408. *The Relationship between Proton Dissociation Constants and the Stability Constants of Complex Ions.*

By J. G. JONES, J. B. POOLE, J. C. TOMKINSON, and R. J. P. WILLIAMS.

The proton, acid, dissociation constants of some derivatives of salicylaldehyde and of 8-hydroxyquinoline (oxine) have been determined, and compared with the stability constants of the complexes formed by the ligands derived from these acids and several cations. The relationship between these quantities is more complicated than has been assumed hitherto. The discussion is supported by reference to the absorption spectra of the metal complexes. The general approach can be extended to other series of ligands.

SEVERAL authors [1,2,3] have suggested that a general linear relation exists between the logarithms of the stability constants, log K, of a series of 1 : 1-complex ions, ML, derived from one metal, M, with a set of similar ligands, L, and the logarithm of the acid dissociation constants, pκ, of the ligands. The general form

$$\log K = a\,\mathrm{p}\kappa + b \quad \dots\dots\dots \quad (1)$$

where a and b are constants, was first used by Bjerrum [3] and much discussed by Martell and Calvin.[2] Specific examples of the relation had been examined earlier.[4,5] Duncan [6] derived a thermodynamic relation:

$$\log K = \mathrm{p}\kappa - [G(^{\circ}_{\mathrm{ML}} - G^{\circ}_{\mathrm{HL}})/\boldsymbol{R}T] + B \quad \dots\dots \quad (2)$$

where G°_{ML} and G°_{HL} are the partial molar free energies of the species ML and HL respectively and B is a constant independent of L. This relation has been further discussed by Irving and Rossotti.[7]

From relation (2) the constant a in equation (1) could only be unity if changes of G°_{ML} and G°_{HL} with ligand compensated one another exactly. If an equation of the general form of (1), where a is not necessarily unity, is to be derived from (2) then the dependence of G°_{HL} upon the ligand must be similar to that of G°_{ML}. Such dependences cannot be deduced from thermodynamic arguments (cf. ref. 7) but require a discussion of the bonding in HL and ML. We recognise here that although both G°_{HL} and G°_{ML} depend similarly upon one property of the ligand, the σ-donor (or -acceptor) power, they must differ in their dependence on its π-donor (or -acceptor) character. Most strong σ donor substituents in ligands are also π donors, *e.g.*, methyl, and most strong σ acceptors are also π acceptors, *e.g.*, nitro, so that a change of substituent in a ligand causes changes in σ- and π-electron densities which are usually in the same direction.

Cations such as the cupric ion are π-electron donors [8] so that they should be less destabilised in a complex than the proton by σ-electron-acceptor substituents which are also π-electron acceptors, and less stabilised by σ-electron donors which are also π-electron donors. Thus the slope a of the plot of log K for cupric complexes against pκ should be less than unity on these grounds alone. Conversely a will exceed unity for a cation which is a π-electron acceptor.

For ligands with substituents not of this general kind (*e.g.*, the chloro-group is a π donor but a σ acceptor), the linear relation between pκ and log K observed for substituents in

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[1] Schwarzenbach, Anderegg, Schneider, and Senn, *Helv. Chim. Acta*, 1955, **38**, 1147.

[2] Martell and Calvin, " The Chemistry of The Metal Chelates," Prentice-Hall, New York, 1953, p. 76.

[3] Bjerrum, *Chem. Rev.*, 1950, **46**, 381.

[4] Bruehlman and Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401.

[5] Britton and Williams, *J.*, 1935, 796.

[6] Duncan, *Analyst*, 1952, **77**, 830, and personal communication.

[7] Irving and Rossotti, *J.*, 1954, 2904, 2910; *Acta Chem. Scand.*, 1956, **10**, 72.

[8] Tichane and Bennett, *J. Amer. Chem. Soc.*, 1957, **79**, 1293.

the general case should no longer be obeyed. The fact that relation (1) holds is somewhat fortuitous and depends upon a particular choice of ligand substituents. Before developing this discussion we will present new evidence that in some series of ligands, and depending on the choice of substituents, relations of the form (1) do not hold and in some others they are far from exact. Equation (1) has no general validity; as this is obvious if ligands of somewhat different character are compared, we shall only compare similar ligands for which the relation has been most intensively examined.

