906. *Spectrophotometric and Thermodynamic Properties of Some Copper and Iron Complexes.*

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The absorption spectra of a number of cupric, cuprous, and ferrous complexes are described and discussed. The stabilities of some of the complexes are also determined. We show that description of the spectra requires a different relative emphasis on σ- and π-bonding in the complexes from that required in discussion of their stability.

THE absorption spectra of transition-metal complexes are relatively well understood. In particular the treatment of *d–d* transitions by ligand-field theory is in excellent agreement with experimental observations in so far as the number of bands and their relative positions are often accurately predictable.[1] Two problems remain, the intensity of the bands and their absolute positions. In this paper we describe an approach to these problems through the study of some cupric complexes. The other common optical transitions of the transition-metal complexes are the intense so-called charge-transfer bands. These transitions are less well understood. In the second part of the paper we examine the charge-transfer spectra of a large number of ferrous and cuprous complexes in an attempt to clarify the nature of these intense absorption bands. We have also examined the stabilities of a number of the complexes of these cations. A comparison between the spectroscopic and the thermodynamic information illustrates the very different effects of change of the ligand substituents on the different properties of the complexes.

Cupric Complexes.—Fig. 1 illustrates the absorption spectra of some typical cupric salts in pyridine. Table 1 lists the positions and intensities of the absorption bands of a series of such salts in the same solvent. The band shape varies little from compound to compound within a group. We shall follow ligand-field theory [1] in relating band positions to the field strength parameter, Δ, and the asymmetry of the bands to distortion from cubic symmetry (Fig. 1). A more detailed discussion follows below. The complexes can be formulated as (A) $Cu(py)_4(carboxylate)_2$, (B) $Cu(salicylaldehyde)_2(py)_2$, and (C) Cu-(salicylaldehyde imine)$_2$(py)$_2$, where py = pyridine. The orders of the wavelengths, (C) $<$ (A) $<$ (B), show a decrease with increase in donor strength of the ligand, as expected,

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[1] Orgel, " An Introduction to Transition-Metal Chemistry," Chapters 5 and 6, Methuen, London, 1960.

TABLE 1.

Spectra of cupric complexes in pyridine.

Anion	$\lambda_{max.}$ (mμ)	ε
Chloride	770	175
Acetate	655	109
Chloroacetate	665	126
Stearate	650	99
Sebacate	650	84
Benzoate	650	111
Isonicotinate	655	111
Picolinate	660	88
Subst. benzoate:		
o-NH_2	660 *	115
m-NH_2	647 *	125
p-NH_2	665 *	115
o-NO_2	660	119
m-NO_2	660	14
p-NO_2	660	103
Salicylaldehyde:		
Unsubst.	725	91
3-NO_2	685	86
5-NO_2	675	113
3,5-$(NO_2)_2$	695	84
5-Cl	740	94
5-Br	680	53
3-Me	725b	110
5-Me	750vb	110
3-MeO	785b	104
5-MeO	780vb	97
2-Hydroxy-1-naphthaldehyde	680	127
Salicylaldehyde deriv.:		
Imine	585	75
Methylimine	635	99
Ethylenedi-imine	605	257
do. (5-Cl)	610s	317
do. (3-MeO)	615s	291
Imine (3-MeO)	600	90
do. (5-Cl)	590	100

* Shoulder at 25 mμ lower. b = broad; s = sharp; v = very.

and the relative sharpness of the peaks suggests that complexes of class (C) are almost regular octahedra (very sharp peaks), those of class (A) are tetragonal (one sharp peak with a broadening at longer wavelengths), and those of class (B) are most asymmetrical (very broad peaks) (Table 1). We note that for the carboxylate complexes the position and intensity of the band change only slightly from ligand to ligand, although there are considerable changes in acid dissociation constants, pK_a. The latter can be used as a guide to σ-donor strength. In contrast, the spectra of the salicylaldehyde complexes are rather sensitive to the nature of substituents in the ligand. Fig. 2 is a plot of $\nu_{max.}$ for this series against pK_a of the ligand. It shows that the weaker bases give rise to the greater spectroscopic splitting factor, Δ. The weakest bases have nitro-substituents, which are strong π-acceptors; the strongest have methoxy- and methyl substituents, which are π-donors. We conclude that the spectra of these complexes are strongly dependent on π-bonding.

