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Stability Orders in Transition Metal–1,10–Phenanthroline Complexes[1]

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Stability constants are measured for complexes of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with some 5-substituted-1,10-phenanthrolines, and are tabulated with other constants reported in the literature. It is found that the order of stabilities for the 1:1 complexes follows the expected series: Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II). The 1:3 complexes follow an anomalous order which is attributed to non-uniformity in the metal ions with respect to the symmetry of the octahedral configuration. An important implication in this interpretation is that the *trans*-configuration of bis-(1,10-phenanthroline)-copper(II) is sterically unstable.

Introduction

Free energy relationships among the chelate compounds of structural similarity have been observed and used to illustrate effects such as those due to variations in ring size, steric factors and solvation.[3] In a few cases, data are available to illustrate the effect of a change in the metal ion for the same set of similar ligands, as, for example, the work of Van Uitert, *et al.*[4] The present work presents data on the stabilities of chelate compounds of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with 1,10-phenanthrolines and attempts to illustrate differences due to changes in the electronegativities of both the metal ion and the ligand.

Experimental

Apparatus and Reagents.—Absorbance measurements were made with these various spectrophotometers: Beckman Model DU with photomultiplier attachment, Cary Model 12 and Cary Model 14. All *p*H measurements were made with a Beckman Model G or GS *p*H meter, using a glass-calomel electrode system. Experimental work was performed at a thermostatically controlled room temperature of 25°. The various 1,10-phenanthrolines used were as listed: 1,10-phenanthroline, 5-methyl-1,10-phenanthroline and 5-nitro-1,10-phenanthroline, obtained from the G. F. Smith Chemical Company, Columbus, Ohio; 5-bromo- and 5-chloro-1,10-phenanthroline, prepared in this Laboratory. Each of the 1,10-phenanthrolines was recrystallized from benzene–petroleum ether mixtures until pure anhydrous compounds were obtained. Stock solutions of the 1,10-phenanthrolines were prepared by weight and were stored in blackened bottles to retard light-catalyzed decomposition. Fe(II), Ni(II), Co(II), Cu(II) and Zn(II) stock solutions were prepared as the chlorides from the pure metals or reagent-grade chloride salts. All solutions were prepared by weight and analyzed for the metal ion by standard methods. Other materials used were of reagent-grade quality. For the partition studies, 2-ethyl-1-hexanol or chloroform was used. Both were especially tested for their ultraviolet transparency at wave lengths above 250 mμ.

Measurement of Stability Constants.—The equilibrium constants for the divalent transition metal complexes with the 5-substituted-1,10-phenanthrolines are defined as

$$K_i = \prod_i k_i = 1/K_{d_i} = \frac{(MPh_i)}{(M)(Ph)^i} \qquad (1)$$

where

M = a divalent transition metal ion

Ph = any of the 5-substituted-1,10-phenanthrolines, as the free base

MPh_i = the 1:1 complex of the metal ion with the 1,10-phenanthroline in question

K_{d_i} = the over-all dissociation constant of the ith complex

k_i = the stepwise formation constant of the ith complex

K_i = the over-all formation constant of the ith complex

The formation function, as defined by Bjerrum,[5] is given by equation 2

$$\bar{n} = \frac{\sum\limits_{i=1}^{3} iK_i(Ph)^i}{1 + \sum\limits_{i=1}^{3} K_i(Ph)^i} = \frac{\sum\limits_{i=1}^{3} i(MPh_i)}{(M)_T} \qquad (2)$$

where the subscript T indicates "total" in the system. A plot of $-\log(Ph)$ against $\bar{n}$ is termed the formation curve. In the case of most of the 1,10-phenanthroline complexes, the calculation of the constants from the formation curve is accomplished by successive approximations using equation 2.

Four distinctly different methods for measuring stability constants were used. Three of these methods (partition, competition and titrimetric-*p*H measurement) give data pertinent to formation curves; the fourth (spectrophotometric) was used to measure the stability constants of only the 1:1 complexes.

The partition method may be applied conveniently because of the selective extraction of only the free base from an aqueous metal ion–metal complex–ligand system. The partition coefficient K_D is defined as

$$K_D = (Ph)_o/(Ph)_w \qquad (3)$$

where the subscripts o and w denote the organic and aqueous phases, respectively; it is easily measured spectrophotometrically using the ultraviolet absorption band of the 1,10-phenanthroline. In a two-phase system containing 1,10-phenanthroline, a single point on the formation curve can best be obtained by the addition of sufficient metal ion to complex one-half of the total 1,10-phenanthroline in the system. In this manner, a direct spectrophotometric measurement of $(Ph)_o$ permits the calculation of both $(Ph)_w$ and $\bar{n}$ from equations 3 and 4.

$$Ph_T - \bar{n}M_T = [K_D v_o + v_w(1 + (H)/K_a)](Ph)_w \qquad (4)$$

In equation 4, v is the volume in liters of the phase indicated. K_a is the acid dissociation constant of the 1,10-phenanthroline in question as defined by equation 5, and the absence of the parentheses about Ph_T and M_T indicates the units are moles.

$$K_a = (H)(Ph)/(PhH) \qquad (5)$$

Irving and Mellor[6] have described in detail and applied to transition metal–1,10-phenanthroline complexes a method for measuring stability constants based on the competition of Fe(II) and another metal ion for the 1,10-phenanthroline. The stability constants of the Fe(II) complexes are presumed known. Formation curve data are obtained by comparison of solutions of corresponding absorbance, in which

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[1] Abstracted from a portion of the Ph.D. Thesis of R. I. Bystroff, Iowa State College, 1959.