The Stability of Metal Oxine Complexes.—In their discussion of the relationship expressed by equation (2) Irving and Rossotti [7] produced evidence which they took to prove linear relationships between the acid dissociation constants of the phenol group of a series of 8-hydroxyquinolines and the stability constants of the individual series of the zinc, nickel, magnesium, uranyl, and cupric complexes. Additional ligands of the same series and their complexes with ferrous and ferric ions have now been examined.[9] As we did not find a simple relation between pκ and log K for these two metals we studied further the complexes of zinc, nickel, and manganous ions with 5-formyl-8-hydroxyquinoline. The conditions used were similar to those of Irving and Rossotti and all calculations of constants are modelled on their methods.[10] Fig. 1 incorporates both sets of results for zinc and nickel ions. Fig. 2 gives data for the ferrous complexes (Table 1). We cannot draw linear plots between pκ_{OH} and log K for these or for the other cations studied.

FIG. 1.

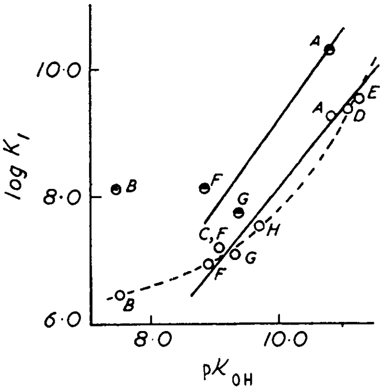

FIG. 2.

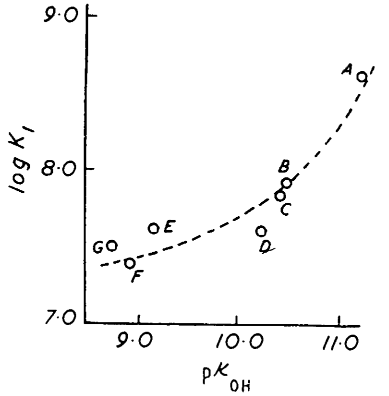

FIG. 1. *The relation between the dissociation constant of the phenolic group of oxines,* pκ_{OH}, *and the stability constants of the nickel,* ●, *and zinc,* ⊙, *oxine complexes.* Full lines, Irving and Rossotti; broken line, present work (see Table 1).

A, 8-Hydroxyquinoline; *B*, 5-formyl-8-hydroxyquinoline; *C*, 8-hydroxy-4-methylquinoline; *D*, 8-hydroxy-5-methylquinoline; *E*, 8-hydroxy-7-methylquinoline; *F*, 8-hydroxycinnoline; *G*, 8-hydroxyquinazoline; *H*, 8-hydroxyquinoxaline; *C,F*, 8-hydroxy-4-methylcinnoline.

FIG. 2. *The relation between the dissociation constant of the phenolic group of oxines,* pκ_{OH}, *and the stability constants of the ferrous oxine complexes (see Table* 1).

A, 8-Hydroxyquinoline; *B*, 5-bromo-8-hydroxy-; *C*, 5-chloro-8-hydroxy-; *D*, 8-hydroxy-5-iodo-; *E*, 5-chloro-8-hydroxy-7-iodo-; *F*, 8-hydroxy-5 : 7-di-iodo-; *G*, 5 : 7-dichloro-8-hydroxy-quinoline.

The linear relation between pκ_{OH} and log K suggested by Irving and Rossotti (full lines in Fig. 1) for some of the same metals and ligands arose because their study was limited to two *particular groups of ligands*: (1) substituted oxines with dissociation constants very near those of oxine itself, and (2) oxines in which a second ring nitrogen atom has been substituted. When a wider range of substituents is used the relation (1) is no longer obeyed. Moreover substituents in this series of ligands have specifically different effects

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[9] Tomkinson and Williams, following paper.
[10] Irving and Rossotti, *J.*, 1953, 3397.

on one metal from those on another, *e.g.*, in ferrous and ferric complexes.[9] Lastly, from eqn. (1) a linear relation might be expected between pκ and the oxidation–reduction potentials of the ferrous–ferric couples, but this is not found.[9]

TABLE 1. *Stability constants of oxine complexes.*

A. 5-Formyl-8-hydroxyquinoline complexes in 50% dioxan–water (v/v) (pκ_{OH} = 7·43).

	Ni^{II}	Fe^{II}	Zn^{II}	Mn^{II}	Fe^{III}
log K_1	8·27	6·90	6·45	5·73	11·7
log K_2	7·56	6·85	6·25	4·97	10·0
log K_3	6·70	5·70	4·95	4·58	8·3

B. Ferrous 8-hydroxyquinoline complexes in 75% dioxan–water (v/v).

Subst.	None	5-Cl	5-Br	5-I	5 : 7-Cl_2	5-Cl, 7-I	5 : 7-I_2
pκ_{OH}	11·22	10·47	10·45	10·27	8·83	9·07	8·96
pκ_{NH}	3·14	1·94	1·93	1·64	~0·9	~1·5	~0·5
log K_1	8·58	7·86	7·92	7·58	7·50	7·61	7·40
log K_2	8·35	8·07	8·19	8·13	7·31	7·80	7·69
log K_3	5·30	4·50	5·30	5·35	4·50	4·84	4·25

The pκ values are practical dissociation constants; for these and other values used in Fig. 1, see ref. 7.

