383. *The Oxidation–Reduction Potentials of Some Copper Complexes.*

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A method is described for determining the formal oxidation–reduction potentials of cuprous–cupric complexes. It is applied to a large number of copper complexes, mostly with 1,10-phenanthrolines, bipyridyls, and other nitrogenous bases. For a series of complexes with differently substituted phenanthrolines and bipyridyls the redox potentials are not simply related to the acid dissociation constants of the ligands. The effect of change of co-ordination number of the ions upon the redox potentials is described, and the causes of changes in co-ordination number are discussed.

THIS paper describes the determination of the oxidation–reduction potentials of a number of copper complexes. As in a previous paper on ferrous–ferric couples[1] the potentials measured are formal mid-point potentials, E'_f. They refer to reversible potentials in a solution of equal concentrations of the oxidised and the reduced form of the element, here cupric and cuprous ions respectively, at some fixed pH and ionic strength. No account has been taken of activity coefficients. (E'_f is the measured potential at an undefined degree of formation of the two complexes $Cu^{I}L_x$ and $Cu^{II}L_y$; $E_f{}^*$ refers to equal degrees of formation of the two complexes; $E_f{}^0$ is the standard potential, traditionally defined.) From the variations of potential with pH, the degree of complex formation is found so that the potentials, $E_f{}^*$, for equal co-ordination of the two ions can be calculated.

EXPERIMENTAL

The procedure for determination of ferrous–ferric couples[1] was modified for cuprous–cupric couples. In the earlier work ferrous and ferric ions were introduced into an acid solution and in a chloride medium. Before the addition of the solid ligand to the solution (from a glass basket) all oxygen was removed from the cell dead-space. Cuprous ions disproportionate in aqueous solution and can only be stabilised by complex formation. In the present series of experiments therefore we made up cupric ion and ligand solutions separately and these were first put into the titration cell.[1] The final cupric-ion concentration was $1{\cdot}75 \times 10^{-4}$M; the ligand concentration depended on the system being investigated but was always at least 3·5 times the total copper concentration. The cuprous ion, as a weighed amount of cuprous chloride, was placed in a short-necked thin-glass bulb which floated on the surface of the cupric ion–ligand solution and was kept vertical by a glass rod which passed through an air-tight gland in the cell-cap. Pushing the rod enabled the bulb to be broken on the bottom of the titration cell. Before de-oxygenation of the cell and its contents the cupric–ligand solution was adjusted to a high pH, if necessary by the addition of sodium hydroxide. It was found advisable to bring the pH of the solution to about one unit above the acid dissociation constant, pK_a, of the ligand so that when the cuprous ion was added to the solution it was converted into its complex and did not disproportionate. The solution and dead-space of the cell were swept free from oxygen as described earlier.[1] This usually required 2—4 hr., after which time the bulb containing cuprous chloride was broken. The cuprous salt dissolved only slowly, especially in purely aqueous media, and the system was usually left overnight (about 12 hr.) before measurements were started. The pH and the E'_f of the solution were measured and subsequently a series of similar measurements were made over a wide range of pH.[1] The pH was adjusted by the addition of concentrated acid or alkali from a microsyringe. Generally the ionic strength of the solutions was held constant by making the aqueous solutions 0·1M in potassium sulphate and the water–dioxan solutions 0·3M in potassium nitrate. Sulphate or nitrate was chosen as a background salt as other anions were known either to form strong complexes with cuprous ions (*e.g.*, chloride), or to give insoluble precipitates with the metal complexes (*e.g.*, perchlorate forms an insoluble cuprous–phenanthroline complex). With both the amino-acid and

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* Some of the results and part of the discussion in this paper were described at the Co-ordination Chemistry Conference in London, 1959. A summary appeared in the Abstracts of the Conference.

[1] Tomkinson and Williams, *J.*, 1958, 2010.

saturated amine systems (see below), ligand concentrations up to 1·25M were employed; the ionic strength is thus higher in these systems. Concentrations of ligands and ionic strengths are given in footnotes to the Tables.

Materials.—" AnalaR " dioxan was purified as described before.[1] Standard cupric solutions were made up by weighing " AnalaR " copper sulphate pentahydrate. Cuprous chloride was prepared by reduction of cupric chloride with aqueous sodium sulphite: [2] the white crystalline salt was stable indefinitely in a vacuum-desiccator.

Most of the phenanthrolines were obtained from the G. F. Smith Chemical Company, a few from British Drug Houses Ltd. They were recrystallised from hot water or benzene–light petroleum until the m. p.s agreed with those given by Smith *et al.*[3] 2-Methyl- and 2-chloro-1,10-phenanthroline had been prepared previously in this laboratory.[4] We prepared 5-aminophenanthroline by reducing an alcoholic solution of the 5-nitro-compound with stannous chloride,[5] and the 4,7-dichloro-compound from the dihydroxy-compound by using phosphorus pentachloride.[6] In contrast to Synder and Freier's report [6] we isolated the dichloro-compound as a white solid which sublimed at about 240° (Found: Cl, 28·75. Calc. for $C_{12}H_6Cl_2N_2$: Cl, 28·4%). The 5-amino-compound was characterised by the spectrum of its 3 : 1 complex with ferrous ion, in agreement with Wilkins *et al.*[5] Wilkins *et al.*[5] also reported that the cuprous 2 : 1 complex with 5-aminophenanthroline is colourless. We found that the complex in 50% water–dioxan has an absorption maximum at 461 mμ (ε 6120). McCurdy *et al.*[7] stated that the intensely orange 2 : 1 complex of cuprous ion and 4,7-diphenyl-1,10-phenanthroline is converted into a colourless monocomplex at pH $<$ 7·0; we found that the 2 : 1 coloured complex existed even at pH 2·0. We cannot explain these discrepancies.

2,2′-Bipyridyl was obtained from British Drug Houses Ltd.; the dimethyl and diphenyl derivatives were obtained from the G. F. Smith Chemical Company.[8] The 4,4′-dicarboxy-derivative was prepared by oxidation of the dimethyl compound [9] and was characterised by the spectrum of the ferrous complex; [10] esterification gave the diethyl ester.[11] 2,2′-Bipyridyl-3,3′-dicarboxylic acid was prepared by oxidation of 1,10-phenanthroline by Bannick and Smith's method.[10] The properties of these compounds agreed with those in the literature. Other bipyridyls were prepared and characterised by Professor G. M. Badger.[12] 2,2′-Biquinolyl was a product from Hopkin and Williams Ltd. We are grateful to Dr. R. G. Wilkins (University of Sheffield) for a gift of 2,2′,2″-terpyridine. Morpholine (L. Light and Co.) was re-distilled before use; pyridine, quinoline, and aniline were redistilled commercial products. Other nitrogen-donor ligands and amino-acids were B.D.H. products, except diglycylglycine which was obtained from Roche Products Ltd.