[2] E. O. Lawrence Radiation Laboratory, Livermore, California.

[3] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, Inc., Englewood Cliffs, N. J., 1952.

[4] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 2736 (1953).

[5] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[6] H. Irving and D. H. Mellor, *J. Chem. Soc.*, 3457 (1955).

the total 1,10-phenanthroline and total metal ion concentrations are the known variables and the total Fe(II) concentration is constant. The principal limitation of this competition method is the small range of the formation curve which can be obtained with sufficient accuracy.

A variation of the method of Bjerrum[5] was used in the present work. A solution of the ligand, of $p\text{H} \leq pK_a$, was prepared. A metal chloride solution of approximately the same pH was prepared and used as titrant. The addition of metal ion to the ligand solution results in proton displacement and a corresponding pH change, from which $\bar{n}$ may be obtained. If the subscript 1 refers to the ligand solution before the titration and 2 to the same solution after the addition of $v_2 - v_1$ ml. of the metal ion titrant, then $\bar{n}$ is related to the difference between the hydrogen ion concentrations of the initial and titrated solutions according to equation 6

$$\bar{n}(\text{M})_{\text{T}_2} = (\text{H})_2 - (\text{H})_1\left[r + \frac{v_1}{v_2}(1 - r)\right] + \frac{K_a(\text{H})_{\text{T}_1}}{(\text{H})_1(\text{H})_2}[(\text{H})_2 - (\text{H})_1] - K_a\left(1 - \frac{v_1}{v_2}\right)(1 - r) \quad (6)$$

The term r denotes the ratio $(\text{H})_{\text{tit}}/(\text{H})_1$, where $(\text{H})_{\text{tit}}$ is the hydrogen ion concentration of the titrant. Ideally, $r = 1$, and the volume changes during the titration can be ignored, so that equation 6 reduces to equation 7

$$\bar{n}(\text{M})_{\text{T}_2} = [(\text{H})_2 - (\text{H})_1]\left[1 + \frac{K_a(\text{H})_{\text{T}_1}}{(\text{H})_1(\text{H})_2}\right] \quad (7)$$

The free-base concentration, (Ph), can be obtained from equation 8

$$(\text{Ph}) = \frac{(\text{Ph})_{\text{T}_2} - \bar{n}(\text{M})_{\text{T}_2}}{1 + (\text{H})_2/K_a} \quad (8)$$

The ionic strength of the solution was constant throughout the titration, and the pH meter was calibrated against solutions of known hydrogen ion concentration at the same ionic strength, so that pH was a direct measure of concentration rather than activity. The over-all change in pH in the course of a titration, under optimum conditions, was seldom more than 0.3 unit, so that increased sensitivity of the Beckman Model GS pH meter was essential for acceptable data.

The spectrophotometric method was applied to the measurement of the acid dissociation constants of several 1,10-phenanthrolines and the stability constants of the 1:1 complexes of Zn(II) and Cu(II) with the 1,10-phenanthrolines. The degree of association α was measured and is defined by equation 9 for the case when excess metal or hydrogen ion is present.

$$\alpha = \frac{(\text{MPh})}{(\text{Ph})_\text{T}} \text{ or } \frac{(\text{HPh})}{(\text{Ph})_\text{T}} \quad (9)$$

Solutions were used in which the metal ion or proton concentrations were the variables, while the total ligand concentration was constant. The degree of association may be expressed in terms of the absorbance A at $\lambda_{\max}$ of the complex

$$\alpha = \frac{A - \epsilon_{\text{Ph}}l(\text{Ph})_\text{T}}{[\epsilon_{\text{MPh}} - \epsilon_{\text{Ph}}]l(\text{Ph})_\text{T}} \quad (10)$$

where l is the cell length in cm., ϵ is the molar absorptivity in liter mole^{-1} cm.$^{-1}$, and $(\text{Ph})_\text{T}$ is the total ligand concentration in mole per liter. It is related to the stepwise dissociation constant and to K_a by equations 11 and 12, respectively.

$$\frac{1}{k_1}\left(1 + \frac{(\text{H})}{K_a}\right) = (\text{Ph})_\text{T}\left[\frac{(\text{M})_\text{T}}{(\text{Ph})_\text{T}} - \alpha\right]\left(\frac{1 - \alpha}{\alpha}\right) \quad (11)$$

$$K_a = \left(\frac{1 - \alpha}{\alpha}\right)(\text{H}) \quad (12)$$

The pK_a Values of 5-Nitro-, 5-Bromo- and 5-Chloro-1,10-phenanthroline.—The pK_a values of the 5-substituted-1,10-phenanthrolines were obtained from spectrophotometric measurements. Series of solutions were prepared in which the ionic strength was constant at 0.1 and the 5-substituted-1,10-phenanthroline concentrations were constant, while the pH was varied from 1.0 to 11.7. Absorbance data at the two principal ultraviolet absorption bands of the 1,10-phenanthrolines were used to calculate α from equation 10 and K_a from equation 12. The average of from four to five results each gave these K_a values: 5-NO$_2$Ph, $(4.7 \pm 0.6) \times 10^{-4}$, 5-ClPh, $(6.7 \pm 0.3) \times 10^{-5}$, 5-BrPh, $(6.3 \pm 0.9) \times 10^{-5}$. These values are listed in Table IV, together with those measured by Brandt and Gullstrom[7] by extrapolation of pH from dioxane–water mixtures.