Alternatively, by plotting log *K* against the sum of the pκ values for the two acidic centres in oxines (pκ_{OH} + pκ_{NH}) we find a somewhat more satisfactory agreement with eqn. (1), but the value of *a* for the cupric complexes is now 0·7 instead of 2·2. Whichever method is adopted of plotting the results, no exact linear relationship is obtained for any cations; the same conclusion can be reached from other data.[11]

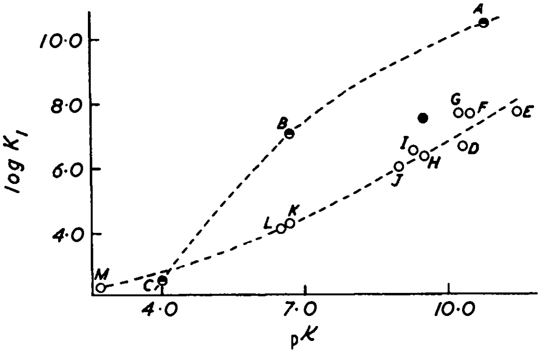

FIG. 3. *The relation between the dissociation constants of salicylaldehydes and the stability constants of the cupric salicylaldehyde complexes,* ○, *as compared with the same data for* 2-*hydroxy*-1-*naphthaldehyde,* ●, *and for a series of acetylacetone complexes,* ◒ *(see Table* 2).

A, Acetylacetone; *B*-trifluoroacetylacetone; *C*, hexafluoroacetylacetone; *D*, salicylaldehyde; *E*, 3-methyl-; *F*, 4-chloro-; *G*, 3-methoxy-; *H*, 5-chloro-; *I*, 5-bromo-; *J*, 3-chloro-; *K*, 3-nitro-; *L*, 5-nitro-; *M*, 3 : 5-dinitro-salicylaldehyde (CHO = 1).

TABLE 2. *Acid dissociation constants and stability constants of cupric complexes of salicylaldehyde derivatives.*

In 50% Dioxan–Water				In 75% Dioxan–Water							
Substituent	pκ	log K_1	log K_2	Substituent	pκ	log K_1	log K_2	Substituent	pκ	log K_1	log K_2
None	9·50	7·05	5·63	None	10·35	6·70	6·00	5-bromo ...	9·25	6·35	5·65
5-methyl ...	9·70	7·15	5·71	3-methyl ...	11·50	7·50	6·70?	5-nitro	6·55	4·10	3·50
5-methoxy	9·65	6·76	5·60	3-methoxy	10·20	7·50	6·40	3-nitro	6·70	4·20	3·40
3-methoxy	9·10	7·17	5·45	3-chloro ...	8·70	5·86	4·90	3 : 5-dinitro	2·60	2·20	1·40?
5-nitro	5·85	4·16	3·60?	4-chloro ...	10·50	7·50	6·50	(2-hydroxy-1-naphthaldehyde	9·35	7·35	6·52)
(Acetyl-acetone	9·70	9·40	8·03)	5-chloro ...	9·35	6·10	5·30				

The acid dissociation constants are practical constants. Values marked (?) are uncertain to ±0·20; others are uncertain to ±0·10. Agreement with Calvin and Wilson's data is satisfactory, differences in conditions of measurement being considered. Values for acetylacetone complexes in Fig. 3 are log K_1—2·0 from ref. 12, and not from this Table.

Stability of Metal Salicylaldehyde Complexes.—Restudying the interaction between derivatives of salicylaldehyde and cupric ions, we obtained the results in Fig. 3. By a

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[11] Albert and Hampton, *J.*, 1954, 505.

suitable choice of substituent pκ and log K cover a very considerable range. Although the linearity expressed by eqn. (1) with $a = 0{\cdot}68$ is obeyed to a good approximation, several marked deviations are found. For example, 4-chloro- and 3-methoxy-salicylaldehyde cupric complexes are abnormally stable relative to the pκ values for these ligands. The general scatter of points about the best straight line will be shown to be significant. In Fig. 3 a curve has been drawn through the points in order to contrast the data with those for the acetylacetone complexes.[12]

