The Thermodynamic Metal–Ligand Stability Constants of Hydroxamic Acids with some Divalent Metal Ions

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The thermodynamic metal–ligand stability constants of *N*-(*m*-chlorophenyl)-*p*-substituted benzohydroxamic acids with Pd^{II}, Cu^{II}, Zn^{II}, Ni^{II}, Co^{II}, Fe^{II}, and Mn^{II} have been determined at 25 °C in 50% (v/v) dioxane–water medium.

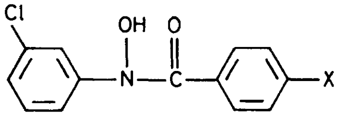
The stability of the complexes mostly follows the order of basicity of the ligands and also the electron-affinity of the metal ions, measured by their ionization potential. The free energy relationship, thermodynamic parameters, transition contraction energy, and ligand field stabilization energy of the complexes have been calculated.

In all the studies made here, the metal–ligand stability constants follow the order:

$$Pd^{II} > Cu^{II} > Zn^{II} > Ni^{II} > Co^{II} > Fe^{II} > Mn^{II}.$$

The new type of chelating agents in analysis have made possible new analytical methods by titrimetric, gravimetric, and colorimetric measurements. The hydroxamic acids have remarkable versatility in organic and inorganic analysis. A knowledge of metal–ligand stability constants offers a means of obtaining fundamental knowledge about the structure of the chelates. It has also been possible to correlate equilibrium data with the electronegativity of metal ions, the steric requirement of chelating agents, and the size of the chelating rings. In view of this it is desirable to determine the stability of the hydroxamic acids with some divalent metal ions.

In the present investigation the thermodynamic metal–ligand stability constants of *N*-(*m*-chlorophenyl)-*p*-substituted benzohydroxamic acids (1) with Pd^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+}, have been determined in 50% dioxane–water media at 25 °C.



(1)

H, F, Cl, Br, or NO_2

Experimental

All the chemicals used were of AR or GR grades of BDH or Merck, respectively.

Reagents.—The hydroxamic acids were synthesised as described elsewhere.[1] These were recrystallised from a mixture of benzene and light petroleum (b.p. 60–80 °C)–diethyl ether (2:1) before use. Tetrabutyl ammonium hydroxide (Bu_4NOH, 0.1 mol dm^{-3}) was used as a titrant. The metal perchlorates were prepared from their oxides. The concentration of metal ions was determined volumetrically.[2,3] Doubly distilled water was redistilled over alkaline $KMnO_4$ and tested for the absence of carbonate.[4] Dioxane was purified by the method of Weissberger.[5]

Apparatus.—A digital Radiometer pH meter Model PHM 84 equipped with combined glass and calomel electrode (G4) was used for the pH measurements.

Procedure.—A weighed quantity of hydroxamic acid, corresponding to a 0.01 mol dm^{-1} solution in a final volume of 50 cm^3, was transferred to a dry titration vessel and 25 cm^3 of freshly distilled dioxane was added. Metal perchlorate (0.01 mol dm^{-3}, 5 cm^3), perchloric acid (0.02 mol dm^{-3}, 5 cm^3), and water (15 cm^3) were added. Due allowance was made for the contraction in volume on mixing the two solvents.[6,7] The titration vessel and contents were then thermostatted (25 ± 0.1 °C) and nitrogen, pre-saturated with the 50% dioxane–water mixture, was bubbled through the solution. The glass and calomel electrodes were placed in the titration vessel. The solution was titrated with tetrabutylammonium hydroxide (0.1 mol dm^{-3}), adding the same quantity in small aliquots and noting the pH meter reading (B), each time.

Calculations.—The thermodynamic metal–ligand stability constants were calculated as described elsewhere.[6,9] The data were fed into a CDC-3600 computer in order to calculate log K_1 and log K_2.[10]

Results and Discussion

A large number of pH titrations were performed at different concentrations of reactants and by varying the metal to ligand ratio. Generally, the free perchloric acid was not added to the solution unless the amount of complex formed at the start of the titration was very large.