" AnalaR " salts were used for buffers, and were dissolved in boiled-out water. The glass electrode was calibrated at pH 4·00 (25°) by 0·05M-potassium trihydrogen diphthalate, and at pH 9·185 (25°) by 0·05M-sodium borate.

Approximately 3N-sodium hydroxide (carbonate-free) was used as titrant in all the pH-titrations and in most of the redox experiments. " AnalaR " potassium trihydrogen diphthalate was the primary standard.

RESULTS AND DISCUSSION

The theory of the method has been given earlier.[1] To illustrate its application we refer to Fig. 1, which consists of a series of plots of the measured potential E'_f against the pH meter reading, pB, for solutions of equal amounts of cuprous and cupric ion in the presence of excess of particular phenanthrolines. The curves consist of four parts. First, at W (highest pB), E_f is independent of pB. Here $\bar{n}_H$, the degree of formation of the

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[2] *Inorg. Synth.*, 1946, **2**, 1.

[3] Smith and Banick, *Talanta*, 1959, **2**, 348.

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

[5] Wilkins, Schilt, and Smith, *Analyt. Chem.*, 1955, **27**, 1574.

[6] Snyder and Freier, *J. Amer. Chem. Soc.*, 1946, **68**, 1320.

[7] McCurdy and Smith, *Analyst*, 1952, **77**, 418, 846.

[8] Smith and Richter, " Phenanthroline Indicators," G. F. Smith Chem. Co., Columbus, Ohio, 1944, where a general discussion of many phenanthrolines and bipyridyls is given.

[9] Case, *J. Amer. Chem. Soc.*, 1946, **68**, 2574.

[10] Bannick and Smith, *Analyt. Chim. Acta*, 1958, **19**, 304.

[11] Case and Maerker, *J. Amer. Chem. Soc.*, 1958, **80**, 2745.

[12] Badger, *J.*, 1956, 616.

acid HL (where L is the phenanthroline), is zero. The pB is well above the pK_a of the ligand. The theoretical slope of the plot,

$$d(E'_f)/d(pB) = -\bar{n}_H\{\bar{n}_{II} - \bar{n}_I\}$$

is also zero. As pB is lowered the concentration of free ligand becomes dependent on hydrogen-ion concentration (*i.e.* on pB), the pK_a value is approached, and $\bar{n}_H$ becomes significantly greater than zero. $d(E'_f)/d(pB)$ takes on a real value, *i.e.*, greater than zero, approaching -1 as $\bar{n}_H$ reaches unity. Hence, over the second region, X, $(\bar{n}_{II} - \bar{n}_I) = 1{\cdot}0$; and as $\bar{n}_I = 2{\cdot}0$ (this is known independently), $\bar{n}_{II} = 3{\cdot}0$. At immediately lower pB values the slope $d(E'_f)/d(pB)$ approaches zero, $(\bar{n}_{II} - \bar{n}_I) = 0{\cdot}0$ (the third part of the plot, Y), and then becomes positive, reaching a value corresponding to $(\bar{n}_{II} - \bar{n}_I) = -1{\cdot}0$ (the fourth part of the plot, Z). For the cuprous–cupric systems we were unable to continue the titrations to still lower $\bar{n}$ values (degrees of complex formation), as the cuprous ion disproportionates. However, we have sufficient information to obtain both a large number of $E_f{}^*$ values and, by using these and the slopes of the redox curves, the stability constants for cupric complexes. In all cases simple acid–base titrations were carried out on the ligand to determine pK_a values at the appropriate ionic strength, and in some cases the stability constants of cupric complexes were measured separately by standard methods in experiments separate from the redox titrations. The source of data in the Tables is noted.

FIG. 1.

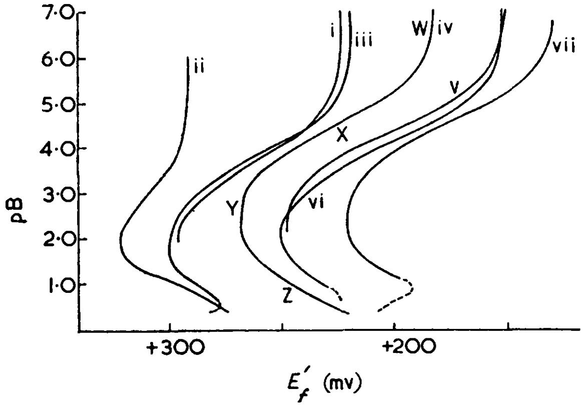

FIG. 2.

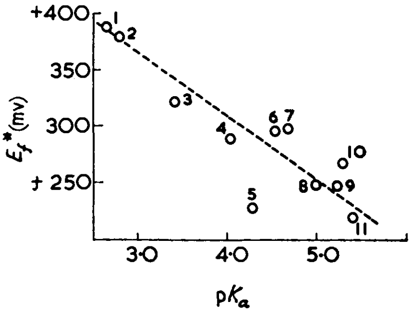

FIG. 1. *Redox potential*–pB *curves for a series of copper phenanthroline complexes in* 50% *dioxan–water solution. The phenanthrolines are*: i, *unsubstituted*; ii, 5-*chloro*; iii, 5-*methyl*; iv, 3,5,6,8-*tetramethyl*; v, 5,6-*dimethyl*; vi, 5-*amino*, vii, 4,7-*dimethyl*.

FIG. 2. *Dependence of the copper–phenanthroline couple potentials,* 2 : 1 *complexes, on the basicity of the ligands. The ligands are phenanthrolines, viz.*: (1) 4,7-*dichloro*; (2) 5-*nitro*; (3) 5-*chloro*; (4) 5-*phenyl*; (5) 4,7-*diphenyl*; (6) *unsubstituted*; (7) 5-*methyl*; (8) 5,6-*dimethyl*; (9) 5-*amino*; (10) 3,5,6,8-*tetramethyl*; (11) 4,7-*dimethyl*.

The results will be given under the heading of the different ligands.

Water.—The standard reduction potential, $E_f{}^0$, of the Cu^{II}–Cu^{I} pair in water at an acid pH is given by Latimer [13] as 0·167 v. We have determined an experimental value of 0·148 v in 0·01N-sulphuric acid at 25° with 0·1M-potassium sulphate salt background: the potentials of a series of solutions, 10^{-2}M in Cu^{II} and of varying Cu^{I} concentration up to 10^{-4}M, were measured. In all cases the concentration of cuprous ion in solution was determined by using the 2,9-dimethylphenanthroline complex. No disproportionation occurred and the Nernst expression for potentials was obeyed. Extrapolation of the straight-line plot to equal concentrations of Cu^{II} and Cu^{I} gives the required $E_f{}^0$ potential.

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[13] Latimer, "Oxidation Potentials," Prentice-Hall, New York, 1958, p. 175.

By a similar procedure the value of this potential in 50% dioxan–water is found to be 0·250 ± 0·01 v.