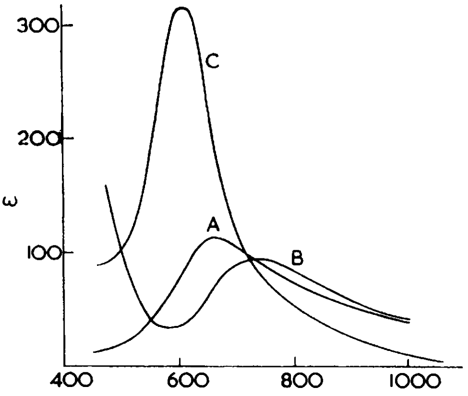

FIG. 1. Absorption spectra of the three groups of cupric complexes described in the text.

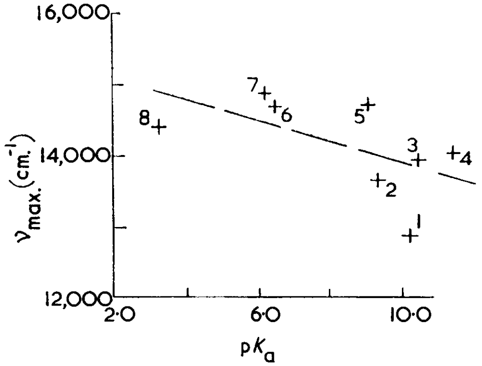

FIG. 2. Relation between the acid dissociation constants of a series of salicylaldehyde complexes and the frequency of the absorption maximum of their cupric complexes in pyridine.

1, 3-MeO$^-$. 2, 5-Cl$^-$. 3, Unsubst. 4, 3-Me. 5, 5-Br. 6, 3-NO_2. 7, 5-NO_2. 8, 3,5-$(NO_2)_2$.

The stabilities of the complexes in dioxan–water [2] indicate a strong dependence of the stability constants of the salicylaldehyde complexes, β_n, on the acid dissociation constants of the ligands. The relation $\log \beta_2 = 0{\cdot}68\text{p}K_a + 1{\cdot}0$ is obeyed approximately. The dependence of stability on π-bonding is apparently much less than that of Δ, causing an opposing dependence of $\nu_{\text{max.}}$ and stabilities upon pK_a. For the benzoates the spectroscopic effects are less noticeable, presumably because the oxygen of a carboxylate ion is not as susceptible to π-bonding with the aromatic ring as is the oxygen of the phenoxide anion of salicylaldehyde. However, we note the absence of a dependence of $\lambda_{\text{max.}}$ upon pK_a even for the benzoates. For the salicylaldehyde di-imines methoxy-substituents again shift the absorption band to longer wavelengths although the pK_a values increase if such groups are present. A more remarkable effect is the relatively high extinction coefficients (250) of the chelated di-imines (derivatives of ethylenediamine), yet the peaks are at longer wavelengths than for the non-chelated di-imines (derivatives of ammonia). We take both facts to suggest that the complexes of the chelated di-imines are very nearly octahedral.[1] The salicylaldehyde methylimine peak is at somewhat long wavelength than for the parent imine, presumably because there is some steric hindrance on chelation. This is also suggested by a broadening of the spectrum which could well arise from removal of degeneracy of the cupric levels. There is, however, no evidence for these differences in structure between the ethylenedi-imine and the methylimine complex from studies on solid complexes.[3]

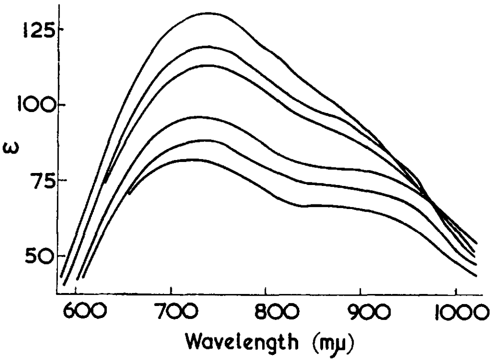

FIG. 3. Absorption spectra of some 2 : 1 complexes of cupric with 2,2′-bipyridyls in aqueous solution. Curves, reading downwards, are for: 5,5′-Et_2-4,4′-Me_2; 4,4′-Me_2; 4,4′-Et_2; 5,5′-Me_2; unsubst.; 4,4′-$(CO_2H)_2$.