Copper(II) with 1.10-Phenanthroline.—The titrimetric pH method was applied to the measurement of the formation curve from $\bar{n} = 1.5$ to 3.0. A typical titration was performed with the following conditions: $v_1 = 40$ ml., $(\text{Ph})_{\text{T}_1} = 4.78 \times 10^{-4}$ M. $(\text{H})_{\text{T}_1} = 5.0 \times 10^{-4}$ M, and the ionic strength μ, adjusted with KCl, $= 0.1$; for the titrant, $(\text{Cu})_\text{T} = 0.989 \times 10^{-2}$ M, $\mu = 0.1$, and $(\text{H})_{\text{tit.}} = 2.05 \times 10^{-4}$ M. The data and results of this titration are shown in Table I. Calculations involving equations 6 and 8 were made using $pK_a = 5.0$. The uncertainty in (Ph) increases as the reaction nears completion. This uncertainty is indicated in Fig. 1.

TABLE I

TITRIMETRIC-pH STUDY OF THE Cu(II)–1,10-PHENANTHROLINE SYSTEM

$v_2 - v_1$, ml.	$(\text{H})_2 \times 10^4$	$\bar{n}\text{M}_{\text{T}_2} \times 10^4$	$\bar{n}$	$(\text{Ph}) \times 10^5$
0.0	0.90	0.00	..	6.3
.10	1.39	0.68	2.77	2.75
.20	1.91	1.30	2.65	1.71
.30	2.49	1.93	2.62	1.09
.40	3.00	2.48	2.53	0.73
.50	3.48	2.97	2.44	.49
.65	4.05	3.55	2.25	.28
.80	4.51	4.01	2.07	.15
1.00	4.83	4.34	1.66	.066
1.10	4.88	4.37	1.65	.057
1.20	4.91	4.41	1.53	.045

The partition method was applied to the measurement of the formation curve from $\bar{n} = 0.5$ to 1.5. The partition coefficient for 1.10-phenanthroline between chloroform and water has been measured and found to be 1040 ± 30 by Grimes,[8] and this value was used in the calculations using equations 3 and 4. Special care was taken to avoid errors due to chloroform evaporation. The hydrogen ion concentration and the ionic strength of the aqueous phase for all solutions were 0.0132 M. Higher chloride concentrations are not desirable because of the extraction of ion pairs. The phases were equilibrated for 1 hr. The 1,10-phenanthroline which was extracted into the chloroform was determined spectrophotometrically, after evaporation of the chloroform and re-solution in 0.1 M hydrochloric acid. The molar absorptivity ϵ_{PhH} in 0.1 M hydrochloric acid is 30,100 liter mole^{-1} cm.$^{-1}$ at 271 mμ. Also the absorption spectra were taken in the chloroform media and the results compared favorably. The results are included in Fig. 1.

The Partition of 5-Nitro-1,10-phenanthroline.—The partition coefficients of 5-nitro-1.10-phenanthroline between chloroform and water and between 2-ethyl-1-hexanol and water were measured spectrophotometrically. Pertinent molar absorptivities, measured independently, are $\epsilon_{5-\text{NO}_2\text{Ph},(\text{CHCl}_3)} = 22{,}500$ (266 mμ). $\epsilon_{5-\text{NO}_2\text{Ph},(\text{C}_8\text{H}_{17}\text{OH})} = 24.100$ (266 mμ), and $\epsilon_{5-\text{NO}_2\text{Ph},(\text{H}_2\text{O})} = 21.300$ (266 mμ). In water the wave length listed corresponds to an isosbestic point; therefore, the absorbance is a measure of $(5\text{-NO}_2\text{Ph})_\text{T}$ and the free-base concentration is obtained from equation 5 and the pH. The results for the partition with chloroform are different at pH 5 to 3.5 than at pH 2. The average result for the higher pH values is $K_\text{D} = 880 \pm 60$ (six results), while at pH 2, $K_\text{D} = 1700 \pm 100$. The results for the partition with 2-ethyl-1-hexanol were obtained only at pH 3.4 to 6.5 and the average K_D was 38.8 ± 2.2. It was found in the studies involving Cu(II) that, although the formation curve is somewhat insensitive to K_D. better agreement with alternate methods for the determination of the formation curve is obtained using $K_\text{D} = 1700$. Grimes[9] has evidence that PhiH species exist at pH values close to pK_a. Such species would tend to cause the observed discrepancies in K_D and would justify the use of the K_D measured in acid.

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(7) W. W. Brandt and D. K. Gullstrom, THIS JOURNAL, **74**, 3532 (1952).

(8) P. G. Grimes, M.S. Thesis, Iowa State College, 1956.

(9) P. G. Grimes, Ph.D. Thesis, Iowa State College, 1958.

Copper(II) with 5-Nitro-1,10-phenanthroline.—The competition method was applied to the measurement of the formation curve from $\bar{n} = 1.1$ to 1.5. Beyond these limits this method cannot give reliable data. For the tris-(5-nitro-1,10-phenanthroline)-iron(II) complex log K_3 was taken to be 18.0, which is the average result Brandt and Gullstrom[7] obtained from rate and equilibrium data. For the 1:1 complex log k_1 was found to be 5.06 in the present work. Three series of solutions were prepared, all of which were 6.19×10^{-5} M in Fe(II). Within each series, $(\mathrm{Ph})_T$ was varied from $(3 \text{ to } 35) \times 10^{-5}$ M. The Cu(II) concentrations were $(1, 5 \text{ and } 10) \times 10^{-5}$ M for each series, respectively. All solutions were maintained at $\mu = 0.1$ and were buffered at pH 4.0. The results are shown in Fig. 1.