Phenanthrolines.—(a) *Substituents in* 3,4,5-*positions.* The most extensive series of measurements have been carried out on a group of substituted phenanthroline complexes. Most of these measurements were made in 50% dioxan–water. The potential–pH relations showed that in nearly all cases both cuprous and cupric ions formed complexes ML_2, but that at high free-ligand concentrations (high pB) the cupric ion gave a $Cu^{II}L_3$ complex (Fig. 1). The formal mid-point potentials, E_f*, of the ML_2 couples are given in Table 1 and the stability constants of some of the complexes in Table 2. The pK_a values of the ligands are included in Table 3. In Fig. 2 the E_f* (ML_2) values are plotted against pK_a. The lower valency state is stabilised relative to the higher at lower pK_a values, as found for the Fe^{II}–Fe^{III} pairs. The copper–phenanthroline potentials fall either above or below the value (0·25 v) for the hydrate pair in the mixed solvent. Taken together with

TABLE 1. *Copper* 1,10-*phenanthroline couples.*

Potentials are expressed in millivolts and are the values determined at the degrees of formation indicated in parentheses, *i.e.*, E_f' ($\bar{n}_{II} : \bar{n}_I$).

Aqueous

Subst. in ligand	pK_a	E_f* (2 : 2)
Unsubst.	4·97	+174
2-Cl	4·20	+400
2-Me	5·30	+337
2,9-Me_2	5·88	+594

50% Dioxan–water

Subst. in ligand	pK_a	E_f* (2 : 2)
Unsubst.	4·53	+296
4,7-Cl_2	~2·65	+387
5-NO_2	2·80	+379
5-Cl	3·43	+321
5-Ph	4·03	+291
4,7-Ph_2	4·30	+229
5-Me	4·65	+299
5,6-Me_2	5·00	+250
5-NH_2	5·23	+248
3,5,6,8-Me_4	5·30	+268
4,7-Me_2	5·40	+220

In all the measurements with these ligands and those of Table 4 (see Tables 1—5), the following conditions were maintained: total ligand = $1·125 \times 10^{-3}$M; total cupric and total cuprous = $1·75 \times 10^{-4}$M. Ionic strength as stated in the text.

TABLE 2. *Stability constants for copper* 1,10-*phenanthrolines.*

Aqueous

Subst. in ligand	log K_1^{II}	log K_2^{II}	log β_2^{II}	log K_3^{II}	log β_2^{I}
Unsubst.		6·64[e]		4·94	15·82 *
				4·90[e]	
,,	8·82[f]	6·57[f]	15·39[f]	5·02	
2-Cl	5·60	4·85	10·45		14·6
2-Me		6·20			16·95 *
		6·21[e]			
,,	7·4	6·4	13·8		
2,9-Me_2	~6·1	~5·6	11·7		19·1

50% Dioxan–water

Subst. in ligand	log K_2^{II}	log β_2^{II}	log K_3^{II}	~log β_2^{I}/β_2^{II}	log β_2^{I}
Unsubst.			4·50	+0·77	
4,7-Cl_2		~10·2[f]	3·25	+2·28	~12·5
5-NO_2			3·25	+2·15	
5-Cl		~11·0[f]	3·72	+1·18	~12·2
5-Ph			4·05	+0·68	
4,7-Ph_2	~5·7		3·75	−0·35	
5-Me	~6·9		4·60	+0·81	
5,6-Me_2	7·15		4·93	0·0	
5-NH_2			5·02	−0·03	
3,5,6,8-Me_4	7·30		4·75	+0·30	
4,7-Me_2	~7·20		4·86	−0·50	

* Calculated from value for log β_2^{II} (Bjerrum, Schwarzenbach, and Sillén, "Stability Constants, Part I," *Chem. Soc. Spec. Publ. No.* 11, 1956). [e] Determined by spectrophotometric method.[4] [f] Determined by pH titration of cupric complex.

the effect of basicity of the ligand upon the potential, this result implies that the unsaturated nature of phenanthrolines stabilises cuprous with respect to cupric ion, but that the greater donor power of the phenanthroline-nitrogen atoms than of water stabilises cupric with respect to cuprous. A very similar situation was observed for iron complexes. It is not permissible, then, to say generally that phenanthrolines stabilise low-valency states though it does seem safe to conclude that increase in π-acceptor strength of phenanthrolines stabilises low-valent and increase in σ-donor strength of phenanthrolines stabilises high-valent complexes. On the other hand, a detailed inspection of Fig. 2 shows that even this generalisation is not applicable in a comparison between individual pairs of substituted phenanthrolines. Low potentials are observed for the systems with a 4- or 5-phenyl substituent. However, we believe that steric hindrance is present in these ligand molecules themselves.

TABLE 3. *Acid dissociation constants.*

(A) *Aqueous solution*

Ligand	$\mathrm{p}K_{\mathrm{NH^+}}$	$\mathrm{p}K_{\mathrm{CO_2H}}$	Lit.
(a) *Subst. in* 1,10-*phenanthrolines*			
Unsubst.	4·97 ± 0·02		4·96 (*a*)
5-NO_2	3·25 ± 0·10		(3·57) (*b*)
2-Cl	4·20 ± 0·02		
2-Me	5·30 ± 0·05		5·42 (*c*)
3,5,6,8-Me_4	5·80 ± 0·05		(5·54) (*d*)
2,9-Me_2	5·88 ± 0·02		(6·17) (*c*
(b) *Subst. in* 2,2′-*bipyridyls*			
Unsubst.	4·50 ± 0·02		4·44 (*c*)
4,4′-Me_2	5·45 ± 0·02		
4,4′-$(CO_2H)_2$		$\mathrm{p}K_1K_2 \sim 7{\cdot}6$	
3,3′-$(CO_2H)_2$	$\leqslant$3·0	3·0 4·63	
(c) *Other* N *bases*			
2,2′,2″-Terpyridine	3·99; 4·69		7·1; 7·1 (*e*)
Pyridine	5·52 ± 0·03		5·45 (*f*)
Quinoline	5·18 ± 0·05		
Aniline	4·80 ± 0·05		4·62 (*g*)
Ammonia			~9·0 (*h*)
Ethylenediamine	7·30 ± 0·05 9·83 ± 0·03		7·49 10·18 (*i*)
Morpholine	8·58 ± 0·03		8·70 (*f*)
Piperidine	11·25		11·28 (*f*)
Imidazole	7·01 ± 0·01		7·12 (*j*)

Ligand	$\mathrm{p}K_{\mathrm{NH^+}}$	$\mathrm{p}K_{\mathrm{CO_2H}}$	Lit.
(d) *Amino-acids*			
Glycine	9·53 ± 0·03	<3·0	9·62; 2·43 (*k*)
α-Alanine	9·62 ± 0·02	<3·0	(9·87; 2·34) (*l*)
Sarcosine	9·73 ± 0·03	<3·0	10·01; 2·24 (*k*)
Diglycylglycine	8·02 ± 0·02	3·30 ± 0·05	(8·09; 3·22) (*m*)
Polysarcosine	~8·7		
Histidine	6·16 9·05 ± 0·02	<3·0	6·05; 9·17 (*n*) (1·82) (*c*)