TABLE 2.

Spectra of 2 : 1 cupric complexes.

1,10-Phenanthrolines (in H_2O).

	Band I		Band II	
Ligand subst.	$\lambda_{\text{max.}}$ (mμ)	ε	$\lambda_{\text{max.}}$ (mμ)	ε
None	710	56	920	45
5-Cl	700	50	940	39
5-NO_2	700	44	950	32
5-Me	720	64	905	55
5-Ph	730	69	910	61
5,6-Me_2	725	78	900	67
3,5,6,8-Me_4	725	81	885	70
4,7-Me_2	740	96	880	70

2,2′-Bipyridyls (in 50% v/v dioxan–water)

	Band I		Band II	
Ligand subst.	$\lambda_{\text{max.}}$ (mμ)	ε	$\lambda_{\text{max.}}$ (mμ)	ε
None	720	86	940	75
5,5′-Me_2	730	88	920	80
4,4′-Et_2	745	170	~900	~100
4,4′-Me_2	735	101	920	90
5,5′-Et_2-4,4′-Me_2	740	112	920	100
5,5′-$(CO_2H)_2$	695	83	950	70
4,4′-Ph_2	710	103	950	> 80
5,5′-$(CO_2Et)_2$	710	70	?	?
4,4′-$(CO_2Et)_2$	700	50	?	?

Table 2 gives the band positions and intensities of some cupric 2,2′-bipyridyl(bipy) and 1,10-phenanthroline(phenan) complexes (cf. Fig. 3). The stability of these complexes is approximately proportional to pK_a.[4] As pointed out there must be considerable π-bond

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[2] Jones, Poole, Tomkinson, and Williams, *J.*, 1958, 2001.

[3] Meuthen and von Stackelberg, *Z. anorg. Chem.*, 1960, **305**, 279.

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

stabilisation in these complexes.[1,2,5] There is also very considerable steric hindrance between the first and the second 1,10-phenanthroline ligand as the difference $\log K_1 - \log K_2 \simeq 4{\cdot}0$ is much greater than the usual difference between the step constants of the cupric ion with chelating ligands, *e.g.*, for ethylenediamine $\log K_1 - \log K_2 \simeq 1{\cdot}0$. Now the different bands of a particular $Cu^{II}(phenan)_2$ or $Cu^{II}(bipy)_2$ complex are usually sufficiently separated for us to allocate bands to transitions (Figs. 3 and 5). We then observe that, whereas band I (750 mμ) (see Fig. 3) shows little dependence of $\lambda_{max.}$ upon ligand substituent, its intensity (or the total area under both bands) increases markedly as pK_a increases[4] (Fig. 4). The position of band II (900 mμ) moves to shorter wavelengths with increasing pK_a while band I moves to slightly longer wavelengths. As the substituents are far from the co-ordination centre and the tetragonal element in the complexes must be increasing in the sequence of basicity we reject any suggestion that a shift toward octahedral symmetry occurs with change of substituent to higher basicity. We suggest instead that the shift of peak I to longer wavelengths is due to the reduction of π-bonding to which transition I will be expected to be sensitive, $d_{zy} \longrightarrow d_{x^2-y^2}$. The shift to shorter wavelengths of peak II is due to increase in σ-bonding, for this transition should be but very little sensitive to π-bonding, $d_{xy} \longrightarrow d_{x^2-y^2}$. The series of observations is common to 1,10-phenanthrolines and bipyridyls. Here, as in the benzoates, salicylaldehydes, salicylaldehydedi-imines, and acetylacetonates,[2] the lack of simple correlations between the positions of ligand field bands and their stabilities does not permit us to use the simple electrostatic model to calculate from absorption spectra contributions to complex stability from *d*-level splitting. As this procedure is not permissible in these simple series it appears most improbable that it can be legitimate in the discussion[1] of the relative stabilities of complexes MX in comparison with MY where X and Y differ more grossly, *e.g.*, where X is water and Y ammonia. The above observations confirm[6] too that when an electron spin resonance spectrum of the cupric ion is to be analysed it will prove to be more valuable