Calvin and Wilson [13] found, but did not comment on, the fact that although there was a rough linear relation between pκ and log K many salicylaldehyde derivatives also gave results deviating strongly from it. For example, the 4-nitro- and 4 methoxy-salicylaldehyde complexes did not behave as expected. Somewhat larger deviations were observed for naphthaldehyde complexes but these were explained by a treatment discussed below. These authors suggested that different series of complexes of aromatic aldehydes, salicylaldehydes, and naphthaldehydes, and a series of complexes of acetylacetone gave rise to relations of type (1) where a is approximately the same for all the series but b changes from series to series. Their best straight lines were of slope $a = 0{\cdot}70$. Now the value of a in this series of ligands is so different from that found [7] in the cupric oxine complexes, $a = 2{\cdot}2$, despite the fact that the dissociation constant of a phenolic group is used as a measure of basicity in both cases, that we decided to examine other series of ligands in order to find how a and b varied with ligand series.

TABLE 3. *Values of the constants in eqn.* (1).

Ligand class	Zinc		Cupric		Nickel		Magnesium		Note *
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	
Acetylacetone †	—	—	0·70	+3·8	0·55	+3·2	—	—	(1)
Oxine ($p\kappa_{OH}$) †	1·10	−3·0	2·20	−11·0	1·40	−4·5	1·00	−6·0	see p. 2003
,, ($p\kappa_{OH} + p\kappa_{NH}$) ...	0·50	+2·0	0·75	+1·5	0·45	+3·5	0·40	−1·0	
Tropolone †	0·70	+1·1	—	—	0·72	+0·6	0·44	+1·8	(2)
Imidodiacetic acid	0·90	−3·3	1·03	−1·0	1·04	−3·8	0·50	−2·3	(5)
	0·85	−3·5	1·33	−5·0	1·10	−4·5	—	—	
Phthalic acid	—	—	0·75	−0·8	0·50	−0·5	—	—	(3)
Phenanthroline	0·40	+4·0	—	—	—	—	—	—	(4)

Ligand class	Ferrous		Ferric		Note
	a	*b*	*a*	*b*	
Phenanthroline	0·85	+3·0	1·50	−1·0	(4)
Oxine † ($p\kappa_{NH} + p\kappa_{OH}$)	0·50	+3·0	0·90	+5·0	see p. 2003
Phenol	—	—	0·97	−1·0	

* See text.

The constants refer to best straight lines drawn through series of points which are often some distance from the lines. The values of a and b are liable to errors of $\pm 0{\cdot}1$ and $\pm 1{\cdot}0$ respectively. Series marked (†) refer to measurements in 50% dioxan–water and unmarked series refer to measurements in water. Change of solvent alters a only slightly but has a considerable effect upon b, although even the latter effect is probably within the " error " of the best straight lines.

Table 3 includes all the relevant data. Many of the complexes involve co-ordination through enolic or phenolic oxygen atoms. In most of the ligand series the ligand binds the cation through at least one other centre. The basicity of the second co-ordinating group is not always known, as for example in salicylaldehyde, so that in plotting the dissociation constant pκ of one of the groups against log K, it is not to be expected that an exact relation, if any, will be found. As we have seen for 8-hydroxyquinolines, use of only one acidic dissociation constant ($p\kappa_{OH}$) causes the linear relation (1) to break down. Several other relevant comments are now given as notes to Table 3

Notes to Table 3.—1. There is a number of exceptional ligands amongst the acetyl acetones and Van Uitert, Fernelius, and Douglas [12] prefer to draw a non-linear relation between pκ and log K at low pκ values (see Fig. 3). Van Uitert *et al.* also point out that the

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[12] Van Uitert, Fernelius, and Douglas, *J. Amer. Chem. Soc.*, 1953, **75**, 457; Van Uitert and Fernelius. *ibid.*, p. 3862.

[13] Calvin and Wilson, *ibid.*, 1945, **67**, 2003.

values of *a* are almost independent of the type of substituent. They give slightly different values to the constant *b* for the series of ligands which have aromatic and aliphatic substituents in acetylacetone respectively.

2. The α- and β-substituted tropolones[14] do not give rise to the same relation; *b* differs although *a* may be the same.

3. 3-Substituted phthalic acids behave exceptionally.[15] Such substituents appear to stabilise the cupric complexes more than expected from the magnitude of pκ. This has also been observed amongst salicylaldehydes.[13]

4. Only a few complexes with different substituents have been studied.[16] The redox potential of the Fe^{II}–Fe^{III} couple has been studied for a more extensive series of substituents. Now the value of the redox potential should be linear with pκ if eqn. (1) holds for both ferrous and ferric complexes, but this is not so.[9] The dipyridyls give a different relation from the phenanthrolines.