The partition method was applied to the measurement of the formation curve between $\bar{n} = 0.5$ and 2.0. The (H) in the aqueous phase was 0.013 M and chloroform was used as the extracting solvent. The K_D and K_a values used in calculations were 1700 and 4.7×10^{-4}, respectively. The absorbance of the 5-nitro-1,10-phenanthroline was measured in the chloroform media. The evaporation technique used with 1,10-phenanthroline gave erratic results and spectral changes with 5-nitro-1,10-phenanthroline, probably because of a greater reactivity of the latter to carbene attack. 5-Nitro-1,10-phenanthroline is also uniquely susceptible to attack by hydroxyl ion, a process observable spectrally at pH 11, and by non-aqueous titration with triethylammonium hydroxide. The results are shown in Fig. 1, along with the data obtained by the competition method.

Spectrophotometric measurements of log k_1 for the 1:1 complex also were performed. A series of solutions was prepared in which $(\mathrm{Ph})_T$ was constant at 2.81×10^{-6} M, $(\mathrm{H})_T = 0.022$ M, and $\mu = 0.1$. The Cu(II) concentrations were varied from $(1 \text{ to } 14) \times 10^{-6}$ M and a solution was prepared with a 100-fold excess Cu(II) to 5-nitro-1,10-phenanthroline in order to determine the molar absorptivity of the mono-(5-nitro-1,10-phenanthroline)-copper(II) species. Absorbance changes were very small under optimum conditions because of the closeness of the molar absorptivities of the Cu-5-NO_2Ph (29,200) and the 5-NO_2PhH (31,400) species at 275 mμ, the wave length of maximum absorption of both species. The data and results are shown in Table II and are included in Fig. 1. Calculations were made using equation 11 and two different values of K_a.

TABLE II

SPECTROPHOTOMETRIC STUDY OF THE Cu(II)-5-NITRO-1,10-PHENANTHROLINE SYSTEM[a]

$(\mathrm{Cu})_T \times 10^6$	A. 275 mμ[b]	α[c]	$k_1 \times 10^{-7}$[d]	$k_1 \times 10^{-7}$[e]
0.00	0.883	..	..	..
2.96	.847	0.61	5.0	9.0
4.94	.839	.74	4.0	7.1
6.92	.837	.78	3.0	5.3
9.89	.836	.80	2.1	3.8
14.83	.832	.86	2.0	3.6
247.0	.824	..	..	..
		Av.	3.2 ± 1.0	5.8 ± 2.3

[a] Cell length, 10 cm. [b] Corrected for free Cu(II) absorption. [c] See equation 10. [d] Calculated using $pK_a = 3.33$. [e] Calculated using $pK_a = 3.57$.

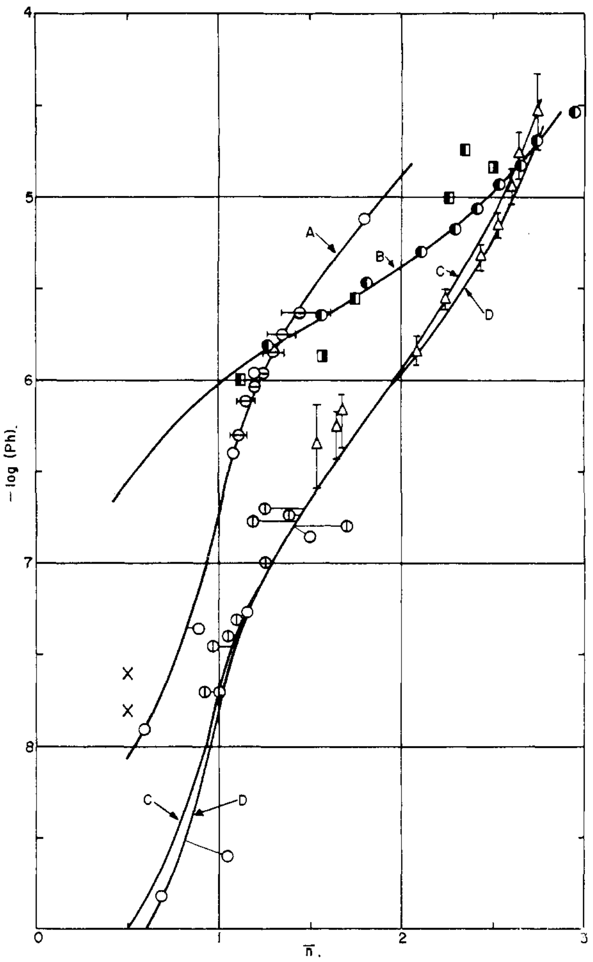

Fig. 1.—Formation curves with Cu(II) and Zn(II), Curve A, Cu(II) and 5-NO_2Ph: O, by partition; ⊖, by competition; ×, by spectrophotometric measurements. Curve B, Zn(II) with 1,10-phenanthroline: ◐, by pH measurements; ■□, data of Yasuda, *et al.*[11]; □■, data of Kolthoff, *et al.*[12] Curve C, Cu(II) with 1,10-phenanthroline: calculated curve using log $k_1 = 9.0$, log $k_2 = 6.7$, log $k_3 = 5.1$. Curve D, Cu(II) with 1,10-phenanthroline: calculated curve using log $k_1 = 9.15$, log $k_2 = 6.65$, log $k_3 = 5.25$; Δ, by pH measurements; O, by partition; ⦶, by competition, data of Irving and Mellor.[6]

Zinc(II) with 1,10-Phenanthroline.—The formation curve from $\bar{n} = 1.0$ to 3.0 was obtained by the titrimetric-pH method. The ligand solution was identical with that used for the corresponding formation curve with Cu(II). The titrant was composed of $(\mathrm{Zn})_T = 0.929 \times 10^{-2}$ M, $(\mathrm{H})_{\mathrm{tit}} = 1.183 \times 10^{-4}$ M and $\mu = 0.1$. The points calculated from the data and equations 6 and 8 are shown in Fig. 1 together with points calculated from the data of Kolthoff, *et al.*,[10] and Yasuda, *et al.*[11] Calculations were performed using $pK_a = 5.0$.