The titration was stopped if at any stage the system became heterogeneous from precipitation of metal as a complex or hydrolysed species, since an essential condition for the determination of the solution stability constants of the complexes is that the system must remain in a homogeneous medium. The ligand to metal ratio in some titrations was varied. This was done to observe any effect due to polynuclear complex formation. The formation function, $\bar{n}$, is independent of metal concentration if the system contains mononuclear complexes only. In all the systems investigated in the present work, no evidence for the formation of polynuclear complexes was observed. The mole ratio of metal salt to ligand in the experiments was generally

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Table 1. Thermodynamic metal–ligand stability constants of *N*-(*m*-chlorophenyl)-p-substituted benzohydroxamic acids in 50% (v/v) dioxane–water media at 25 °C.[a]

Metal ions	Constants	Substituent (X)							
		C_2H_5O	CH_3O	CH_3	H	F	Cl	Br	NO_2
	pK_a	11.04	10.90	10.70	10.51	10.38	10.20	10.24	10.04
	log K_1	10.99	10.90	10.66	10.55	10.42	10.23	10.20	10.03
Pd^{II}	log K_2	9.49	9.32	9.10	8.85	8.72	8.51	8.58	8.30
	log K_1	10.37	10.28	10.05	9.94	9.80	9.61	9.60	9.41
Cu^{II}	log K_2	8.70	8.52	8.25	8.02	7.88	7.68	7.68	7.48
	log K_1	8.25	8.07	7.80	7.50	7.36	7.16	7.13	6.92
Zn^{II}	log K_2	6.55	6.40	6.15	5.90	5.75	5.55	5.52	5.32
	log K_1	7.82	7.66	7.41	7.24	7.10	6.88	6.86	6.68
Co^{II}	log K_2	6.05	5.90	5.65	5.45	5.32	5.12	5.12	4.92
	log K_1	7.79	7.65	7.38	7.21	7.07	6.86	6.84	6.65
Ni^{II}	log K_2	6.00	5.80	5.60	5.43	5.30	5.10	5.09	4.90
	log K_1	6.87	6.70	6.45	6.15	6.00	5.80	5.76	5.58
Fe^{II}	log K_2	5.80	5.60	5.30	5.04	4.89	4.69	4.65	4.40
	log K_1	6.70	6.49	6.25	6.02	5.88	5.67	5.64	5.45
Mn^{II}	log K_2	5.57	5.40	5.15	4.91	4.77	4.57	4.54	4.34

[a] The values of log K_1 and log K_2 are the average of five titrations. The standard deviation for the values of log K_1 is ±0.04 and for log K_2 is ±0.05.

Table 2. Thermodynamic metal–ligand stability constants of *N*-(*m*-chlorophenyl)benzohydroxamic acid with metal ions in 50% dioxane–water at 35 °C.

Metal ions	log K_1	log K_2	log K_1/K_2
Mn^{2+}	5.87	4.76	1.11
Fe^{2+}	6.01	4.89	1.12
Co^{2+}	7.06	5.29	1.77
Ni^{2+}	7.04	5.28	1.76
Cu^{2+}	9.75	7.83	1.92
Zn^{2+}	7.32	5.72	1.60

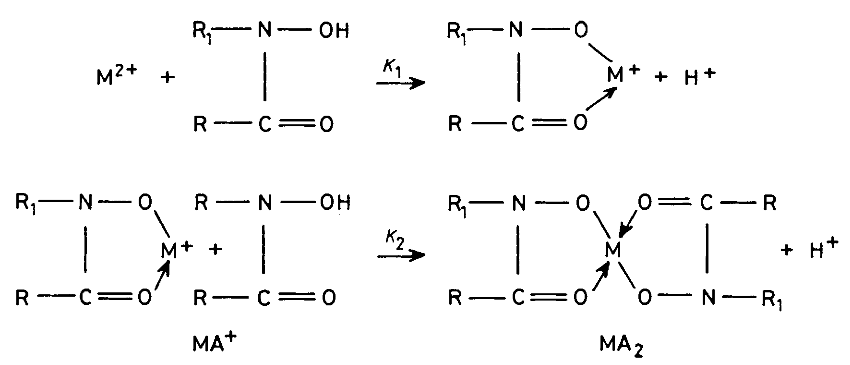
maintained at 1:10 although a few studies were also made at different ratios.

The average values of stability constants in 50% (v/v) dioxane–water at 25 °C are given in Table 1. The values of stability constants for *N*-(*m*-chlorophenyl)benzohydroxamic acid in 50% (v/v) dioxane–water media at 35 °C are given in Table 2 for comparison only.

Hydroxamic acids are known to act as bidentate ligands and form chelates with metal ions.[11–13] Bivalent metal ions examined here form solid inner complexes with hydroxamic acids.[12–14] The metal to ligand ratio in these complexes is 1:2 showing a co-ordination number 4 for the metal ion. The titration data and the formation curves indicate that in solutions too the maximum complexation involves the four co-ordinated species, and no penta- or hexa-co-ordinated species is formed. The two complex species which are formed stepwise can be explained by the reactions below, where K_1 and K_2 are the first and second stepwise metal chelate stability constants.