5. A re-plot of the data for the imidodiacetates[8] does not give a good linear relation so that values of *a* and *b* quoted may be in considerable error. There is some disagreement between the two sets of data.[1,8]

The surprising fact revealed by Table 3 and its notes is that, although a rough linear relation is found between log *K* and pκ for certain types of simple substituent, *e.g.*, for methyl, chloro-, and nitro-groups in salicylaldehyde, most authors stress that the relation fails if the conjugated system of the ligand extends through carbon chains, *e.g*, a phenyl substituent in acetylacetone, a change from salicylaldehyde to naphthaldehyde, or the change from dipyridyl to *o*-phenanthroline amongst imines. Now it is usually supposed that a substituent such as a nitro-group interacts with a conjugated hydrocarbon in much the same way as an extension of the conjugation: there should thus be changes in both σ- and π-electron densities throughout the molecule. Such changes might well alter the stability of HL in a manner different from that of ML. In order to exaggerate such differences it is preferable to examine a group of ligands in which the same single substituent is placed in the *ortho*-, *meta*-, and *para*-positions to the acidic centre in turn rather than merely to vary the substituent in one of these positions. The effects of such changes in the position of one substituent are known in salicylaldehydes and 8-hydroxyquinolines (Table 4). The expected relation between pκ and log *K* is no longer observed. Now if we restrict our examination of the relation (1) to the 4- and 5-substituted salicylaldehydes,

TABLE 4.

Relative stabilities of complexes of cupric ion with salicylaldehydes substituted *ortho*, *meta*, and *para* to the hydroxyl groups (*i.e.*, at positions 3, 4, and 5 respectively).

Substituent		*ortho*	*meta*	*para*	Solvent
Nitro	pκ	6·0	7·4	5·9	50% dioxan
	$\log K_1$	4·15	4·9	4·35	
Methoxy	pκ	9·10	9·3	9·65	50% dioxan
	$\log K_1$	7·17	7·5	6·76	
Chloro	pκ	8·70	10·50	9·35	75% dioxan
	$\log K_1$	5·86	7·50	6·10	

Relative stabilities of complexes of zinc and nickel ions with 8-hydroxyquinolines having aza-substituents *ortho*, *meta*, and *para* to the nitrogen group (*i.e.*, 8-hydroxy-cinnoline, -quinazoline, and -quinoxaline respectively).

	ortho	*meta*	*para*
$(p\kappa_{NH} + p\kappa_{OH})$	10·61	12·89	10·30
$\log K_1$ (Zinc)	6·93	7·48	7·07
$\log K_1$ (Nickel)	9·48	10·56	9·66

The relative order of stabilities *para* > *ortho* for π-electron acceptors differs from that, *ortho* > *para*, for π-electron donors. *meta*-Substituted complexes are more stable when the substituent is a π-electron donor.

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[14] Bryant, Fernelius, and Douglas, *J. Amer. Chem. Soc.*, 1953, **75**, 3784; Bryant and Fernelius, *ibid.*, 1954, **76**, 1696.

[15] Yasuda, Suzuki, and Yamasaki, *J. Phys. Chem.*, 1956, **60**, 1649.

[16] Brandt and Gullstrom, *J. Amer. Chem. Soc.*, 1952, **74**, 3532.

we find that the 4-substituents give rise to a relation in which *a* and *b* differ from those giving the best straight line through the points for 5-substituents. (The 3-substituents are exceptional in another manner, see footnote.) One explanation of the two relationships is immediately apparent. The cupric ion gains in stability relative to the hydrogen ion if the substituent is a π-electron acceptor, *e.g.*, a 5-nitro-group, as the cupric ion can act as a d_ϵ-electron donor. On the other hand a 5-chloro-group, a π-electron donor, makes the copper complex less stable than the hydrogen complex. The 4-substituents affect the electron density on the phenol oxygen atom much less than the 5-substituents so that the π-electron changes with 5-substituents are greater than with 4-substituents. Hence there are two relations, one referring to *para*-substituents (to the hydroxyl group) having the smaller slope, *a*. The curvature of the line in Fig. 3 can thus be explained. The absorption spectra of the cupric complexes also provide evidence that the π-electron interaction in the metal complexes does occur in the manner described. Extension of conjugation, *e.g.*, in going from dipyridyl to *o*-phenanthroline, will lower the π-electron density on nitrogen or oxygen atoms but will have little effect upon σ-electron density. This is why the *o*-phenanthroline complexes are more stable than those of dipyridyl, two ligands of very similar basicity.