Zinc(II) with 5-Nitro- and 5-Chloro-1,10-phenanthroline.—The spectrophotometric method was used to measure the log k_1 for the complexes of Zn(II) with 5-nitro- and 5-chloro-1,10-phenanthroline. The data were obtained in a manner identical to that used for the spectrophotometric method with Cu(II) and 5-nitro-1,10-phenanthroline but were more extensive, being obtained at three different wave lengths, 231, 275 and 300 mμ for the 5-nitro-1,10-phenanthroline, and 215, 230 and 274 mμ for the 5-chloro-1,10-phenanthroline studies. The results expressed in terms of $(1/K_1)(1 + (\mathrm{H})/K_a)$ were $(1.0 \pm 0.1) \times 10^{-4}$ and $(4.8 \pm 0.1) \times 10^{-4}$ for the 5-nitro- and the 5-chloro-1,10-phenanthroline complexes, respectively. Both studies were performed at an ionic strength of 0.1. The acidities were (H) = 0.0112 M for the 5-nitro- and 0.022 M for the 5-chloro-1,10-phenanthroline study. The log k_1 values listed in Table IV are shown as calculated using the pK_a values measured in this work and those measured by Brandt and Gullstrom.[7]

Nickel(II) with 5-Nitro-1,10-phenanthroline.—The partition method was used to obtain points on the formation curve from $\bar{n} = 0.5$ to 2.5. The 2-ethyl-1-hexanol-water system was used, and the extracted free base was determined spectrophotometrically in the organic media at 266 mμ. The points, shown in Fig. 2, are scattered to some extent. For the lowest $\bar{n}$ values, a spectral shift indicated possible extraction of some of the complex. The slowness

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(10) I. M. Kolthoff, D. L. Leussing and T. S. Lee, THIS JOURNAL, **73**, 390 (1951).

(11) M. Yasuda, K. Sone and K. Yamasaki, *J. Phys. Chem.*, **60**, 1667 (1956).

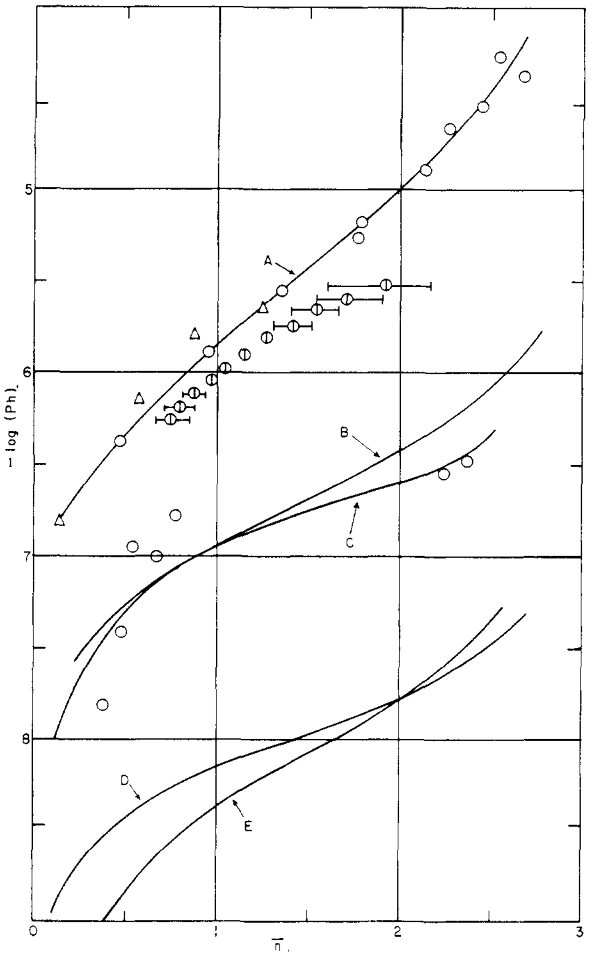

Fig. 2.—Formation curves with Co(II) and Ni(II), Curve A, Co(II) and 5-NO_2Ph: O. by partition with 2-ethyl-1-hexanol; Δ. by partition with chloroform; ⊕, by competition. Curve B, Co(II) and 1.10-phenanthroline: calculated from the data of Irving and Mellor.[6,25] Curve C. Ni(II) and 5-NO_2Ph: O, by partition. Curve D, Ni(II) and 1.10-phenanthroline: calculated from the data of Irving and Mellor.[25] Curve E. Ni(II) and 1,10-phenanthroline: calculated from the data of Margerum.[26]

of the formation reaction dictated that the solutions be equilibrated for 24 to 48 hr. The pH of the aqueous phases was between 4.26 and 4.61. Until it is possible to investigate the nature of the spectral shift mentioned, the stability constants calculated from the present data shall remain questionable.

Cobalt(II) with 5-Nitro-1,10-phenanthroline.—The partition method was applied to obtain the entire formation curve. 2-Ethyl-1-hexanol was used as the extracting solvent. and the 5-nitro-1,10-phenanthroline was determined spectrophotometrically in the organic media at 266 mμ. To illustrate the composition of solutions used in the partition studies, more complete data are given for this system in Table III and Fig. 2.

Part of the formation curve also was obtained by the partition method using the chloroform-water system. The aqueous phases were pH 4.0 to 5.0 and μ = 0.1. The K_D value used was 1700. The results are also shown in Fig. 2.