	$\mathrm{p}K_{\mathrm{NH^+}}$	$\mathrm{p}K_{\mathrm{SH}}$	$\mathrm{p}K_{\mathrm{CO_2H}}$	Lit.
(e) *Sulphur compounds*				
L-Cysteine	8·11	10·02	<3·0	8·48; 10·55 (*n*)
2-Mercaptoethylamine	8·30	10·95		8·35; 10·81 (*n*)
Thioglycollic acid		10·18 ±0·04	3·45 ±0·03	9·78; 3·58 (*n*)
Benzylidenebisthioglycollic acid			3·09 3·98	
Ethylenebisthioglycollic acid			3·19 3·81	

(f) *Arsenic compound*	p*K* values of the CO_2H groups	Lit.
Phenylarsinediacetic acid	3·61; 4·93	3·60; 5·03 at 20° (*p*)

TABLE 3. (*Continued.*)

(B) 50% v/v *Dioxan–water*

Ligand	pK_{NH^+}	Extrapolated val. for H_2O obtained by Smith (*d*)
(a) *Subst. in* 1,10-*phenanthrolines*		
Unsubst. ...	4·53 ± 0·03	(4·86)
4,7-Cl_2	2·65 ± 0·10	(3·03)
5-NO_2.........	2·80 ± 0·05	(3·57)
5-Cl	3·43 ± 0·03	
5-Ph	4·03 ± 0·03	(4·72)
4,7-Ph_2	4·30 ± 0·05	(4·84)
5-Me	4·65 ± 0·05	(5·23)
5,6-Me_2	5·00 ± 0·03	
5-NH_2	5·23 ± 0·03	
3,5,6,8-Me_4	5·30 ± 0·02	
4,7-Me_2	5·40 ± 0·02	pK_{OH}
4,7-$(OH)_2$ ...	11·5 ± 0·1	7·28 ± 0·03 2·55 ± 0·05
(b) 2,2′-*Biquinolyl*	3·10 ± 0·10 3·64 (75% EtOH) (*q*)	

Ligand	pK_{NH^+}	
(c) *Subst. in* 2,2′-*bipyridyls*		
Unsubst.	3·62 ± 0·02	
5,5′-$(CO_2Et)_2$ ...	0·85 (spectra)	
5,5′-$(CO_2Me)_2$ ...	—	
4,4′-$(CO_2Et)_2$ ...	2·45 ± 0·10	
4,4′-Ph_2	3·25 ± 0·05	
5,5′-Me_2	3·97 ± 0·03	
4,4′-$(phenethyl)_2$	3·98 ± 0·05	
6,6′-Me_2...........	4·23 ± 0·02	
4,4′-Et_2...........	4·38 ± 0·02	
4,4′-Me_2...........	4·40 ± 0·03	
5,5′-Et_2-4,4′-Me_2	4·59 ± 0·03	
4,4′-$(CO_2H)_2$......		pK_{CO_2H} 4·25; 4·77
5,5′-$(CO_2H)_2$......		$pK_1 + pK_2 \sim 9·5$
(d) 8-Hydroxyquinoline (*r*)	4·13 ± 0·02	pK_{OH} 10·88 ± 0·03

References: (*a*) Pflaum and Brant, *J. Amer. Chem. Soc.*, 1954, **76**, 6215. (*b*) Brandt and Gullstrom, *ibid.*, 1952, **74**, 3532. (*c*) Ref. 4. (*d*) Schilt and Smith, *J. Phys. Chem.*, 1956, **60**, 1546. (*e*) Brandt and Wright, *J. Amer. Chem. Soc.*, 1954, **76**, 3082. (*f*) Bruehlman and Verhoek, *ibid.*, 1948, **70**, 1401. (*g*) Golumbic, *ibid.*, 1952, **74**, 5777. (*h*) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1947. (*i*) Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 307. (*j*) Edsall, Felsenfield, Goodman, and Gurd, *J. Amer. Chem. Soc.*, 1954, **76**, 3054. (*k*) Basolo and Chen, *ibid.*, 1954, **76**, 953. (*l*) Monk, *Trans. Faraday Soc.*, 1951, **47**, 292. (*m*) Evans and Monk, *ibid.*, 1955, **51**, 1244. (*n*) Li and Manning, *J. Amer. Chem. Soc.*, 1955, **77**, 5225. (*o*) Albert, *Biochem. J.*, 1952, **50** 690. (*p*) Pettit, D.Phil. Thesis, Oxford, 1960. (*q*) Peard and Pflaum, *J. Amer. Chem. Soc.*, 1958, **80**, 1593. (*r*) Ref. 1 gives pK_{NH^+} 4·08, pK_{OH} 10·82.

Herbstein and Schmidt[14] have shown that all the individual rings in benzo[*c*]phenanthrene (I) are distorted out of the conventional stereochemical formulation to give relief from the "overcrowding" of hydrogen atoms at positions 1 and 2 (Fig. 3) (this was pointed out to us by Dr. J. Halpern). By analogy with this system, a 4(7)- or 5(6)-phenyl substituent in phenanthroline cannot undergo free rotation about a bond *xy* (cf. II), so that such a phenyl group is out of the plane of the phenanthroline molecule and its mesomeric effects will be modified. No steric hindrance can occur in 4,4′-diphenyl-2,2′-bipyridyl (III) and the potential of the copper couple is, as expected, higher than that for the parent 2,2′-bipyridyl system (see Table 4). A consideration of the ligand pK_a values and the corresponding copper potentials shows that the effect of an "out of plane" phenyl group is not simple.

The plot of pK_a against $\log K_3^{II}$ for the cupric complexes shows a general dependence on pK_a, the strongest bases forming the strongest complexes (Fig. 4). The few $\log K_2^{II}$ and $\log \beta_2^{II}$ values obtained suggest that similar considerations apply to these complexes (Table 2). The cupric–phenylphenanthroline complexes have exceptionally low stability. Presumably there is a rough linearity between $\log \beta_2^{II}$ and pK_a of the form

$$\log \beta_2^{II} \simeq a \, . \, pK_a + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and similarly

$$\log \beta_2^{I} \simeq a' \, . \, pK_a + b' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Such relations would account for the change in E_f^* with pK_a if $a > a'$ and $b' < b$. In an earlier paper[15] we have pointed out that, where approximately linear relations such

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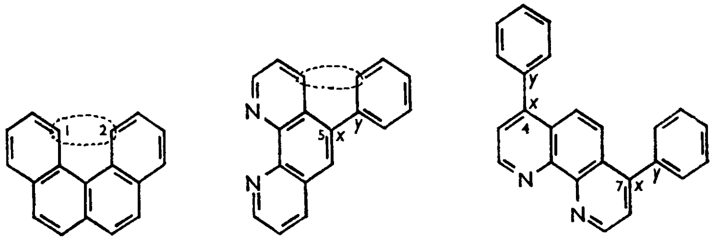
[14] Herbstein and Schmidt, *J.*, 1954, 3302.