Correlation between Ionisation Constants and Stability of the Complex.—It has been pointed out by several workers[13–24] that an approximately linear relationship exists between the logarithms of the stability constants of a series of metal complexes derived from one metal ion with a set of closely related ligands. Hence it is expected that a more basic ligand should form more stable complexes. A linear relationship between metal complexes of *N*-arylhydroxamic acids and their pK_a values is obtained.

The overall stability constants (log K_1, K_2) and log K_1 of divalent metal ions are plotted against pK_a values of cor-



M = Pd, Cu, Zn, Co, Ni, or Mn

Table 3. Empirical correlation between pK_a and $\log K_1$ of *N*-(*m*-chlorophenyl)-*p*-substituted benzohydroxamic acid metal complexes in 50% (v/v) dioxane–water at 25 °C.

Metal ion	$\log K_1 = mpK_a + c$		
	m	c	r
Pd^{2+}	0.96	0.40	0.995
Cu^{2+}	0.96	−0.18	0.995
Zn^{2+}	1.34	−6.57	0.998
Co^{2+}	1.14	−4.75	0.998
Ni^{2+}	1.14	−4.81	0.998
Fe^{2+}	1.33	−7.83	0.995
Mn^{2+}	1.24	−6.99	0.998

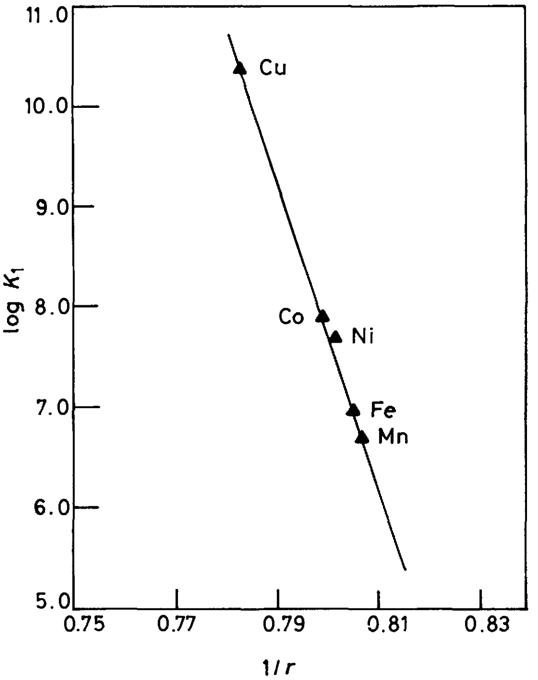


Figure 1. Variation of $\log K_1$ of *N*-(*m*-chlorophenyl)-*p*-ethoxybenzohydroxamic acid *versus* $1/r$ of the metal ions.

responding hydroxamic acids. Those which show a linear relation (the empirical relationship $pK_a = m \log K_1 + C$) are given in Table 3.

It is evident, from the pK_a values of hydroxamic acids and logarithms of the successive stability constants of the corresponding metal–ligand complexes given in Table 1 that the introduction of *para*-substituents has a parallel effect on proton–ligand and metal–ligand stability constants in the following manner:

pK_a $C_2H_5O > CH_3O > CH_3 > H > F > Cl > Br > NO_2$
$\log K_1$ $C_2H_5O > CH_3O > CH_3 > H > F > Cl > Br > NO_2$
$\log K_2$ $C_2H_5O > CH_3O > CH_3 > H > F > Cl > Br > NO_2$
$\log \beta_2$ $C_2H_5O > CH_3O > CH_3 > H > F > Cl > Br > NO_2$

Order of Stability Constants.— The sequence for complexes of Pd^{II}, Cu^{II}, Zn^{II}, Ni^{II}, Fe^{II}, Co^{II}, and Mn^{II} with hydroxamic acid is a result of the factors (*a*) ionic radii and (*b*) electronegativity, measured by ionization potential and ligand field stabilization energy (LFSE). Maley and Mellor[25] and later Irving and Williams[26,27] have shown the order of stability constants for the divalent metal ions to be:

$$Mn^{II} < Fe^{II} < Zn^{II} < Co^{II} < Ni^{II} < Cu^{II} < Pd^{II}$$

The stability constants of hydroxamic acids follow almost the same order:

$$Mn^{II} < Fe^{II} < Ni^{II} < Co^{II} < Zn^{II} < Cu^{II} < Pd^{II}$$

The stability constants are invariant for $\log K_1$ ($\log K_2$ or $\log \beta_2$) with hydroxamic acids and divalent ions of the 3d transition series (Table 1). Beyond Mn^{II} the constants increase with increasing atomic number reaching a maximum with $3d^9$ Cu^{II}; a decrease is observed with $3d^{10}$ Zn^{II} as follows:

$$Mn^{II} < Ni^{II} < Cu^{II} > Zn^{II}$$

Taking the $3d^5$ and $3d^{10}$ systems as a base line (no crystal field stabilization, Figure 4), it is seen that there is an extra stability for $3d^9$, Cu^{II}, while the stability is less for $3d^8$, Ni^{II}. There is a crystal field correction increasing to a maximum at Cu^{II} and falling abruptly to zero at Zn^{II}.[28,29] The Zn^{2+} hydroxamate complexes have higher stability compared with Ni^{2+}. The same trend is also reported with several hydroxamic acids and other ligands.[18–24,30]

The hydrolysis constant of Zn^{II} is greater than that of Ni^{II} indicating a greater affinity of Zn^{2+} ion for the –OH group. The hydroxamic acid, with a functional grouping N(OH)–C=O, resembles the –OH group carrying a negatively charged oxygen ion. If the bonding involved were purely ionic, then the smaller Zn^{2+} ion[31] would be expected to form a stronger complex than Ni^{2+}, as observed here.

It has been observed that the Co^{II} hydroxamate complexes have higher stability constants compared with Ni^{II}. A similar order was reported by Agrawal *et. al.* for other hydroxamic acids[32] and other ligands *viz.* 4-nitro-2-aminophenol[33] and 8-hydroxy-2-methylquinolinol.[34–36]

Ionic Charge and Radius.—It has been observed from the stability constant data reported hitherto for the metal ion complexes of hydroxamic acids that the metal–ligand stability constants increase, in general, with increasing ionic potential (charge/radius) of the metals. A plot of the stability of various metal chelates ($\log K_1$) *versus* reciprocal of the ionic radius is linear for all hydroxamic acids reported here (Figure 1).

Ionisation Potential and Electronegativity.—Attempts have been made by several authors[18–24,29] to correlate the stability constants for a series of complexes of hydroxamic acids with ionization potential and an approximately linear correlation is observed.

Nieborer and McBryde[37] have developed a correlating numeral index Q defined as:

$$Q = (a\,\delta Z X_M + b\,X_M^2)/(a + b) \qquad (1)$$

and have obtained a linear relationship for plots of $\log K_1$ *vs.* Q for various metals and more than thirty ligands. The spectral assignment of Q values to metals are given in Table 4. It is evident (Table 4) that the index is independent of the nature of the ion and that a characteristic plot (Figure 2), of $\log M_A$ *vs.* Q can be established in each case for hydroxamic acid.

The plots of the stability constants of metal ions *vs.* Q and ionization potential are given in Figures 2 and 3. In each case a straight line is obtained. The points corresponding to Cu^{II} complexes with all these ligands do not fall on the straight lines but are always above them. The higher magnitude of the stability constants for the complexes of copper has been attributed[18–24,29] to the unique electronic configuration due to tetragonal distortion of the octahedral symmetry as a result of

Table 4. Q-Values for N-(m-chlorophenyl)-p-substituted benzohydroxamic acid metal complexes.

Metal ions	x_m	Q	r
Mn^{2+}	1.55	2.75	0.99
Fe^{2+}	1.83	3.50	0.98
Co^{2+}	1.88	3.65	0.99
Ni^{2+}	1.91	3.74	0.99
Cu^{2+}	1.99	4.20	0.99
Zn^{2+}	1.65	3.42	0.99
Pd^{2+}	2.20	4.62	0.98