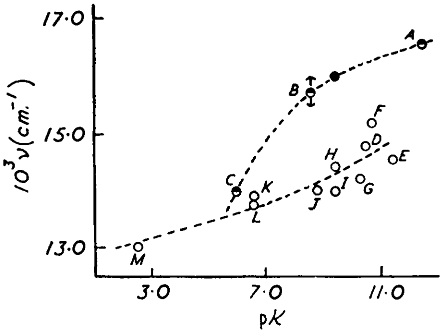

Fig. 4. *The relation between the acid dissociation constants of a series of salicylaldehydes and the frequency of the maximum in the absorption spectra of the cupric salicylaldehyde complexes* ○.

Corresponding data are given for 2-hydroxy-1-naphthaldehyde, ●, and for a series of acetylacetones, ◒.

A, Acetylacetone; *B*-trifluoroacetylacetone; *C*, hexafluoroacetylacetone; *D*, salicylaldehyde; *E*, 3-methyl-; *F*, 4-chloro-; *G*, 3-methoxy-; *H*, 5-chloro-; *I*, 5-bromo-; *J*, 3-chloro-; *K*, 3-nitro-; *L*, 5-nitro-; *M*, 3 : 5-dinitro-salicylaldehyde (CHO = 1).

Absorption Spectra of Cupric Complexes.—We use the theory of the visible absorption spectrum of cupric ion given elsewhere.[17] The ground state is stabilised relative to the excited state either by increase of σ-donor or π-acceptor properties of the ligands. We assume that the σ-properties of the ligand are related to the pκ values so that the lower the pκ the lower the frequency of the absorption maximum. If no other effect had to be taken into account a linear relation might be expected between these quantities.

Fig. 4 shows that relative to those of salicylaldehyde, acetylacetone and naphthaldehyde complexes have absorption spectra at shorter wavelengths than expected on the basis of their respective pκ values. This implies that these ligands act as better d_ϵ electron acceptors from the cupric ion, as mentioned above. This stabilisation is due to electron migration in the opposite direction to that proposed by Calvin and Wilson,[13] who concluded that the π electrons of the ligand were stabilised by the cation. 3- or 5-Substituents * which are π-electron donors shift the absorption band to lower frequencies and longer wavelengths, and π-electron acceptors shift the band to higher frequencies, than expected on the basis of pκ values. As an example we can compare the cupric complexes of 5-nitro- and 5-bromo-salicylaldehyde. The bromo-group, a π-electron donor, destabilises the ground state but the nitro-group stabilises it relative to the respective pκ values. The absorption maxima of the two complexes are at very similar wavelengths, as expected.

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* Some of the 3-substituted salicylaldehydes form complexes with cupric ion which are considerably more stable than the corresponding 5-substituted complexes, *e.g.*, 3-methoxy. The absorption spectra and step stability constants of these complexes are anomalous when compared with 4- and 5-substituted ligand complexes.[24]

[17] Williams, *J.*, 1956, 8.

Other features of Fig. 4 will be discussed elsewhere. Further evidence can be drawn from the study of the fluoro-derivatives of acetylacetone.[18] In Fig. 4 the plot for cupric acetylacetone derivatives shows that for a given change of pκ the position of the absorption maximum changes more rapidly than in the salicylaldehyde complexes. The stability of the acetylacetone complexes also changes more rapidly with pκ (Fig. 3). The difference between the two series of ligand complexes is attributable to the π-donor character of the fluoro-substituents in the acetylacetone derivatives as compared with the π-acceptor character of the nitro-groups in the salicylaldehyde complexes.

We now return to the 8-hydroxyquinoline series. The different correlation between pκ and log K obtained by Irving and Rossotti,[7] and by ourselves arose partly from choice of the substituent and partly from the use of only pκ_{OH} (instead of pκ_{NH} + pκ_{OH}) as a measure of basic strength. Using either method of examining the data, however, we find that the 5-formyl-8-hydroxyquinoline complexes are more stable than expected from the pκ value of the ligand. This we now suggest is due to the strong π-electron acceptor character of this substituent. A convincing illustration of the influence of such π-electron acceptor properties in this series is provided by a comparison of the effects of aza-substituents (Table 4); such substituents "*meta*" to the nitrogen group are less effective than those "*ortho*" or "*para*" in stabilising the metal complexes relative to its basicity (pκ_{NH} + pκ_{OH}) in any one of the series of complexes of ferrous,[11] cupric, or zinc [7] ion. This is to be expected as an aza-substituent acts as a π-electron acceptor but it can only be effective when *ortho* or *para* to the co-ordination position. The position of the absorption band in the ferrous complexes [19, 20] confirms that an aza-substituent so placed acts as a strong π-electron acceptor. The parallel with the discussion of the three mononitrosalicylaldehyde cupric complexes is obvious.