[15] Jones, Poole, Tomkinson, and Williams, *J.*, 1958, 200.

as (1) and (2) are found, a is a useful measure of σ-acceptor strength and b a useful measure of π-donor strength of a cation.

(b) *Substituents in 2,9-positions.* 2,9-Substituents introduce considerable steric hindrance in the four-co-ordinate cupric complexes,[4,16] ML_2, which are usually planar. On the other hand, no steric hindrance is expected in the tetrahedral ML_2 cuprous complexes.[13] The potentials of the couples (Table 1) show how steric hindrance rather than basicity controls the relative stability of the two valency states. With these ligands no cupric complexes ML_3 were formed at the ligand concentrations used by us. The destabilisation of the Cu^{II} state is evident on examining the $\beta_2{}^{I}/\beta_2{}^{II}$ ratios and the lower stability of these cupric–phenanthroline complexes than of the parent-base complexes (Table 2). These sterically hindered complexes will be more fully discussed in a later paper.



(I) (II) (III)

FIG. 3. *Steric hindrance in some aromatomic hydrocarbons, see text.*

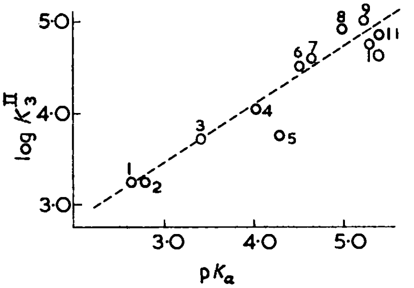


FIG. 4. *The third step stability constant,* $K_3{}^{II}$, *of a series of cupric complexes compared with the basicity of the ligands. The ligands are listed as for Fig. 2.*

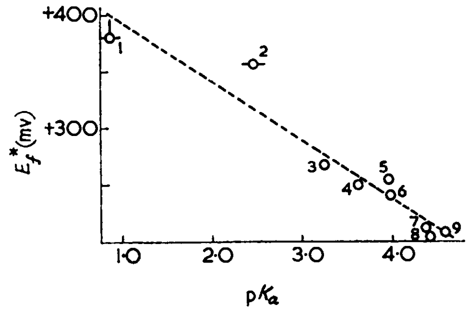


FIG. 5. *Dependence of the copper–bipyridyl couple potentials,* 2 : 1 *complexes, on the basicity of the ligands. The ligands are 2,2′-bipyridyls, viz.*: (1) *5,5′-diethoxycarbonyl*; (2) *4,4′-diethoxycarbonyl*; (3) *4,4′-diphenyl*; (4) *unsubstituted*; (5) *5,5′-dimethyl*; (6) *4,4′-diphenethyl*; (7) *4,4′-diethyl*; (8) *4,4′-dimethyl*; (9) *5,5′-diethyl-4,4′-dimethyl.*

The cuprous complexes with 2(9)-substituted phenanthrolines show increasing stability with increasing basicity (Table 2).

Bipyridyl.—The change of E_f^* with ligand basicity in the bipyridyl series (ML_2 complexes; Table 4) is similar to that for phenanthrolines (see Fig. 5). For a given value of pK_a the bipyridyl couple has much the lower potential, indicating that bipyridyls stabilise the cupric relative to the cuprous ion more than does the corresponding phenanthroline. We attribute this difference to the weaker π-acceptor character of bipyridyl consequent on its lower conjugation. On the other hand, the 2,2′,2″-terpyridine, which is more highly conjugated, does not stabilise the cuprous ion as effectively as bipyridyl. The former

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[16] Irving and Williams, *Analyst*, 1952, **77**, 813.

ligand, however, forms but a 1 : 1 complex with both the cuprous and the cupric ion: the Cu^{II} ion is co-ordinated to all three nitrogen atoms whereas this is unlikely for the Cu^{I} ion. This difference in co-ordination number would explain the strong stabilisation of the cupric state. 6,6′-Dimethyl-2,2′-bipyridyl and the similar ligand, 2,2′-biquinolyl, stabilise cuprous relative to cupric for much the same reason as that given for the relative stabilisation of cuprous by 2,9-substituted phenanthrolines. The rather limited number of stability constants determined for the copper bipyridyls indicates trends (Table 5) similar to those noted for the phenanthroline complexes.

TABLE 4. *Copper–bipyridyl couples.*

(A) *Aqueous*

Subst. in 2,2-bipyridyl	pK_a	E_f* (2 : 2)
Unsubst.	4·50	+120
4,4′-Me_2	5·45	+91
4,4′-$(CO_2^-)_2$	—	+150
		E_f* (1 : 1)
3,3′-$(CO_2^-)_2$		+213
(2,2′,2″-Terpyridine)	4·69, 3·99	−80

(B) 50% *Dioxan–water*

Subst. in 2,2′-bipyridyl	pK_a	E_f* (2 : 2)
Unsubst.	3·62	+251
5,5′-Et_2-4,4′-Me_2	4·59	+210
4,4′-Me_2	4·40	+204
4,4′-Et_2	4·38	+215
4,4-(Phenethyl)$_2$	3·98	+243
5,5′-Me_2	3·97	+251
4,4′-Ph_2	3·25	+269
4,4′-$(CO_2Et)_2$	~2·45	+357
5,5′-$(CO_2Et)_2$	0·85	~+380 ($\bar{n}_{II}$ ~2)
4,4′-$(CO_2^-)_2$		+234
4,4′-$(CO_2H)_2$		+300?
5,5′-$(CO_2^-)_2$		+234
6.6′-Me_2	4·23	>+750
(2,2′-Biquinolyl)	~3·10	~+770

TABLE 5. *Stability constants for copper bipyridyls.*

Aqueous

Ligand	log K_1^{II}	log K_2^{II}	log β_2^{II}	log K_3^{II}	log β_2^{I}
2,2′-Bipyridyl		~5·6		3·20	13·18 *
,,	8·15[f]	5·50[f]	13·65[f]	3·30[f]	
4,4′-Me_2 deriv.				3·72	

50% *Dioxan–water*

Ligand	log K_2^{II}	log β_2^{II}	log K_3^{II}	log β_2^{I}/β_2^{II}	log β_2^{I}
Subst. in 2,2′-bipyridyl					
Unsubst.	~5·25			0·0	
5,5′-$(CO_2Et)_2$				+2·17	
4,4′-$(CO_2Et)_2$		~9·6		+1·80	~11·4
4,4′-Ph_2				+0·30	
5,5′-Me_2	5·48			+0·10	
4,4′-(Phenethyl)$_2$				−0·10	
4,4′-Et_2	~6·2		~2·9	−0·58	
4,4′-Me_2			3·25	−0·77	
5,5′-Et_2·4,4′-Me_2			~3·25	−0·67	

	log K_1^{II}	log K_2^{II}	log β_2^{II}	log K_1^{I}	log β_2^{I}
6,6′-Me_2	4·88[f]	~2·6	~7·48		~15·8
(2,2′-Biquinolyl) (aq.)	4·27	3·46	7·73		~16·5
2,2′,2″-Terpyridine (aq.)	~13·0[e]			~9·3	

[e, f] See Table 2.

