ltd.), which could be read to 0·001 pH unit; its output was also applied to a Rectiriter recording milliammeter (Texas Instruments Inc.). The electrodes used were internally shielded glass and saturated calomel.

RESULTS and DISCUSSION

In the present work, interference by species such as chloride or sulphite ions has been avoided by using pure 1 : 2 copper(I)–(substituted phenanthroline) complexes.

Results of potential measurements at three temperatures are summarised in Figs. 1 and 2. The slopes of the lines are the theoretical values from equation 1. Formal potentials at $I = 0\cdot15$ for both couples, and at $I = 0\cdot075$ for the dimethylphenanthroline couple, also lie on these lines. Standard oxidation–reduction potentials (referred to the hydrogen electrode) obtained from these lines are given in Table 2, together with the formal potentials at $I = 0\cdot15$.

TABLE 2.

Standard and formal oxidation–reduction potentials of 1 : 2 copper complexes of 2,9-dimethyl- and 2-chloro-1,10-phenanthroline.

	E°, in volts			E_f, in volts	
1,10-Phenanthroline deriv.	10°	20°	30°	20°, $I = 0\cdot15$	25°, $I = 0\cdot3$
2,9-Dimethyl	0·6233	0·6240	0·6248	0·5992	0·594 *
2-Chloro	0·4668	0·4668	0·4666	0·4412	0·400 *

* Ref. 2.

Changes of standard entropy, ΔS°, and enthalpy, ΔH°, for the oxidation–reduction equilibria were calculated from

$$-\Delta G^\circ = -\Delta H^\circ + T\Delta S^\circ.$$

For both the 2,9-dimethyl- and the 2-chloro-1,10-phenanthroline couple the changes of standard entropy are small ($\Delta S^\circ = 1\cdot8$ and ~ 0 e.u., respectively), indicating that the oxidation–reduction potentials are due mainly to enthalpy terms. The change of standard enthalpy for the first of these couples, −13·88 kcal., is 3 kcal. more negative than that of the second, −10·76 kcal. Because the complexes of the same oxidation state for the two

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[7] Güntelberg, *Z. phys. Chem.*, 1926, **123**, 199.

[8] Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publns., London, 2nd edn., 1959, p. 468.

[9] Ref. 8, p. 231.

couples are of similar size and charge, hydrational effects are unlikely to contribute significantly to this difference in ΔH° values. This leaves ligational enthalpy as the major factor in accounting for the difference, which is probably due, mainly, to differences in steric interactions in the copper(II) complexes. To facilitate discussion of such steric effects, stepwise formation constants have been obtained for some metal complexes of 2,9-dimethyl-1,10-phenanthroline. These results are summarised in Table 3.

Bivalent metal ions of the first transition series are believed to exist in aqueous solution mainly in the form, $M(H_2O)_6^{2+}$, in which six water molecules are disposed octahedrally around the metal ion (except that, because of the Jahn–Teller effect, this structure is vertically distorted in the hydrated cupric ion). Formation of bis-complexes, ML_2, with bidentate ligands such as 1,10-phenanthroline, may result in *cis*- and *trans*-configurations (A) and (B). Leybold atomic models show that the hydrogen atoms at positions 2 and 9 of

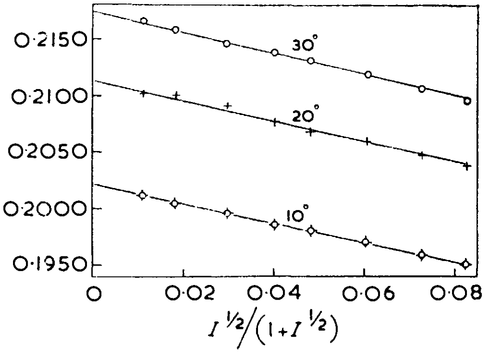


FIG. 1.

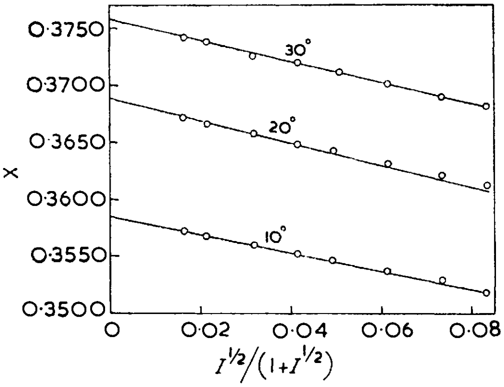


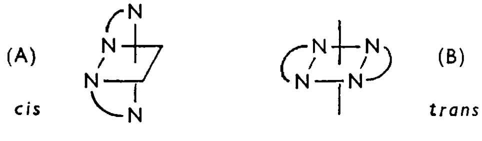
FIG. 2.