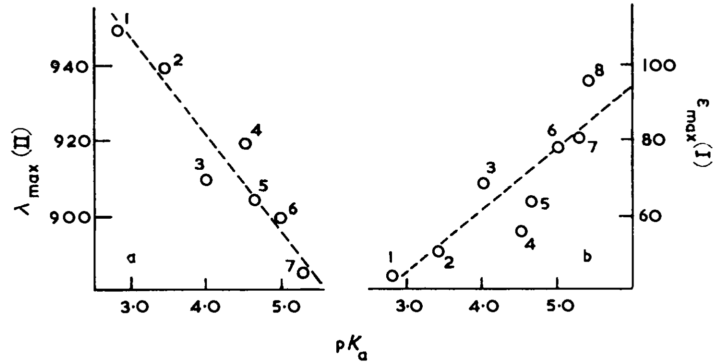

FIG. 4. Relations between $\lambda_{max.}$ (II) and pK_a and between ε (I) and pK_a for a series of 2 : 1 cupric complexes with 1,10-phenanthrolines. 1, 5-NO_2; 2, 5-Cl; 3, 5-Ph; 4, unsubst.; 5, 5-Me; 6, 5,6-Me_2; 7, 3,5,6,8-Me_4.

TABLE 3.

Step stability constants.

1,10-Phenanthroline derivative	log K_1	log K_2	og K_3
Unsubst.	8·80	6·64	4·94
2-Methyl	7·40	6·40	V. small
2,9-Dimethyl	~6·10	~5·60	V. small

[5] Williams, *Discuss. Faraday Soc.*, 1958, **26**, 123.

[6] Maki and McGarvey, *J. Chem. Phys.*, 1958, **29**, 31, 35.

to determine σ-bonding from the value of $g_{||}$ than from $g_{\perp}$ which is liable to be very sensitive to π-bonding.

Gross steric hindrance to planar binding of two phenanthroline molecules can be introduced by substituents in the 2-position. The cupric complexes should be driven from octahedral toward tetrahedral symmetry with distortion in both cases as steric hindrance increases. The electron energy levels of the cupric ion should become inverted as the change in symmetry takes place[1] (Fig. 5). We expect then that the more intense band will be at the longer wavelength in tetrahedral (distorted) complexes. The spectra of the complexes are shown in Fig. 6, where this prediction is born out. There is also a considerable increase in intensity, so that the transition probability is increased about three times on going to the tetrahedral complex. This change is expected as a tetrahedron lacks a centre of inversion. There is a gradual change in the spectrum from the phenanthroline to the 2,9-dimethyl-1,10-phenanthroline by way of the 2-methylphenanthroline complex. There is, moreover, a remarkable change in the step stability constants,[4] as shown in Table 3.

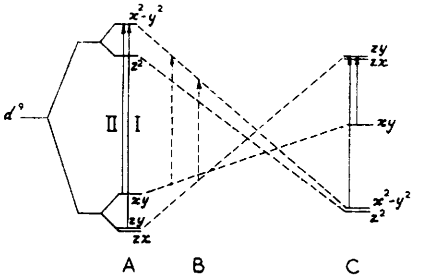

FIG. 5. Electron levels in cupric complexes indicating the transitions I and II which are resolved in the 2,2′-bipyridyl complexes (Fig. 3), and the effect of change of field symmetry from octahedral with tetragonal distortion (A) to tetrahedral with distortion (C). B is an intermediate case.