Other Nitrogen-donor Ligands.—Ammonia forms a 4 : 1 cupric complex and a 2 : 1 cuprous complex.[17] The measured E_f value, at 25° in a 2M-ammonium nitrate background at a high pH, where both complexes are fully formed, was +1 mv, in excellent agreement with a value of 0·00 obtained by Bjerrum [17] at 18°. Our result and the cupric stability constants determined at 25° by Spike *et al.*[18] lead to a calculated potential E_f* for the two 2 : 1 complexes of +308 mv, cuprous ion binding the ligand the more strongly.

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[17] Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 307.

[18] Spike and Parry, *J. Amer. Chem. Soc.*, 1953, **75**, 3770.

With ethylenediamine both ions form a 2 : 1 complex, but the cupric ion is four-co-ordinated whereas the cuprous ion is but two-co-ordinated. This explains the very low potential (Table 6) of this couple, compared with those of the phenanthroline and bipyridyl couples.

TABLE 6. *Copper systems with other nitrogen donors.* (*Aqueous*) E'_f ($\bar{n}_{\text{II}} : \bar{n}_{\text{I}}$) *values.*

Ligand	pK_a	$E'_f(1:2{\cdot}5)$	$E'_f(\bar{n}_{\text{I}} - \bar{n}_{\text{II}} = 2)$	E_f^* (3 : 3)	E_f^* (4 : 4)
Aniline	4·80	+240 (pL = 1·0)			
Quinoline	5·18	—	+351 (pL = 1·45)		
Pyridine	5·52	—	—	+304	~+300

Ligand	pK_a	E_f^* (2 : 2)	E'_f (4 : 2)
Ammonia ...	9·0	+308	+1 (pL ~0·0)
Ethylene-diamine ...	7·30, 9·83	−360	
Morpholine ...	8·58	+250	
Piperidine ...	~11·25	(+145)?	

Ligand	pK_a	E_f^* (2 : 2)
Glycine	9·53	−160
Alanine	9·62	−130
Sarcosine	9·73	~−130
8-Hydroxy-quinoline ...	4·13	~−375 *
Imidazole	7·01	+317
Histidine	9·05, 6·16	E'_f (2 : 1) = −170 †

* In 50% dioxan–water. † At pL ~2·5.

Measurements were made as follows: Total solution volume 80 ml. containing in each case total cupric = total cuprous = $1{\cdot}4 \times 10^{-5}$ moles and total ligand (in moles) pyridine $3{\cdot}0 \times 10^{-2}$, quinoline $1{\cdot}72 \times 10^{-2}$, aniline $8{\cdot}8 \times 10^{-3}$, morpholine $1{\cdot}28 \times 10^{-2}$, piperidine $8{\cdot}0 \times 10^{-2}$, ethylenediamine $8{\cdot}0 \times 10^{-2}$, glycine $9{\cdot}9 \times 10^{-2}$, alanine and sarcosine $9{\cdot}9 \times 10^{-2}$ (in these cases the ionic strength was not controlled during the titrations, *i.e.*, there was no added salt); imidazole $8{\cdot}0 \times 10^{-4}$, histidine $8{\cdot}0 \times 10^{-4}$, ethylenebisdithioglycollic acid $1{\cdot}0 \times 10^{-3}$, phenylarsinediacetic acid $1{\cdot}0 \times 10^{-3}$ (in these cases the ionic strength was held constant by the salt background of 0·1M-potassium sulphate). Stability constants in Table 7 refer to the same conditions.

For a similar reason glycine, α-alanine, and sarcosine give very low potentials. The substituted amines, aniline and morpholine, like ammonia, bind cuprous more strongly than cupric ions at low $\bar{n}$ values. The cupric complexes are weak and in the morpholine system $\bar{n}_{\text{II}}$ only just reached 3 even with 1·0M-ligand; the potentials measured in this solution are positive relative to the hydrate couple whereas at this ligand concentration in the case of ammonia the potential is strongly negative with respect to the hydrate couple. Any explanation of these differences depends upon an understanding of the co-ordination of the two ions and it is not sufficient to state that a donor ligand such as a primary amine stabilises the high-valent state. In pyridine solutions the co-ordination of the two copper ions is not very different over a wide range of pH, and the 3 : 1 and probably the 4 : 1 complexes of both ions are formed. The cuprous ion is stabilised relative to cupric at all $\bar{n}$ values. For unsaturated ligands, then, the co-ordination number of the cuprous ion appears to be four rather than two. In quinoline solutions the co-ordination of the cupric ion is restricted to $\bar{n} \leqslant 2$ but that of the larger cuprous ion again approaches four. We presume that steric hindrance reduces the stability of the cupric complexes. With quinoline, as with sterically hindered phenanthrolines and bipyridyls, the copper couple potential is high.

With the imidazoles there is no evidence of a higher complex than 2 : 1 of cuprous ion, but cupric ion forms a 3 : 1 and a 4 : 1 complex. The E_f^* (2 : 2) value shows that cuprous ion binds the ligand more strongly. Thus all the 2 : 1 copper complexes (with ammonia, pyridine, quinoline, aniline, morpholine, and imidazole) are more stable in the cuprous than the cupric form to about the same degree (~2 kcal./mole).

Histidine forms complexes with cupric and cuprous copper, but we and other workers[19] have found the systems somewhat complicated. Our work agrees with earlier findings[19] that at a high pH (pH ≈ 10 and pL ≈ 2·5) histidine forms a 2 : 1 chelate complex with cupric copper, presumably through the four nitrogen atoms. At the same pH the redox potential–pH curves (Fig. 6) indicate a 1 : 1 complex with the cuprous ion presumably co-ordinated through both the imino- and the amino-nitrogen atom. The potential of this system is very low (Table 6). At lower pH values (<7) it appears from the redox

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[19] Leberman and Rabin, *Nature*, 1959, **185**, 747.

potential–pH curve (Fig. 6) that a 2 : 1 histidine–cuprous complex exists and the co-ordination of the cupric ion is still two. The Cu$^{\rm I}$ cation is presumably bound only through imino-nitrogen atoms. This is expected from a comparison with the cuprous–imidazole system. When the concentration of histidine is the same as that of the total copper, the cupric ion forms a 1 : 1 complex which hydrolyses at high pH.[19] Stability constants for the complexes are included in Table 7.