FIG. 1. Determination of standard oxidation–reduction potential for the 1 : 2 copper complexes of 2,9-dimethyl-1,10-phenanthroline (DMP). The ionic strength of an aqueous solution of copper sulphate (5×10^{-5}M), bis-DMP-copper(I) sulphate ($2{\cdot}5 \times 10^{-5}$M), and DMP (2×10^{-4}M) was adjusted with sodium sulphate (0·1M).

The quantity $X = E_{\text{obs.}} + \frac{RT}{F} \ln \frac{[CuL_2^{2+}]}{[CuL_2^{+}]}$, in volts.

FIG. 2. Determination of standard oxidation–reduction potential for the 1 : 2 copper complexes of 2-chloro-1,10-phenanthroline, ClP. The ionic strength of an aqueous solution of copper sulphate ($2{\cdot}5 \times 10^{-5}$M), ClP ($1{\cdot}25 \times 10^{-4}$M), and bis-ClP-copper(I) sulphate (○ = $1{\cdot}25 \times 10^{-5}$M; + = $6{\cdot}25 \times 10^{-6}$M) was adjusted with sodium sulphate (0·1M).

X, as for Fig. 1.



pairs of 1,10-phenanthroline molecules are in contact in the *trans*-form of the bis-(1,10-phenanthroline)copper(II) complex, and Jørgensen [10] has postulated, on spectroscopic evidence, that this complex exists in the *cis*-configuration. Steric hindrance is greatly increased by the introduction of 2- and 9-substituents,[11] preventing *trans*-complex formation. The bulkiness of the chloro- and methyl groups limits the number of ways in which 2-chloro- and 2-methyl-1,10-phenanthroline can be disposed in their *cis*-complexes and (according

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

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

TABLE 3.

Thermodynamic stepwise formation constants of metal complexes of 2,9-dimethyl-1,10-phenanthroline.

(At ionic strengths less than 0·004 and on the basis of $-\log f_i = Az_i^2I^{\frac{1}{2}}$.)

Cation	pH range	$\bar{n}$	T (c)	log K_1	log K_2	Titration (see below)
Cu^{2+}	3·39—4·63	0·43—1·24	15°	6·36	5·49	a
Cu^{2+}	3·67—5·09	0·50—1·39	20	6·19	5·36	b
Cu^{2+}	3·31—4·46	1·06—1·66	20	6·28	5·58	e
Cu^{2+}	3·84—4·67	0·56—1·17	30	5·99	5·31	c
Cu^{2+}	3·97—4·98	0·59—1·27	42	5·82	5·09	d
Fe^{2+}	4·69—6·36	0·04—0·32	20	2·79	—	f
Zn^{2+}	4·32—5·72	0·13—1·25	20	3·40	4·43	g

Acid dissociation constant, pK_a° (mean ± max. deviation) *

15°	20°	30°	42°
5·814 ± 0·026	5·785 ± 0·025	5·715 ± 0·042	5·598 ± 0·026

* By titration of 10^{-3}M-solution; evaluated over 9/10ths of the titration by the complete Henderson–Hasselbach equation with activity-coefficient corrections.

Titration data used in obtaining stability constants

$[Cu(NO_3)_2] = 5 \times 10^{-5}$M, $[L]_T = 10^{-4}$M, titrated with 0·1M-$HClO_4$.

(a) At 15°.

pH	4·625	4·427	4·280	4·166	4·073	3·928	3·816	3·725	3·616	3·527	3·454	3·390
−log [L]	5·642	5·773	5·875	5·955	6·021	6·123	6·207	6·278	6·360	6·434	6·490	6·546
$\bar{n}$	1·237	1·128	1·044	0·970	0·908	0·800	0·720	0·658	0·575	0·523	0·461	0·430

(b) At 20°.

pH	5·089	4·741	4·515	4·353	4·227	4·125	4·039	3·968	3·848	3·752	3·672
−log [L]	5·308	5·516	5·663	5·770	5·857	5·929	5·991	6·038	6·126	6·195	6·154
$\bar{n}$	1·390	1·235	1·113	1·010	0·926	0·855	0·798	0·734	0·644	0·564	0·499

(c) At 30°.

pH	4·666	4·465	4·316	4·199	4·103	3·955	3·838
−log [L]	5·476	5·604	5·702	5·781	5·847	5·947	6·035
$\bar{n}$	1·172	1·048	0·945	0·857	0·783	0·647	0·558

(d) At 42°.

pH ...	4·980	4·680	4·479	4·330	4·213	4·117	3·969
−log [L]	5·157	5·337	5·462	5·558	5·634	5·698	5·793
$\bar{n}$	1·273	1·133	1·007	0·898	0·803	0·720	0·593