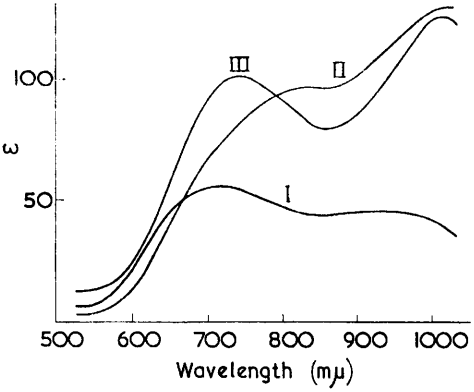

FIG. 6. Absorption spectra of the 2 : 1 cupric complexes with (I) 1,10-phenanthroline, and (II) 2-methyl- and (III) 2,9-dimethyl-1,10-phenanthroline.

The stability data suggest that the co-ordination around the cupric ion changes from octahedral to tetrahedral on addition of the first ligand, which is consistent with the spectroscopic observations. In this series of complexes the wavelengths of the transitions are not very different in the octahedral and tetrahedral complexes. Theory would predict an ~50% reduction of field strength on change to the lower co-ordination. Possibly the unexpected size of the field strength in the tetrahedral complexes arises from reduction of the Cu–N distances owing to the greatly reduced steric hindrance between ligands in the complexes of lower co-ordination number.

A spectrum of interest is that of the 4,7-dihydroxy-1,10-phenanthroline–cupric complex. Maximum absorption is at 460—470 mμ and the extinction coefficient is ~1250. The wavelength of the *d–d* transition is shorter and the extinction coefficient greater than in any other known cupric complex, raising the problem whether *d–d* transitions may be dissociated from charge-transfer transitions in extreme cases. We shall treat this problem in another paper.

We have also measured the spectra of the cupric complexes of $Ph{\cdot}As(CH_2{\cdot}CO_2^-)_2$ and $S(CH_2{\cdot}CO_2^-)_2$: neither of these ligands has a very marked effect on the position of the *d–d* band of the cupric ion relative to its position in water, whereas both increase the intensity of the bands considerably. As in previous papers we take the intensity changes to reflect changes in covalency, although there is no evidence for this type of change from

Δ values. The stability constants for the ligand $S(CH_2{\cdot}CO_2^-)_2$ with several cations follow the Irving–Williams stability series.[7] These complexes provide another example of the persistence of this stability order even when Δ in the complexes is not markedly different from the value in water.[5]

Charge-transfer Spectra.—We have drawn attention earlier [8] to the similarity in absorption spectra between the spectra of $Cu^I(phenan)_2$ and $Fe^{II}(phenan)_3$ spectra. We have now made a large number of additional measurements which are summarised in Table 4. There is still a general linear correlation between $\lambda_{max.}(Cu^I)$ and $\lambda_{max.}(Fe^{II})$, but it is not as exact as was found for the more limited range. Incidentally we note that the $\lambda_{max.}$ values for the charge-transfer bands of Cu^I–O_2 (600 mμ) in hæmocyanin and of Fe^{II}–O_2 (900 mμ) in hæmoglobin as well as of Cu^I–S^- (300 mμ) in the cuprous and Fe^{II}–S (400 mμ) in the ferrous salt of cysteine lie near the same line. In charge-transfer spectra there appears to be a correlation between Fe^{II} (low spin) and Cu^I spectra extending over some 400 mμ. We are now seeking similar correlations with other reducing cations, *e.g.*, low-spin chromous and vanadous.

TABLE 4.

Absorption spectra of some cuprous and ferrous complexes.