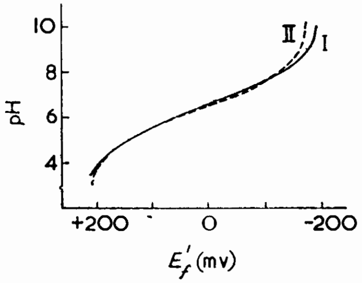

FIG. 6. *Redox potential–*pH *curves for copper–histidine complexes.* (I) *Total copper,* 3·5 × 10^{-4} *mole/l.*; *total ligand,* 10^{-2} *mole/l.* (II) *Total copper,* 3·1 × 10^{-3} *mole/l.*; *total ligand,* 10^{-2} *mole/l.*

Sulphur and Arsenic Ligands.—We have found from a study of absorption spectra that the anionic species of ethylenebisthioglycollic acid forms a monomeric 1 : 1 cupric complex; the species is very probably as inset. The exact nature of the cuprous species is uncertain, but at low pH's when the ligand is fully protonated the cuprous ion is co-ordinated only to sulphur. Potentials measured at pH 1—5 are all + ~400 mv, indicating considerable stabilisation of the cuprous state. We attribute this in part to π-bond formation between the vacant outer *d*-orbitals of the sulphur atom and the fully filled 3*d*-orbitals of the cuprous ion, and in part to polarisation. The full interpretation of the redox curve involves the " early " dissociation of the carboxyl groups in the cuprous complex, *i.e.*, they are titrated at a lower pH than they are in the uncomplexed ligand (see Tables 3 and 7).

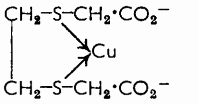

TABLE 7. *Stability constants of various copper complexes.*

Aqueous

Ligand	log$_{10}$ (Stability constants)
Pyridine	log $K_1^{\rm I}$ = 3·90 ± 0·10; log $K_2^{\rm I}$ = 2·70 ± 0·10
	log $K_3^{\rm I}$ = 1·3 ± 0·2; log $K_4^{\rm I}$ = 0·8 ± 0·2
	* log $\beta_3^{\rm I}$ = 8·29
,,	log $K_1^{\rm II}$ = 2·52, log $K_2^{\rm II}$ = 1·86, log $K_3^{\rm II}$ = 1·31, log $K_4^{\rm II}$ = 0·85
Glycine	log $K_3^{\rm II}$ = 0·47; * log $\beta_2^{\rm I}$ ~10·0
,, ...	log $K_3^{\rm II}$ ~1; log $\beta_2^{\rm II}$ = 15·2
Alanine	log $K_3^{\rm II}$ ~0·05; * log β_2^1 ~9·6
,, ...	log $\beta_2^{\rm II}$ = 15·0
Sarcosine	* log $\beta_2^{\rm I}$ ~9·2, using log $\beta_2^{\rm II}$ = 14·6
Imidazole	log $K_1^{\rm II}$ = 4·33, log $K_2^{\rm II}$ = 3·28, log $K_3^{\rm II}$ = 2·7, log $K_4^{\rm II}$ = 1·9
	log $\beta_4^{\rm II}$ = 12·21, log $\beta_2^{\rm I}$ = 10·44
,, ...	log $K_1^{\rm II}$ = 4·20, log $K_2^{\rm II}$ = 3·47, log $K_3^{\rm II}$ = 2·84, log $K_4^{\rm II}$ = 2·0
,, ...	log $\beta_2^{\rm I}$ = 10·87
Histidine	log $\beta_2^{\rm II}$/log $K_1^{\rm I}$ = 7·62, log $K_1^{\rm II}$ = 10·3 (pH titrn.)
,, ...	log $K_1^{\rm II}$ = 10·5
Ammonia	* log $\beta_2^{\rm I}$ = 10·55, using log $\beta_4^{\rm II}$ = 13·05 (Ref. 29)
Ethylenediamine	* log $\beta_2^{\rm I}$ = 11·4, using log $\beta_2^{\rm II}$ = 20·0 (Ref. 29)
Ethylenebisthioglycollic acid	log $K_1^{\rm II}$ ~4·8 (pH-titrn.); log $\beta_n^{\rm I}$ = 4·37 + 2·9n (pK_a values for the CO_2H groups in probable 1 : 1 Cu$^{\rm I}$ complex are 2·44, 2·71)
Phenylarsinediacetic acid ...	log $K_1^{\rm II}$ ~2·5 (ref. 24): log $\beta_n^{\rm II}$ = 3·95 + 1·7n (pK_a values for 1 : 1 Cu$^{\rm I}$ complex, are 2·70, 3·96)
	50% Dioxan–water
8-Hydroxyquinoline	* log $\beta_2^{\rm I}$ ~14·7, using log $\beta_2^{\rm II}$ = 25·4 and the unsteady E_f* value.

* log β^1 values calc. from log $\beta^{\rm II}$ (Bjerrum, Schwarzenbach, and Sillén, " Stability Constants, Part I," *Chem. Soc. Spec. Publ. No.* 11, 1956); log $\beta^{\rm II}$ values calc. from those recorded for log $\beta^{\rm II}$. For ethylenediamine (Bjerrum, Schwarzenbach, and Sillén, " Stability Constants, Part I," *Chem. Soc. Spec. Publ. No.* 11, 1956) give log β_2^1 10·8.

Pettit[20] has shown that the cupric ion forms a 1 : 1 species with phenylarsinediacetic acid. Again we found that the cuprous ion is bound only through the arsenic atom at a low pH, and the redox curve is interpreted as for the previous sulphur system. The high potentials observed between +400 and +450 mv at pH 2·5—7·5 are similarly attributed to the described dative π-bonding and polarisation.

Several other ligands containing sulphur groups were examined, but they were oxidised by the cupric ion. The acid dissociation constants of the ligands are given in Table 3.

The Co-ordination Number of the Cuprous Ion.—The present work is in line with earlier suggestions that there is no simple co-ordination number for the cuprous ion. In combination with saturated ligands which are strong σ-donors and weak π-acceptors, *e.g.*, NH_3, it is 2-co-ordinate. With strong π-acceptors, *e.g.*, pyridine, phenanthroline, it is 4-co-ordinate. Four-co-ordination is also common in complexes with halides, $CuCl_4^{3-}$, and uncharged sulphur donors, $Cu^I[S{:}C(NH_2)_2]_4$. The chemistry of silver(I) complexes is similar: two-co-ordinated silver is particularly stable with ammines and four-co-ordinated in complexes with uncharged sulphur ligands.[21] The halide, thiocyanate, and cyanide complexes are somewhat intermediate in character: a high co-ordination number is found with π-acceptors. The two-co-ordination state of the cuprous ion with saturated ligands has long been attributed to *sp*-hybridisation, the energy gap between *s*- and *p*-states being so large in the Group IB elements as to prevent effective use of sp^3-hybridisation. An alternative explanation, the mixing of *s*- and *d*-states, can lead to the same result.[22] We favour the explanation given by Chatt[23] for the change to higher co-ordination number with the unsaturated ligands. The polarisation of ten 3*d*-electrons in a simple electrostatic field does not lead to crystal-field stabilisation. On molecular-orbital theory mixing of the *d*-states with ligand states will permit this polarisation provided the ligand is unsaturated; for, although there can be no energy gain from $d_\sigma\sigma_L$-mixing (L refers to a ligand orbital) where both d_σ and σ_L are full orbitals, there can be considerable gain from $d_\pi\pi_L$ mixing if π_L (the bonding or anti-bonding state of the ligand) are empty. Two linear bonds stabilise but one d_ϵ-orbital, whereas two such orbitals are stabilised in tetrahedral co-ordination.