Amongst ferric oxine complexes, those of 5-formyl- and 5-cyano-8-hydroxyquinoline are rather less stable than expected on the basis of pκ values. The ferric ion acts as a π-electron acceptor, unlike the other cations discussed here. It is in part this difference between the ferric ion and the ferrous ion that causes the plot of redox potential against basicity to take such a singular form.[9, 20] Albert and Hampton's [11] data show similar differences between ferrous and ferric aza-substituted oxine complexes, although the authors did not comment upon these peculiarities. Lastly, amongst *para*-substituents in ferric phenoxides bromo and methyl stabilise but nitro destabilises the ferric complex relative to the respective pκ values of the ligands as in the oxine complexes.[21] In each of these series the absorption spectra of ferric complexes support the conclusion that substituents have opposed effects upon the stability of the ferric and ferrous ground states.[19]

Now all the cations considered above are derived from transition elements which can act as *d*-electron donors or acceptors. The magnesium ion should behave differently. It is not noticeably more stable in cinnoline than in quinazoline complexes,[7] implying that the π-electron density has little importance in the stability of magnesium complexes.

Change of a *with Cation.*—We now discuss eqn. (1) more generally, and assume that deviations from the relation can be understood in such terms as those discussed. For aromatic ligands and d_ϵ-electron donor cations the slope a tends to a value lower than unity owing to the compensating effect of π interactions. As expected, the value of a is closer to unity for aliphatic ligands, when there are no π effects, for series of cupric, nickel, or zinc complexes, *e.g.*, imidodiacetates (Table 3). We also consider the effect on the slope of a change of cation.

In a simple electrostatic model, with charge e_1 on the ligand and charge e_2 on the cation, the energy of interaction is e_1e_2/d where d, the distance of separation, can be put equal to the radius of the cation plus a constant, $r + c$. If a change in substituent changes e_1

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[18] Belford, Martell, and Calvin, *J. Inorg. Nuclear Chem.*, 1956, **2**, 11.
[19] Williams, *J.*, 1955, 137.
[20] Williams, *Chem. Rev.*, 1956, **56**, 299.
[21] Milburn, *J. Amer. Chem. Soc.*, 1954, **77**, 2064.

only, then there will be a linear relationship between pκ and log K. The slope will not be unity, but will depend on the differential of e_1e_2/d with respect to e_1, *i.e.*, e_2/d, and will increase with increasing cationic charge and decreasing d. This is found to be so. For example, for lanthanum ($e_2 = 3$) the slope is greater than for barium ($e_2 = 2$) in a series of acetylacetone complexes.[12]

A somewhat more obscure relationship is observed for ions of the same charge but of different size. Our model suggests that the bigger the cation, *i.e.*, the bigger r, the smaller the value of a. In the cases of the barium acetylacetone and calcium imidodiacetate complexes, a is smaller than for the complexes of the larger cupric ion. In the series of cations Cu^{II}, Ni^{II}, Co^{II}, Mn^{II} the magnitude of the slope a falls in that order, *i.e.*, the stability order found by Irving and Williams. However there is little difference in the size of the cations in this series as compared with the changes in a. (This series of a values implies that there cannot be a general relation of unit slope between log K_{ML} for one metal and log $K_{M'L}$ for another, where M and M′ are both in this series of cations.[7]) The order is also the order of the electronegativity of the cations. This parallel was pointed out by Schwarzenbach *et al.*;[1] it implies that a is proportional to the polarisation of the ligand by the cation. Such polarisation can only be expressed in terms of a detailed treatment of the molecular orbitals in transition-metal complexes and here we shall not concern ourselves further with the problem.

The Values of b *in Equation* (1).—We make the same assumption as in the discussion of a. A comparison of eqns. (1) and (2) shows that b is a composite constant. It comprises the difference in partial molar free energy of the cation and proton, B (independent of the ligand), and terms which are dependent on the ligand, as is shown by eliminating log K between the two equations whereupon we obtain

$$(G^\circ_{ML} - G^\circ_{HL})/\boldsymbol{R}\boldsymbol{T} = (1 - a)\mathrm{p}\kappa - (b - B) \qquad . \quad . \quad . \quad . \quad . \quad (3)$$

For two ligand series which give rise to the same constant a the term $(b - B)$ will measure the additional stabilisation of one series of ligands, *e.g.*, salicylaldehydes, as compared with another, *e.g.*, acetylacetone, and is assumed here to be independent of the substituents within each series. (We have already shown that this is not exactly true when 4-substituted are compared with 3- or 5-substituted salicylaldehydes but the order of the effect is smaller than the one we are about to discuss.) Table 3 shows that b [or $(b - B)$] changes considerably from aliphatic to aromatic ligands in the order imidodiacetic acid $\ll$ phthalic acid $<$ salicylaldehyde (Fig. 3) $<$ naphthaldehyde $<$ acetylacetone $\ll$ oxine.