	Cuprous		Ferrous			Curpous		Ferrous	
2,2′-Bipyridyl subst.	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	2,2′-Bipyridyl subst.	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
None	434	5270	523	9200	4,4′-$(CO_2Et)_2$	483	7130	545	14,000
5,5′-Et_2-4,4-Me_2 ...	430	5530	525	10,700	5,5′-$(CO_2Et)_2$	496	4150	~570	~2000
4,4′-Me_2	430	5700	530	9900	5,5′-$(CO_2Me)_2$	492	?	No colour?	
4,4′-Et_2	437	6150	530	10,600	4,4′-$(CO_2^-)_2$	457	7600	538	11,100
6,6′-Me_2	455	6460	—	—	4,4′-$(CO_2H)_2$	482	8300	547	11,000
4,4′-$(Ph{\cdot}CH_2{\cdot}CH_2)_2$	433	6180	532	11,000	5,5′-$(CO_2^-)_2$	455	~4000	562	5500
5,5′-Me_2	436	6800	512	9520	5,5′-$(CO_2H)_2$	475	?	—	—
4,4′-Ph_2	463	10,300	550	21,700	3,3′-$(CO_2^-)_2$ ...	U.V.		U.V.	
					3,3′-$(CO_2H)_2$ ...				

Measurements refer to 50% v/v dioxan–water solutions, except for the Fe^{II} complex with diethyl 2,2′-bipyridyl-5,5′-dicarboxylate which was investigated in 75% dioxan–water.

During the measurements on the ferrous–bipyridyl complexes we found that the maximum intensity of the spectrum of the diethyl 2,2′-bipyridyl-5,5′-dicarboxylate complex (FeP) was very low. We therefore investigated the stability and spectra of the step complexes of this ligand in some detail. The three step stability constants were obtained by the method of corresponding solutions: they are given in Table 5 with, for comparison, those of the ferrous–1,10-phenanthroline complex.

TABLE 5.

Stability constants of ferrous–diethyl 2,2′-bipyridyl-5,5′-dicarboxylate and, in parentheses, ferrous–1,10-phenanthroline.

	log β_n *	$\lambda_{max.}$	ε
FeP_1	2·5 (5·9)	520 (450)	100 (~1,000)
FeP_2	4·5 (?)	545 (?)	300 (?)
FeP_3	6·5 (2·15)	570 (510)	2,000 (11,000)

* Probable error ±0·30.

We conclude that, unlike the tris-1,10-phenanthroline complex, the complex FeP_3 is not a low-spin complex, but is an equilibrium mixture of the two spin forms containing a large proportion of the high-spin ion. At room temperature there is not more than 20% of the low-spin form. This has been confirmed by direct measurement of the magnetic moments in solution, which will be reported in a later paper. The proportion of the two

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[7] Irving and Petit, unpublished work.

[8] Williams, *J.*, 1955, 137.

forms is strongly dependent on temperature, as judged by changes of absorption spectra. We also find the tris-4,4′-dicarboxylate complex to be virtually wholly in the low-spin form. This ligand has a higher basicity (pK_a 2·45) than the 5,5′-compound (pK_a 0·85), but the two ligands have very similar absorption spectra with the cupric ion, *i.e.*, the values of Δ are similar. We therefore suggest that the low-spin–high-spin equilibrium is not controlled so much by the value of Δ, the spectroscopic splitting parameter [determined from the study of the spectra of high-spin (*e.g.*, cupric) complexes] as by changes in π-bonding. The 5,5′-dicarboxylate ligand is a relatively poor π-acceptor, as the substituent groups are *meta* to the nitrogen, whereas the 4,4′-groups are *para* and are strong π-acceptors. Now we have already shown that the *d–d* transitions of the cupric ion are very sensitive to π-bonding between the ligand and the cation. We conclude that the high-spin–low-spin equilibrium is even more sensitive to π-bonding. This is not so surprising when it is remembered that the low-spin state is merely a very highly excited *d*-state configuration relative to the high-spin state.

Experimental.—Materials. Preparation of the substituted salicylaldehydes has been described.[2] The benzoic acids were commercially available. The substituted bipyridyls were given to us by Professor G. M. Badger (Adelaide University, Australia). The substituted phenanthrolines have been described elsewhere.[4] The procedure used for determination of the stability constants of the copper complexes has been published.[2,4] The stability constants for the stepwise formation of the ferrous complex of diethyl 2,2′-bipyridyl-5,5′-dicarboxylate were obtained by the method described below. Absorption spectra were measured on a Unicam S.P. 600, a Beckman DU, or the recording Beckman spectrophotometer. The degrees of complex formation in the solutions were known from the measurements of the stability constants.