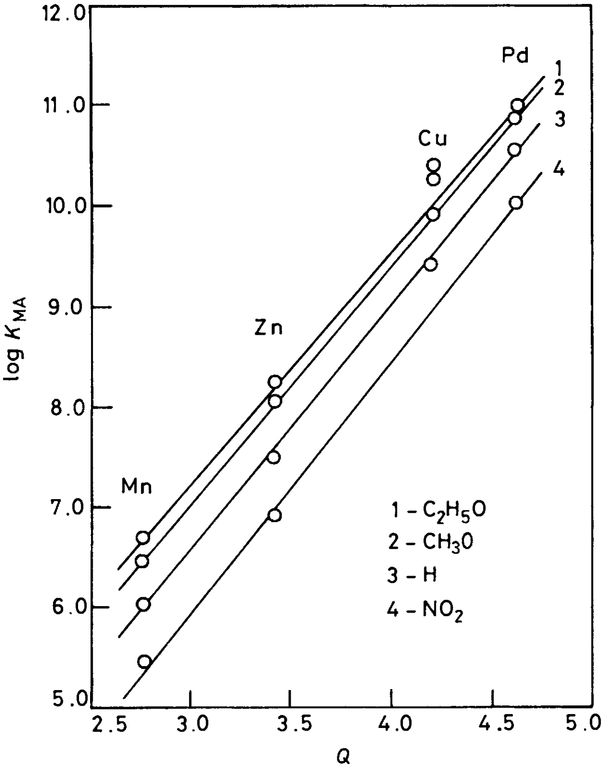


Figure 2. Plot of log K_{MA} *versus* Q.

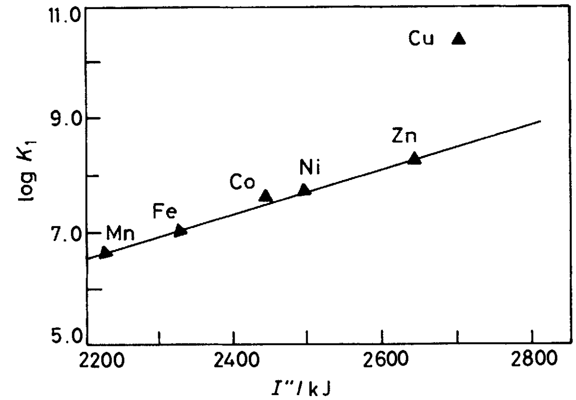


Figure 3. Variation of log K_1 of N-(m-chlorophenyl)-p-ethoxybenzohydroxamic acid with ionization potential of metal ions.

the Jahn–Teller effect. The Cu^{2+} ion, with its d^9 configuration, provides one of the best opportunities for observation of this distortion to an appreciable extent.

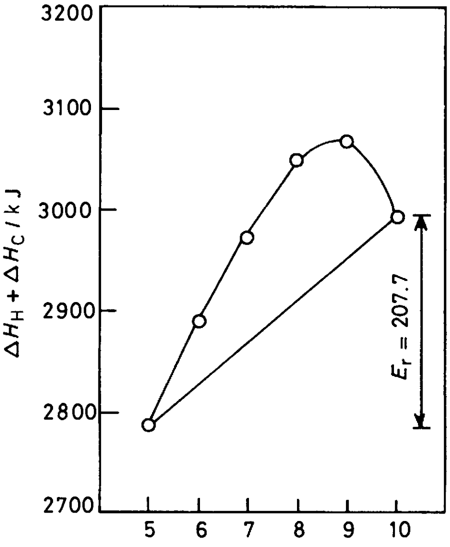


Figure 4. Variation of (ΔH_H + ΔH_C) values with a number of $3d^n$ (Mn–Zn) metal ions.

Ligand Field Stabilization Energy.—The stability constants of complexes are related to the free energy changes and consequently to the temperature independent heat of reaction:

$$-RT \ln k = \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (2)$$

These values are shown in Figure 4 and Table 5. The lower line in Figure 4 represents the same value corrected for orbital-stabilizing energy arising from the ligand field treatment of the complexes. This shows the regular increase in ΔH_C with increasing atomic number.

George and McClure[38] have defined the transition series contraction energy E_r (Mn–Zn), as the heat of reaction for

$$Zn^{2+}\ (g) + MnA^{2+}\ (n\ aq.) \longrightarrow Zn^{2+}\ (n\ aq.) + Mn^{2+}\ (g)$$

and this may be calculated from equation (3), where $\Delta H_H(M^{2+})$

$$E_r = -\Delta H_H(Zn^{2+}) + \Delta H_C(Zn^{2+}) + \Delta H_H(Mn^{2+}) + \Delta H_C(Mn^{2+}) \qquad (3)$$

is the heat of hydration of the transition metal ion, M^{2+} (g) = M^{2+} (aq.), $\Delta H_C(\Delta H^{\circ})$ is the heat of complex formation, and E_r is the transition series contraction energy from Mn to Zn ($3d^5$–$3d^{10}$).