The competition method was applied to this system in a manner similar to that for copper. The compositions of the solutions used were identical to those with Cu(II) except that higher concentrations of Co(II), (2 to 20) × 10^{-5} M. were necessary to compete significantly with the Fe(II). The results are shown, along with the experimental uncertainty, in Fig. 2.

TABLE III

PARTITION STUDY OF THE Co(II)-5-NITRO-1.10-PHENANTHROLINE SYSTEM[a]

Ph_T × 10^6, moles	Co_T × 10^6, moles	pH	$(Ph)_o$ × 10^4	$(Ph)_w$ × 10^6	$\bar{n}$
0.876	0.86	4.50	0.178	0.426	0.48
2.63	1.27	4.85	0.535	1.28	0.964
5.40	1.80	4.80	1.12	2.68	1.37
11.0	2.76	4.75	2.32	5.56	1.78
24.5	4.90	4.60	5.32	12.7	2.14
34.6	15.15	4.60	2.70	6.75	1.80
56.6	15.15	4.60	8.63	21.6	2.27
64.1	8.08	4.60	16.6	41.3	2.68
66.4	15.15	4.60	11.4	28.4	2.45
107.7	20.2	4.60	21.8	54.7	2.54

[a] v_o = 25 ml., v_w = 50 ml., μ = 0.1, K_D = 40.

The Stability of the Mono-(5-substituted-1,10-phenanthroline)-iron (II) Complexes.—The spectrophotometric method described by Kolthoff, *et al.*,[12] was applied to the measurement of the 1:1 complexes of Fe(II) with 1,10-phenanthroline, 5-nitro-. 5-methyl- and 5-bromo-1,10-phenanthroline. The method requires the knowledge of the stabilities of the 1:3 complexes. With the exception of the 5-bromo-1.10-phenanthroline complex, these were taken from the data of Brandt and Gullstrom.[7] The 1:2 complex with Fe(II) was assumed to be negligible in all aqueous systems. Solutions were prepared with excess Fe(II), as described by Kolthoff.[12] and buffered at pH 4 with sodium formate and hydrochloric acid while maintaining the ionic strength at 0.1. The log k_1 values were obtained as a linear function of the corresponding log K_3 values; as log K_3 for the 5-bromo-1,10-phenanthroline complex has not been measured. log K_3 was inferred from the substituent effect data of Brandt and Gullstrom[7] and the pK_a measured in this work. The stability constant results are presented in Table IV.

Results

Table IV summarizes the stability constants and pK_a values pertinent to a comparison of the substituent effect in transition metal–1,10-phenanthroline complexes. Constants listed without reference are taken from the present work. Formation curves calculated from the constants listed for the Zn(II), Cu(II), Ni(II) and Co(II) complexes are shown in Figs. 1 and 2 in relation to the experimental data. In the case of Cu(II) with 1,10-phenanthroline, two sets of constants are used to indicate the sensitivity of the constants to the experimental error. Both calculated curves can be said to fit the data. A close fit to the data by the calculated formation curve for Ni(II) with 5-nitro-1,10-phenanthroline is not warranted, and the stepwise constants are to be regarded as very approximate. The over-all constant, log K_3, should be a lower limit if it is found that the 1:1 complex indeed extracts. The Co(II) curve is drawn through the partition method data. The curve from the competition data is parallel to this curve and would indicate log k_1 values 0.2 unit larger. The discrepancy is reasonable in light of the uncertainty in log K_3 for the tris-(5-nitro-1,10-phenanthroline)-iron(II) complex and in the K_D used.

The log k_1 values for the Fe(II) complexes are related to pK_a values by the equation log k_1 = 0.596 pK_a + 2.93, while the equation of the substituent effect for the 1:3 complexes, obtained from the data of Brandt and Gullstrom,[7] is log K_3 = 2.5

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(12) I. M. Kolthoff, D. L. Leussing and T. S. Lee, This Journal, **72**, 2173 (1950).

$pK_a + 9.15$. From the experimentally derived relationship $\log k_1 = {}^1/_3 \log K_3 - 1.123$, obtained for the 5-bromo-1,10-phenanthroline–Fe(II) system, and the preceding substituent effect relationships, one may calculate values for $\log k_1$, $\log K_3$, and pK_a for the iron complexes and the free base of 5-bromo-1,10-phenanthroline, respectively. These are 5.45, 19.7 and 4.2. The pK_a value is in agreement with the independent spectrophotometric measurement, and $\log K_3$ is identical with that found for the tris-(5-chloro-1,10-phenanthroline)-iron(II) complex, which is reasonable in light of the closeness of the inductive constants for chlorine and bromine. These results give credence to the assumption of linear free energy relationships in these transition metal complexes.

It should be pointed out that some discrepancies evident in Table IV undoubtedly are due to inadequate consideration of the limitations of the method used. In this category fall the examples $\log k_3 = 1.1$ and $\log k_1 = 6.3$ for Zn(II) and Cu(II), respectively, with 1,10-phenanthroline.