The Co-ordination of the Cupric Ion.—The hydrated cupric ion is now considered to be 6-co-ordinate. In aqueous ammonia and ethylenediamine, only four of the water molecules of the hydrate are replaced readily, but it is known that a fifth and perhaps a sixth can be exchanged for ammine groups at very high ammine concentrations.[24] For non-aqueous solvents Graddon[25] has shown recently that five-co-ordination appears to be quite common[26] in cupric complexes but he found no evidence for six-co-ordination. In the present paper we have shown that in aqueous solutions of phenanthrolines and bipyridyls all six water molecules of the cupric complex ion are replaced relatively readily (Table 2). It is clear that the number of equivalent co-ordination positions about the cupric ion is not a simple number independent of the ligand.

We shall next consider those features of the ligand which we consider important in deciding the number of more or less equivalent ligand molecules taken up by the cupric ion. The size of the cupric ion is such that in the absence of polarisation it would be expected to be co-ordinated by six groups of the size of the oxygen or nitrogen atom. This can be deduced from Pauling's radius-ratio rules. Use of either an electrostatic or a molecular-orbital model for the polarisation of the ion, d^9 system, by the six ligands leads

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[20] Petit, D.Phil. Thesis, Oxford, 1960.

[21] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 264, 276.

[22] Orgel, Tenth Solvay Conference, ed. Stoops, Brussels, 1956, p. 289.

[23] Chatt, " Chemistry of the Co-ordination Compounds," Pergamon Press, London, 1958, p. 515.

[24] Bjerrum, " Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941; ref. 17.

[25] Graddon, *Nature*, 1959, **183**, 1610.

[26] Llewellyn and Waters, *J.*, 1960, 2639; Cox and Corbridge, *J.*, 1956, 594.

to an energy separation of the $d_{x^2-y^2}$ and d_{z^2}-orbitals of the cupric ion (Jahn–Teller effect). Thus, either two or four of the six-co-ordination positions should be favoured starting from an octahedral field. Öpik and Price [27] considered that four positions were favoured rather than two, but Knox [28] pointed out that this is not necessarily so. In crystals, both distortions of the octahedron are known. However, none of these discussions make clear what is implied by the " field " of a ligand. On an electrostatic model the concept of the field of an uncharged ligand is the sum of the dipole and the induced dipole at the equilibrium distance of the ligand from the cation. The " field " on a molecular-orbital model is similar, being the sum of factors which are a property of the ligand alone and its polarisation due to the drift of electrons from the ligand orbitals into the empty cation orbitals (we consider π-bond formation later). Thus on either model the field contains a polarisation term which is very sensitive to interatomic distance. At short distances, therefore, a highly polarisable ligand, L_1, may form a more stable complex than a highly polar ligand, L_2, but at long distance the ligand L_2 would interact the more strongly. L_1 could be a nitrogen donor, *e.g.*, ammonia or phenanthroline, and L_2 an oxygen donor, *e.g.*, water. A large cation (*e.g.*, calcium) which is weakly polarising does not form co-ordination compounds with either ammonia or 1,10-phenanthroline in the presence of water. A small highly polarising symmetrical cation (*e.g.*, nickel), which undergoes equal polarisation in the six directions of an octahedron, forms six co-ordinate complexes, all six positions then interacting equivalently with the ligands. Now the fifth and the sixth position in the co-ordination sphere of the cupric ion behave as in the calcium ion, while the other four positions behave as in the nickel ion; that is to say, the order of preferred ligands at the fifth and the sixth position is $SO_4^{2-} > H_2O > NH_3$ as for calcium, whilst at the other four positions it is $NH_3 > H_2O > SO_4^{2-}$. From the interatomic distances in crystals we find that the cupric ion has a radius of approximately 1·0—1·1 Å perpendicular to the plane of the four most strongly held ligands (compare the radius of the calcium ion 0·97 Å), while in this plane the radius is but 0·70 Å. In the plane, polarisation of the ligand is of greater importance, while polarity is most important perpendicular to the plane. Primary amines, such as ammonia and ethylenediamine are more polarisable than water, and therefore the cupric ion takes up but four amine groups. The formation of complexes with unsaturated ligands requires the discussion of a further polarisation of the cupric ion. The six d_ϵ-electrons of the cupric ion are best stabilised by an octahedral field of six equal π-acceptor ligands. Unsaturated aromatic amines can fill this function. With such ligands the co-ordination number of the cupric ion will depend upon the relative importance of the two terms—the $d_\epsilon\pi_L$-bonding and the $d_\gamma\sigma_L$-bonding. In phenanthroline and bipyridyl complexes the latter is reduced in strength by the steric hindrance between two di-imine molecules held in the same plane. This can be seen from the values of $\log K_1$ and $\log K_2$ which are 8·8 and 6·5 for 1,10-phenanthroline and 8·1 and 5·5 for 2,2-bipyridyl, to be compared with 10·4 and 9·6 for ethylenediamine. Thus Jahn–Teller stabilisation must be lost in the 2 : 1 phenanthroline and bipyridyl complexes, and the cupric ion behaves more nearly as a spherically symmetrical ion, going on to add a third ligand. The lower stability of the cupric–phenanthroline and –bipyridyl complexes than the nickel complexes at the ML_2 and ML_3 stages, but not at the ML stage,[29] is due then to the matching of prefered directions of polarisation of the nickel cation with the ligand geometry and to the absence of such a match in the cupric complexes. As the Jahn–Teller stabilisation is present in the cupric hydrates, cupric complexes which cannot benefit from tetragonal distortion will always be unstable. The ligand-field stabilisation energy is sufficient to make the nickel complexes more stable than the cupric complexes only in the presence of such a steric selectivity. The more general case is that the greater

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[27] Öpik and Price, *Proc. Roy. Soc.*, 1957, *A*, **238**, 425.

[28] Knox, *J. Chem. Phys.*, 1959, **30**, 991.

[29] Bjerrum, Schwarzenbach, and Sillén, " Stability Constants, Part I, Organic Ligands," *Chem. Soc. Spec. Publ. No.* 11, 1956.

polarising power of the cupric ion produces the stability order $Cu^{II} > Ni^{II}$, as is illustrated in the ML complexes of both phenanthroline and bipyridyl.

We are grateful to Professor G. M. Badger, Dr. H. Irving, and Dr. R. G. Wilkins for gifts of chemicals. The work was carried out while one of us (B. R. J.) held a D.S.I.R. research fellowship.

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[*Received, August* 15*th*, 1960.]