The LFSE, ΔH, in a complex of $3d^n$ transition metal ion M^{2+} may be obtained from the enthalpy change if it is assumed that all the Mn^{2+} to Zn^{2+} complexes have the same symmetry *viz.* octahedral or tetrahedral.[38] Hence $\Delta H(M^{2+}) = \Delta H_C(M^{2+}) - 0.2(n-5)E_r - \Delta H_C(Mn^{2+}) - \Delta H_H(Mn^{2+})$, where n is the number of d electrons.

A plot of (ΔH_H + ΔH_C) of N-(m-chlorophenyl)-p-methylbenzohydroxamic acid complexes as a function of 3d electron in the metal ion is shown in Figure 4. The values of hydration energy, ΔH_H, are those given by George and McClure.[38] The LFSE, ΔH, of the complexes was calculated by taking the difference between the actual values taken from the interpolation curve obtained by joining the (ΔH_H + ΔH_C) values for Mn^{II} and Zn^{II} complexes. The values obtained from the curve were of the differences of those increases from Mn^{II} and reach a minimum at Zn^{II}, above the former line, which was obtained by joining the (ΔH_H + ΔH_C) values for the complexes of Mn^{II} and Zn^{II} (Table 4). The stabilization energy thus increases from $3d^5$ to $3d^8$ and drops to $3d^{10}$; this follows the field stabilization energy order $Ni^{2+} > Cu^{2+}$.

Table 5. d*H*, Ligand field stabilization ernergy.[a]

Metal ion	ΔG°/kJ 25 °C	35 °C	ΔS°/J 25 °C	35 °C	$\Delta H^\circ(\Delta H_C)$/kJ	ΔH/kJ	$(\Delta H_H + \Delta H_C)$/kJ	$0.2E_r(n\text{–}5)$	δ_H
Mn^{2+}	62.4	62.8	134.8	135.0	52.8	2 736.3	2 789.1	0.0	
Fe^{2+}	63.9	64.2	180.3	179.0	51.1	2 845.1	2 896.2	41.5	60
Co^{2+}	72.5	72.9	191.1	190.8	58.8	2 916.2	2 975.1	83.1	105
Ni^{2+}	72.2	72.7	222.5	222.6	56.3	2 995.7	3 052.0	124.6	140
Cu^{2+}	101.4	104.0	484.7	504.1	66.9	2 999.5	3 066.4	166.2	115
Zn^{2+}	76.5	77.0	184.6	184.7	63.4	2 933.4	2 996.8		

[a] E_r(Mn–Zn) = 207.7

Table 6. Values of *B* for *N*-(*m*-chlorophenyl)-*p*-substituted benzohydroxamic acids.

Metal ion	*B*	*r*	θ
H^+	1.000	1.000	0.00
Pd^{2+}	0.962	0.995	−0.04
Cu^{2+}	0.958	0.995	+0.57
Zn^{2+}	1.342	0.998	+3.01
Co^{2+}	1.238	0.998	+3.27
Ni^{2+}	1.141	0.998	+3.30
Fe^{2+}	1.333	0.995	+4.36
Mn^{2+}	1.238	0.998	+4.49

Table 7. Values of *C* for *N*-(*m*-chlorophenyl)-*p*-substituted benzohydroxamic acids.

Substituent (X)	*C*	*r*	σ
H	1.000	1.000	—
C_2H_5O	0.938	0.999	+0.55
CH_3O	0.961	1.003	+0.39
CH_3	0.965	0.999	+0.19
F	1.002	0.999	−0.13
Cl	1.007	0.999	−0.31
Br	1.008	0.999	−0.27
NO_2	1.011	0.999	−0.47

The Ratio of Successive Stability Constants.—As the tendency of a metal ion to take up ligand is proportional to the number of vacant sites, the ratio between consecutive constants, is, to a certain extent, determined statistically.[39] For ionic ligands the coulombic attraction is more for, *e.g.*, Mn^{2+} as compared to MA^+. As such, $\log K_1 - \log K_2$ is usually positive.[40] In the studies of the complexes of hydroxamic acids, for all the systems $\log K_1 - \log K_2$ is positive and lies within the range 1.0–2.0 log units.