Discussion

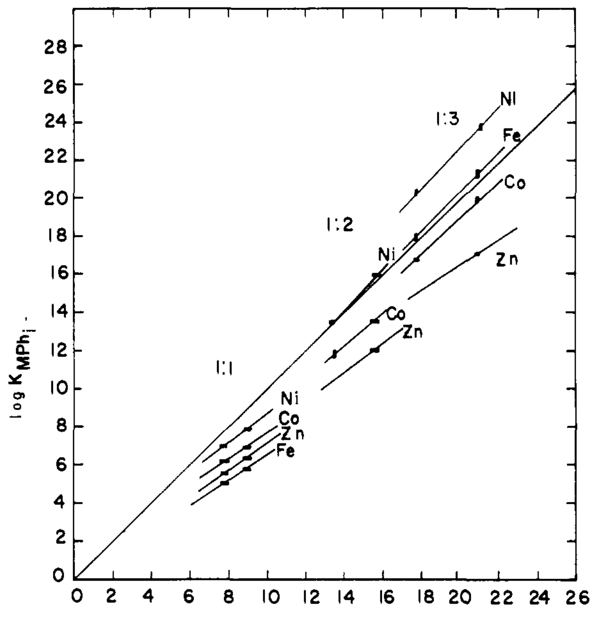

Fig. 3.—The substituent effect in various metal–1,10-phenanthroline complexes relative to that of the corresponding Cu(II) complex.

In Fig. 3 the log K_i values for Zn(II), Ni(II), Co(II) and Fe(II) are plotted against the corresponding log K_i values for the Cu(II) complexes of 1,10-phenanthroline and 5-nitro-1,10-phenanthroline. In this manner, both the relative substituent effects and the relative order of stabilities are illustrated, as the number of ligands attached to the metals varies from 1 to 3. The order of stabilities of the 1:1 complexes follows the Irving–Williams series,[13] Fe < Co < Ni < Cu > Zn, as expected. The metal hybrid orbitals used in bonding have energies which parallel the second ionization potentials of the respective metals. The stabilities of the 1:3 complexes do not follow such an order, however. The substituent effects fall in the same order as that of the stabilities for both the 1:1 and 1:3 complexes. It may be possible that some correlation exists between the relative stabilities and the relative substituent effects, as theory would predict,[14] but present data are not sufficiently precise to illustrate this point conclusively. As a first approximation, the lines in Fig. 3 pass through the origin. Such an empirical correlation may prove useful in predicting stabilities of metal complexes whose constants may be difficult to measure directly. In this respect, Irving and Rossotti[15] have called attention to the value of correlative diagrams of various types, similar to Fig. 3, which can be useful to the analytical and inorganic chemist.

The question of the unusual order of stabilities of the 1:3 complexes may be better understood qualitatively if two points are considered: (1) the metal ions in question exhibit more pronounced differences in orbital character than has been assumed in regarding hexacovalent complexes as perfect octahedra, and (2) the fixed N–N distance and angular orientation of the orbitals in 1,10-phenanthroline suggest that this ligand will tend to form equivalent metal–nitrogen bonds and, therefore, 1:3 complexes with a high degree of symmetry.

The first point must be discussed primarily in terms of the ligand-field theory concepts which have been described by Nyholm, Orgel and Jørgensen[16] and Griffith and Orgel.[17] It is understood that under the action of a cubic field, the 3d orbitals are split in energy into a lower non-bonding triply degenerate set, d_ϵ, which correspond to the d_{xy}, d_{xz} and d_{yz} gaseous metal ion orbitals, and a higher set, d_γ, which correspond to the d_{z^2} and $d_{x^2-y^2}$ orbitals. The latter orbitals then participate in the formation of σ-molecular orbitals with the appropriate ligand orbitals. The $12 + n$ ligand and metal ion electrons occupy the $3d^24s4p^3$ bonding orbitals, the non-bonding $3d_\epsilon$ and the antibonding $3d_\gamma$ orbitals, in that order. The octahedral configuration can be said to be established by the d^2sp^3 hybrid orbital configuration, but the presence of d_ϵ (t_{2g}) and d_γ (e_g) electrons are capable of distorting the symmetry by the Jahn–Teller effect.[18] In general, an uneven distribution of electrons among the three d_ϵ or the two d_γ orbitals will result in minor distortions in the former case and sizable distortions if the antibonding d_γ orbitals are involved. The Cu(II) hexacovalent complexes, with a $d_\epsilon^6 d_\gamma^2 d_\gamma^1$ configuration, exhibit the Jahn–Teller effect to an extent which varies with the basic strength of the ligands. The presence of three electrons in the two antibonding d_γ orbitals results in a repulsive force on the axially located ligands. The resulting tendency is that Cu(II) forms square planar complexes with weakly held axial monodentate ligands, so much so that 1:3 Cu(II) complexes

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(13) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

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(15) H. Irving and H. Rossotti, *Acta Chem. Scand.*, **10**, 72 (1956).

(16) R. S. Nyholm, L. E. Orgel and C. K. Jørgensen, "Quelques Problemes de Chimie Minerale," Reports of the Tenth Solvay Conference, R. Stoops, Bruxelles, 1956.

(17) J. S. Griffith and L. E. Orgel, *Quart. Revs.*, **11**, 381 (1957).

(18) L. E. Orgel, *J. Chem. Soc.*, 4756 (1952).