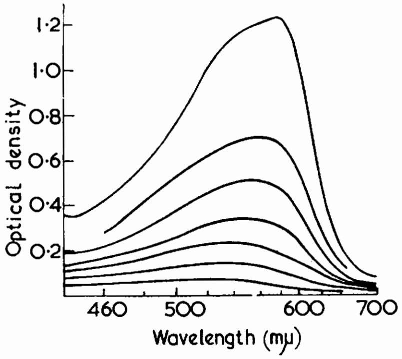

FIG. 7. Ferrous complex with diethyl 2,2′-bipyridyl-5,5′-dicarboxylate. [Fe^{II}] = 2 × 10^{-3}M. Ligand concns. are 2·0 × 10^{-3}M for the lowest and 16·0 × 10^{-3}M for the top curve, with 2·0 × 10^{-3}M intervals. The solvent is 75% dioxan–water and 0·1N-sulphuric acid.

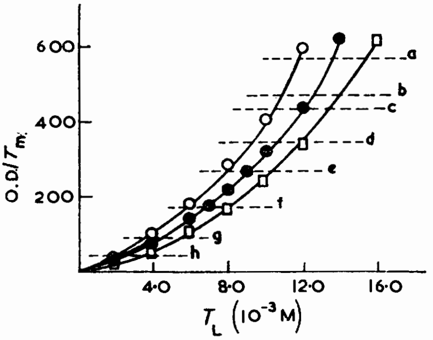

FIG. 8. Corresponding solutions, positions of equal optical density (O.D.)/T_M, at different T_L, and three ferrous concentrations, *viz.*: ○, 0·5 × 10^{-3}M; ●, 1·0 × 10^{-3}M; □, 2·0 × 10^{-3}M. Other conditions as for Fig. 7.

Diethyl 2,2′-bipyridyl-5,5′-dicarboxylate complexes. The absorption spectra of 0·002M-solutions of ferrous sulphate and ligand, at the various strengths indicated, and all in 0·1N-sulphuric acid and 3 : 1 dioxan–water, appear in Fig. 7. The procedure of corresponding solutions[9] is to vary both T_M (total ferrous) and T_L (total ligand), giving solutions of equal optical density at a chosen wavelength. Our measurements at 540 mμ are plotted in Fig. 8. From this graph, plots of T_M against T_L (Fig. 9A) for equal optical density (see broken lines on Fig. 8) are obtained. The slope of the lines gives $\bar{n}$, the degree of formation, and the intercept

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[9] Fronaeus, *Acta Chem. Scand.*, 1951, **5**, 139.

on T_L ($T_M = 0$) gives $[L]$ (the concentration of free ligand). The formation function of pL against $\bar{n}$ so obtained is given in Fig. 9B. By curve-fitting methods the values of K_1, K_2, and K_3 were derived. The method of corresponding solutions is open to considerable error, as is recognised in the quoted constants. Extinction coefficients were then calculated.

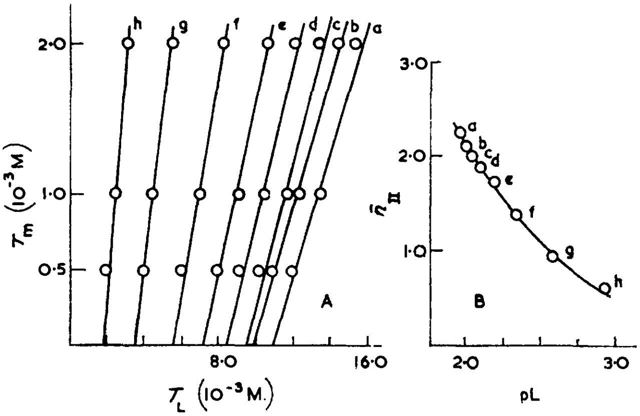

FIG. 9. (A) Plots of T_L against T_M at equal optical density (see Fig. 8). (B) The resulting plot of $\bar{n}$ against $-$log [free ligand].

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