(e) At 20°. $[Cu(NO_3)_2] = 5 \times 10^{-4}$M, $[L]_T = 10^{-3}$M, $[H_2SO_4] = 5 \times 10^{-4}$M, titrated with 0·1M-KOH. pK_a of H_2SO_4 taken as 1·87.

pH	3·309	3·375	3·451	3·538	3·641	3·768	3·928	4·143	4·463
−log [L]	5·867	5·803	5·755	5·701	5·638	5·575	5·464	5·337	5·151
$\bar{n}$	1·066	1·116	1·168	1·228	1·295	1·367	1·451	1·548	1·660

(f) At 20°. $[FeSO_4] = 4 \times 10^{-4}$M, $[L]_T = 10^{-3}$M, titrated with 0·1M-HCl. Log K_1 was constant within ±0·08 over the accessible range of $\bar{n}$ (hydrolysis occurs in less acid solution) so that no estimate of K_2 could be obtained.

pH	6·362	6·243	6·134	6·032	5·938	5·845	5·754	5·662
−log [L]	3·184	3·202	3·229	3·263	3·297	3·339	3·384	3·434
$\bar{n}$	0·320	0·264	0·239	0·228	0·213	0·208	0·201	0·195
pH	5·570	5·475	5·375	5·269	5·153	5·022	4·870	4·686
−log [L]	3·489	3·549	3·617	3·694	3·783	3·888	4·018	4·182
$\bar{n}$	0·184	0·170	0·155	0·135	0·113	0·094	0·067	0·041

(g) At 20°. $[Zn(ClO_4)_2] = 5 \times 10^{-4}$M, $[L]_T = 10^{-3}$M, titrated with 0·1M-HCl.

pH	5·719	5·592	5·479	5·377	5·283	5·195	5·110	5·030
−log [L]	3·793	3·826	3·863	3·901	3·939	3·977	4·018	4·059
$\bar{n}$	1·254	1·181	1·107	1·033	0·957	0·880	0·803	0·724
pH	4·952	4·872	4·792	4·709	4·623	4·531	4·430	4·319
−log [L]	4·101	4·148	4·197	4·253	4·313	4·382	4·462	4·555
$\bar{n}$	0·645	0·567	0·489	0·412	0·337	0·264	0·196	0·134

Titrations (a), (b), (c), and (d) of copper(II) solutions were carried out under comparable conditions, and were used in obtaining estimates of entropy changes for the reactions, from the relation, $d(\boldsymbol{R}T \ln K)/(dT = -\Delta S$. Values of log K_1 and log K_2 from these titrations are believed to be accurate to within about ±0·05 logarithm unit. Results from titration (e) are less reliable because of the more limited range of $\bar{n}$ and because of the need to correct for incomplete ionisation of sulphuric acid.

to atomic models) formation of the *cis*-complex of 2,9-dimethyl-1,10-phenanthroline with copper(II) ion is prevented. Bis-(2,9-dimethyl-1,10-phenanthroline)copper(II) probably has a configuration intermediate between *cis*-octahedral and tetrahedral.

It had been thought that steric effects would be unimportant in the formation of 1 : 1 metal complexes of 2,9-dimethyl-1,10-phenanthroline. If so, the stability constants of these complexes might be expected to be greater than those of 1,10-phenanthroline itself. This is because, in related ligands, log K_1 usually increases with the pK_a of the ligand (because similar factors govern σ-bonding by metal ions and protons). Thus, Banks and Bystroff [12] found, for 1 : 1 ferrous complexes of some 5-substituted-1,10-phenanthrolines, log $K_1 \approx 0{\cdot}596\mathrm{p}K_a + 2{\cdot}93$. The experimental values of log K_1 (4·2 [11] and 2·80, respectively) for the ferrous complexes of 2-methyl- and 2,9-dimethyl-1,10-phenanthroline (pK_a 5·42 [11] and 5·785) indicate stabilities of only 1/100 and 1/3000 of those predicted by the equation. Similarly, the 1 : 1 copper(II) and zinc complexes of 2,9-dimethyl-1,10-phenanthroline have values of log K_1 about 3 logarithm units less than for the unsubstituted phenanthroline complexes.[12] Atomic models suggest that this drop is due to a steric effect: the methyl groups need to occupy positions round the metal ion which are normally filled by water molecules. Thus, with phenanthrolines unsubstituted in positions 2 or 9, only two water molecules have to be removed in forming a 1 : 1 complex according to the equation, $\mathrm{M(H_2O)_6}^{2+} + \mathrm{L} \rightleftharpoons \mathrm{ML(H_2O)_4}^{2+} + 2\mathrm{H_2O}$, leaving two water molecules in the plane of the organic ligand. With 2-methylphenanthroline one of these water molecules, and with 2,9-dimethylphenanthroline both of these water molecules, must be displaced in forming a 1 : 1 complex. In the latter case, it is possible that one of these water molecules may remain in an intermediate position in the plane, giving a trigonal bipyramidal structure. For copper(II) ion, formation of the 1 : 2 complex requires the loss of most of the ligand-field stabilisation associated with the 1 : 1 complex, as well as leading to gross distortion from an octahedral structure. Both steps in complex formation thus include energetically unfavourable processes and hence lead to lower stability constants than would be expected. The temperature-dependence of $\boldsymbol{R}T$ log K_1 and $\boldsymbol{R}T$ log K_2 for these copper(II) complexes shows that little net entropy change ($\Delta S = 0 \pm 5$, 4 ± 5 e.u., respectively) occurs in these reactions.