of bidentate ligands, such as $Cu(en)_3$,[19] are unstable with respect to the square planar complex, such as $Cu(en)_2(H_2O)_2$. Jørgensen[20] has used a spectral criterion for the tetragonal character of the Cu(II) complexes, namely, the magnitude of the $t_{2g} - e_g$ transition in the Cu(II) relative to that in the Ni(II) complexes. His data indicate that $Cu(Ph)_3$, $Cu(Dipy)_3$,[21] $Cu(Dipy)_2(H_2O)_2$ and $Cu(Ph)_2(H_2O)_2$ are very nearly perfect octahedra, in contrast to many other complexes with both mono- and bidentate ligands. It is evident that the two 1:2 complexes named do not have coplanar nitrogen atoms but appear to be primarily of the *cis* configuration. This observation is borne out by the stability constants of the 1,10-phenanthroline complexes of Cu(II) in Table IV. The 1:2 complex is so much less stable than the 1:1 complex that it is highly unlikely that the 1:2 complex could be of the *trans* configuration, which would, like $Cu(en)_2(H_2O)_2$, have closely similar stepwise stability constants. Adoption of the *cis* configuration, on the other hand, could conceivably suppress the Jahn–Teller effect because of the steric rigidity of 1,10-phenanthroline. The refusal of the additional stability generally acquired through the Jahn–Teller effect and its concomitant octahedral distortion can only appear as a decreased over-all stability of the 1:2 and 1:3 complexes and a less distorted octahedral symmetry. While this picture will explain the unusual stability order of the 1:3 complexes discussed earlier, it does not suggest the reason why the *trans*-$Cu(Ph)_2(H_2O)_2$ complex is unstable. It is proposed that the hydrogen atoms present in the 2- and 9-positions in 1,10-phenanthroline and in the 3- and 3′-positions in 2,2′-bipyridyl are capable of sterically interfering with the adoption of the *trans* configuration. It should be noted in this respect that such steric effects would not be expected in the Fe(II), Co(II), Ni(II) and Zn(II) complexes, because the Jahn–Teller effect should be minor or non-existent for the configurations $d_\epsilon^6 d_\gamma^0 d_\gamma^0$, $d_\epsilon^5 d_\gamma^1 d_\gamma^1$, $d_\epsilon^6 d_\gamma^1 d_\gamma^1$ and $d_\epsilon^6 d_\gamma^2 d_\gamma^2$, respectively. Furthermore, Cu(II) would present the smallest ionic radius in this series, although no data are yet available for the 1,10-phenanthroline complexes, making steric considerations plausible. Orgel[16,22] has suggested an alternative possibility that π-bonding could stabilize the *cis* configuration much more than the *trans* in $Cu(Ph)_2(H_2O)_2$, but this conclusion was based in part on stability constants[23] which now can be regarded as erroneous.

TABLE IV

STABILITY CONSTANTS AT 25° OF SOME TRANSITION METALS WITH 5-SUBSTITUTED-1,10-PHENANTHROLINES

Metal	log $k_1^{a,b}$		log $k_2^{a,b}$		log $k_3^{a,b}$		log K_3^c	
1,10-Phenanthroline, pK_a: 4.77 A,[28,29] 4.96 F,[28,29] 4.857 A,[30] 5.02 A[31]								
Zn(II)	6.36	A	5.64	A	5.2	A	17.0	
	6.43	E[10]	5.72	C[10]	4.85	C[10]	17.0	
	6.6	C[10]	..		..		..	
	6.47	B[24]	5.5	B[24]	1.1	B[24]	13.1	
	..		5.9	A[11]	4.8	A[11]	..	
Cu(II)	9.15	C	6.65	A,C	5.25	A	21.05	
	9.0	C	6.7	A,C	5.1	A	20.9	
	8.8	C[25]	6.57	C[25]	5.0	C[25]	20.4	
	6.3	A[23]	6.15	A[21]	5.5	A[23]	17.9	
Ni(II)	8.6	B[26]	8.1	B[26]	7.55	B[26]	24.25	
	8.0	C[25]	8.0	C[25]	7.9	C[25]	23.9	
Co(II)	7.02	C[25]	6.70	C[25]	6.38	C[35]	20.1	
Fe(II)	5.85	B	..		..		21.3	B[7,28,29]
	5.85	B[12]	..		..		21.5	D[7,28,29]
5-Nitro-1,10-phenanthroline, pK_a: 3.57 A,[7] 3.33 B								
Zn(II)	5.6^d	B	..		..		..	
	5.4^e	B	..		..		..	
Cu(II)	8.0	C	5.47	C,E	4.2	C	17.7	
	7.8^d	B	..		..		..	
	7.6^e	B	..		..		..	
Ni(II)	7.57	B[26]	..		..		..	
	7.0	C	6.4	C	7.0	C	20.4	
Co(II)	6.25	C	5.41	C	4.63	C	16.3	
	6.44^f	E	5.60^f	E	4.82^f	E	16.8	
Fe(II)	5.06	B	..		..		18.1	D[7]
	..		..		..		17.8	B[7]
5-Bromo-1,10-phenanthroline, pK_a: 4.20 B								
Fe(II)	5.45^g	B	..		..		19.7^g	
5-Chloro-1,10-phenanthroline, pK_a: 4.26 A,[7] 4.18 B								
Zn(II)	5.85	B	..		..		..	
	5.72	B	..		..		..	
Fe(II)	..		..		..		19.7	D,B[7]
5-Methyl-1,10-phenanthroline, pK_a: 52.6 A.[11] 5.23 A[7]								
Zn(II)	..		6.0	A[11]	5.0	A[11]	..	
Ni(II)	8.7	B[26]	..		..		..	
Fe(II)	6.05	B	..		..		22.3	B

[a] Values stated without ref. are from this work, in which ionic strengths are all 0.1 *M* in KCl, except for log k_1 for Cu(II) with 1,10-phenanthroline for which $\mu = 0.0132$. [b] Methods are coded: A, *p*H measurements; B. spectrophotometric equilibrium; C, partition; D, kinetics; E, competition, F, conductivity. [c] Methods and references listed for direct measurements only. [d] Calculated using $pK_a = 3.57$. [e] Calculated using $pK_a = 3.33$. [f] Taken from a formation curve drawn parallel to partition data. [g] Computed indirectly using the substituent effect.

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(19) en represents ethylenediamine.

(20) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

(21) Dipy represents 2,2′-dipyridyl.

(22) *Cf.* ref. 16, pp. 341–342.

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