Linear Free-energy Relationship.—The standard free energy of a reaction, ΔG°, can be expressed as a function of the number of independent variables represented by *w*, *x*, *y*, and *z*. A change in ΔG° is then given by the equation (4).

$$d(\Delta G^\circ) = (\delta\Delta G^\circ/dw)_{x,y,z}dw + (\delta\Delta G^\circ/\delta x)_{x,y,z}\,dx + \ldots \quad (4)$$

Nieborer and McBryde[41] considered the standard free-energy change for metal complex formation in a reaction series to be a function of two variables, and obtained the following two important relationships:

$$\log K_{MA} = B\log K_{M_sA} + [\log K_{MA_0} - B\log K_{M_sA_0}] \quad (5)$$

$$\log K_{MA} = C\log K_{MA_0} + [\log K_{M_sA} - C\log K_{M_sA_0}] \quad (6)$$

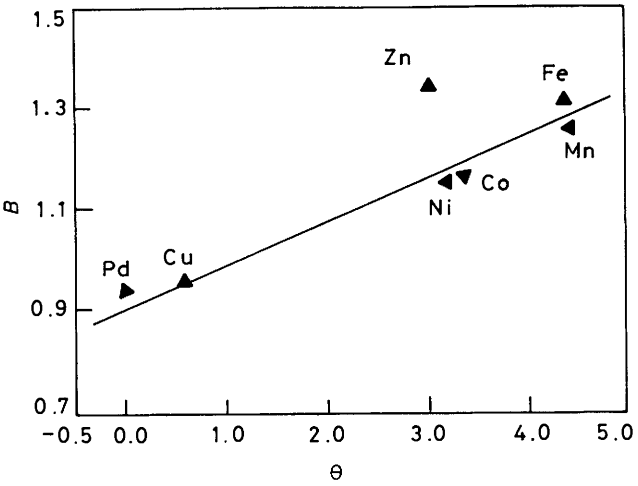


Figure 5. Plot of *B versus* θ.

Equations (5) and (6) compare the stabilities of the complexes of two related ligands (A and A_0) with series of metal ions M, and may be said to describe the quasi-substituent effect. Tests on equations (5) and (6), using the data of *N*-(*m*-chlorophenyl)-*p*-substituted benzohydroxamic acids reacting with several metal ions, are summarised in Table 6. Nieborer and McBryde[41] have noted two principal modes of behaviour. In one, there was mutual dependence of *B* on the particular metal ions compared and of *C* on the particular ligands compared. All other values of *B* and *C* were found to be unity, irrespective of the metal ion or ligand compared.

N-(*m*-Chlorophenyl)-*p*-substituted benzohydroxamic acid data is employed in the regression analysis of the slopes of *B* and *C*. The appropriate statistical information for seven metal ion systems which illustrate the mutual dependence of *B* on the metal ion and *C* on the ligand is compiled in Tables 6 and 7 and Figures 5 and 6.

Stabilization Factor.—Irving and Da Silva[42,43] suggested a new parameter, sf, which measures the additional stabilization caused by the formation of bonds, and obtained a more fundamental relationship demonstrating that this parameter was a linear function of the Hammett factor. In general, no direct correlation of the stability constants of metal complexes with the Hammett σ-factor has been feasible. However, Da Silva and Calado[44] demonstrated that it is possible to obtain good fundamental correlation with the Hammett factor and a parameter (sf) which they derived on thermodynamical grounds.

In the present case the parameter sf has been calculated for the metal complexes of the hydroxamic acids. These results are shown in Table 8 and Figure 7. The correlation is given in

Table 8. Stabilization factor (sf) for *N*(-*m*-chlorophenyl)-*p*-substituted benzohydroxamic acid complexes.