That log K_2 for the zinc complex of 2,9-dimethyl-1,10-phenanthroline is greater than log K_1 accords with results for the zinc ammines, where a similar increase has been attributed to the increasing relative stability of the tetrahedral configuration as one passes from the octahedral $\mathrm{Zn(H_2O)_6}^{2+}$ ion.[13] The steric strains discussed above are unimportant in tetrahedral structures which are presumably adopted in the 1 : 2 complexes of zinc and copper(I). However, this simple explanation fails to explain why the normal sequence, $K_1 > K_2$, is found for zinc complexes with ethylenediamine and some other diamines.

The stability constant, β_2^{I}, of the bis-(2,9-dimethyl-1,10-phenanthroline)copper(I) complex at 20° and $I = 0{\cdot}15$ (mainly sodium sulphate) was calculated from the identity [14]

$$E^\circ_{\mathrm{CuL_2^{2+},CuL_2^{+}}} = E^\circ_{\mathrm{Cu^{2+},Cu^{+}}} - 2{\cdot}3026(\boldsymbol{R}T/\boldsymbol{F})(\log \beta_{\mathrm{Cu^{2+}}} - \log \beta_{\mathrm{Cu^{+}}}),$$

with $E^\circ_{\mathrm{Cu^{2+},Cu^{+}}} = 0{\cdot}164$ v at 20° (calculated from Fenwick's value,[15] 0·167 v at 25°, with correction for the small entropy change [16]), and log $\beta_2^{\mathrm{II}} = 11{\cdot}63$ (obtained by pH-titration). The value, log $\beta_2^{\mathrm{I}} = 19{\cdot}54$ at 20°, agrees reasonably with the similarly determined one of 19·1 at 25° and $I = 0{\cdot}3$, reported by James and Williams.[2] It is greater than for similar complexes with 2-chloro-, 2-methyl-, and unsubstituted 1,10-phenanthroline,[2] as expected from the greater basicity of the ligand. Attempts to obtain

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[12] Banks and Bystroff, *J. Amer. Chem. Soc.*, 1959, **81**, 6153.

[13] Orgel, " An Introduction to Transition-Metal Chemistry," Methuens, London, 1960, p. 82.

[14] Perrin, *J.*, 1959, 290.

[15] Fenwick, *J. Amer. Chem. Soc.*, 1926, **48**, 860.

[16] Hugus, *J. Amer. Chem. Soc.*, 1951, **73**, 5459; Wagman, *ibid.*, p. 5463; Latimer, " Oxidation Potentials," Prentice-Hall, New York, 1952, p. 184.

log K_2, and hence log K_1, by rapid-reaction spectrophotometric measurements on fully formed complex solutions added to solutions of varying acid concentration were unsuccessful.

Stability constants of some bivalent cations with 2,9-dimethyl-1,10-phenanthroline at 25° and $I = 0{\cdot}1$, obtained by a distribution method, have recently been reported.[17] Although log β_2 (= 7·7) for the 1 : 2 zinc complex agrees with the present result, log $K_1 = 4{\cdot}1$ and log $K_2 = 3{\cdot}6$ are, respectively, 0·7 logarithm unit higher and 0·8 logarithm unit lower than our values which, in turn, support the figure, log $K_1 = 3{\cdot}1$, reported[18] from potentiometric titrations at 25° in 0·1M-KNO_3. Similarly, our results for copper(II) complexes accord with log $K_1 = {\sim}6{\cdot}1$, log $K_2 = {\sim}5{\cdot}6$, at 25° in 0·1M-K_2SO_4, from redox measurements,[2] but not with the recent values,[17] log $K_1 = 5{\cdot}2$, log $K_2 = 5{\cdot}8$. The causes of the discrepancies, which may be due to differences inherent in the potentiometric and the distribution method, are not known.

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