Calvin and Wilson explained a part of this order of b, namely salicylaldehyde $<$ naphthaldehyde $<$ acetylacetone, on the basis of resonance between the cation and the ligands. This resonance entailed the transfer of charge from the ligand to the cation. We do not accept this interpretation but believe that the transfer of charge which *in part* controls $(b - B)$ is the transfer of d_ϵ electrons of the cation, *e.g.*, cupric, to the ligand. The ligand series for which $(b - B)$ is greatest, oxine or acetylacetone, is also the series for which the cupric absorption band is at the shortest wavelength for a given pκ. Following our argument concerning spectra the ligand order given above appears to be dominated by the order of the ability of the ligands to accept electrons through π bonding.

It must not be assumed that the only factor affecting $(b - B)$ is π-bonding. There may well be differences in solvation between ML and HL which are independent of the dissociation constant within a given series but are sensitive to changes from one series of ligands to another. For example, we consider that solvation differences contribute to the difference in relative position between the acetylacetone and naphthaldehyde series in Figs. 3 and 4. Such solvation factors will be of some importance even within a given series, so that a strict linear relation between pκ and log K cannot be expected. Solvation effects should be more or less independent of the cation, especially for cations of similar charge, whereas the changes in $(b - B)$ due to π bonding should depend on the cation. A case in point is the effect of aromatic substituents in acetylacetone complexes upon the $p\kappa$–log K relations.[13] Such substituents have the same effect in barium, cerium, nickel, or cupric complexes and we suspect that the factor common to these different series of cation complexes is one of solvation rather than of π bonding.

This paper has been restricted largely to a discussion of relation (1) for bivalent cations. The relation is less applicable to univalent and null-valent cations where π-bonding is more important. For univalent cations this was shown by Basolo and Murman.[22] Studying the case of the combination of ligands with a cation on which the charge has been neutralised by complex formation with anions we found that there is no relation of the form of eqn. (1).[23] This in turn is due to the increasing importance of π-effects as the valency of the cation is reduced.

EXPERIMENTAL

Materials.—8-Hydroxyquinoline derivatives were gifts. The salicylaldehydes were prepared by conventional methods. Additional details will be given later of the cupric salicylaldehyde complexes.[24] " AnalaR " metal salts were used to determine stability constants.

Methods.—These are well established.[7, 8] pH Titrations were used to determine the acid dissociation constants and stability constants of metal complexes. In all cases water–dioxan was used as solvent. The ionic strength in the solutions was constant at 0·3M by addition of sodium perchlorate (cupric experiments) or sodium chloride (other cation experiments). Sodium hydroxide was carbonate free.

The absorption spectra of the complexes were measured on a Unicam S.P. 600 spectrophotometer with matched cells. For the cupric salicylaldehyde complexes the measurements were made in 75% dioxan–water, *i.e.*, the same medium as that in which the stability constants were determined, when this was practicable. All measurements were made at a sufficiently high pH to ensure that the degree of complex formation was $\bar{n} = 2{\cdot}0$. In several cases the spectra were also measured in 50% dioxan–water. No differences were observed in the position of the absorption spectra between the two solvent media. The 5-chloro- and 3 : 5-dinitrosalicylaldehyde cupric complexes were too insoluble in either solvent to permit the determination of their absorption spectra. These spectra were measured in 50% methanol–dioxan by adding a ten-fold excess of ligand in dioxan to cupric chloride in methanol and then raising the pH by adding enough concentrated potassium hydroxide in methanol to neutralise 75% of the ligand. In order that these spectra could be referred to the parent salicylaldehyde complex the same measurements were made with the latter. There was a shift of some 35 mμ to shorter wavelengths from the aqueous solvent to the methanol solvent, and this was allowed for. We did not attempt to analyse the spectra further for, although there are three overlapping *d–d* transitions of the cupric ion in the visible region of the spectrum, only one maximum was observed in any measurement. The positions of the maxima in the acetylacetone complexes were taken as 620 mμ for acetylacetone, 625—675 mμ for trifluoroacetylacetone, and 710 mμ for hexafluoroacetylacetone. The first value is that observed in 75% dioxan–water and differs very slightly from the mean of the two peak maxima in chloroform (606 mμ).[18] The other values are those observed in chloroform.[18]

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[22] Basolo and Murman, *J. Amer. Chem. Soc.*, 1955, **77**, 3484.
[23] Jillot and Williams, *J.*, 1958, 462.
[24] Jones, Poole, and Williams, to be published.