Metal ions	Constants	Substituent (X)						
		H	CH_3O	CH_3	F	Cl	Br	NO_2
	pK_a	10.51	10.90	10.70	10.38	10.20	10.24	10.04
	ΔpK_a		−0.39	−0.19	+0.13	+0.31	+0.27	+0.47
Pd^{II}	$\log \beta_2$	19.40	20.22	19.76	19.14	18.74	18.78	18.33
	$\log K_L$	−1.62	−1.58	−1.64	−1.62	−1.66	−1.70	−1.75
	sf		−0.04	+0.02	0.00	+0.04	+0.08	+0.13
	σ		−0.33	−0.33	+0.37	+0.60	+0.20	+1.01
Cu^{II}	$\log \beta_2$	17.96	18.80	18.30	17.68	17.29	17.28	16.89
	$\log K_L$	−3.06	−3.00	−3.10	−3.08	−3.11	−3.20	−3.19
	sf		−0.06	+0.04	+0.02	+0.05	+0.14	+0.73
	σ		−0.33	−0.33	+0.37	+0.60	+0.20	+0.01
Zn^{II}	$\log \beta_2$	13.40	14.47	13.95	13.11	12.71	12.65	12.24
	$\log K_L$	−7.62	−7.33	−7.45	−7.65	−7.69	−7.83	−7.84
	sf		−0.29	−0.17	+0.03	+0.07	+0.21	+0.22
	σ		−0.33	−0.33	+0.37	+0.60	+0.20	+1.01
Co^{II}	$\log \beta_2$	12.69	13.56	13.06	12.42	12.00	11.98	11.60
	$\log K_L$	−8.33	−8.24	−8.34	−8.34	−8.40	−8.50	−8.48
	sf		0.09	+0.01	+0.01	+0.07	+0.17	+0.15
	σ		−0.33	−0.33	+0.37	+0.60	+0.20	+1.01
Ni^{II}	$\log \beta_2$	12.64	13.45	12.98	12.37	11.96	11.93	11.55
	$\log K_L$	−8.38	−8.35	−8.42	−8.39	−8.44	−8.55	−8.53
	sf		−0.03	+0.04	+0.01	+0.06	+0.17	+0.15
	σ		−0.33	−0.33	+0.37	+0.60	+0.20	+1.01
Fe^{II}	$\log \beta_2$	11.19	12.30	11.75	10.89	10.49	10.41	9.98
	$\log K_L$	−9.83	−9.50	−9.65	−9.87	−9.91	−10.07	−10.10
	sf		−0.33	0.18	+0.04	+0.08	+0.24	+0.27
	σ		−0.33	−0.33	+0.37	+0.60	+0.20	+1.01
Mn^{II}	$\log \beta_2$	10.93	11.89	11.40	10.65	10.24	10.18	9.79
	$\log K_L$	10.09	−9.91	−10.00	−10.11	−10.16	−10.30	−10.29
	sf		−0.18	−0.09	+0.02	+0.07	+0.21	+0.20
	σ		−0.33	−0.33	+0.37	+0.60	+0.20	+1.01

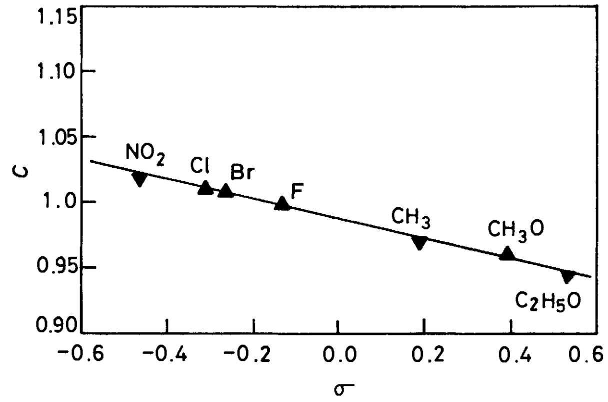


Figure 6. Plot of *C versus* σ.

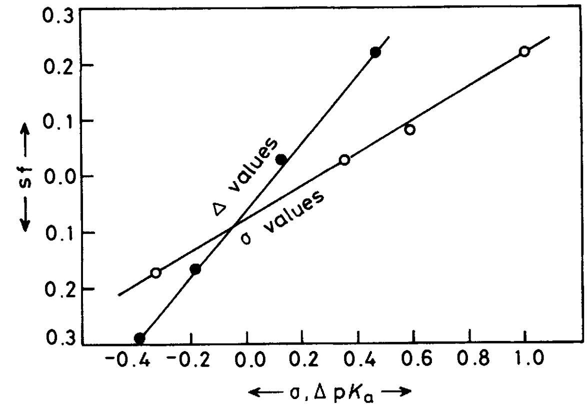


Figure 7. Plot of sf *versus* ○ σ and ● ΔpK_a for Zn^{II}.

tabular and graphical form, and the symbols used have the following meanings:

K_{HA}, the dissociation constant of the ligand HA, is given by

$$K_{HA} = [H][A]/[HA];$$

MA_n, the stability constant (overall) of the metal complex, is given by

$$MA_n = MA_n/[M][A]^n;$$

K_A, the ratio of constant $K_A : \beta_{MA_n} (K_{HA})^n$, is given by

$$\beta_{MA_n}/(\beta_{HA})^n;$$

and sf, the stabilization factor, is given by

$$sf = \log K_A - \log K_A$$

The data given in Table 8 for hydroxamic acids show a good correlation between a plot of sf *versus* σ, Figure 7. The accuracy of the fit can be judged by calculating the correlation coefficient, which is around 0.999. Further, the straight lines obtained have positive slopes, indicating that the complexing reactions are favoured by electron-withdrawal from the reaction centre. This is taken to imply that the stabilization is caused by dative metal to ligand π-bonding.

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