Quantitative Study of Chelates of Pyridine-2-aldoxime

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Acid dissociation constants of pyridine-2-aldoxime and its affinity for various metal ions were determined by means of potentiometric titrations. Stable chelates were formed with the following metal ions, listed in order of stability: ferric > cupric > cobaltous > ferrous > nickelous > mercuric > zinc > cadmium >manganous. Calcium and magnesium ions showed no evidence of chelate formation. The unusually high stabilities of the cobaltous and ferrous chelates suggest that the oxime exhibits a specific affinity for these ions. All of the 1 : 1 chelates showed a strong tendency to hydrolyze, as indicated by results obtained from titrations of solutions containing the reactants in a 1 : 1 ratio. Colored species were formed in the ferrous, ferric, cobaltous, nickelous, and cupric systems. In particular, the ferrous chelate formed an intense red solution, suggesting possible application of the oxime as an analytical reagent for ferrous ion.

THE CHELATING ability of the oxime group has been recognized for some time; however, relatively little work on the stability of oxime chelates has been reported in the literature. A notable exception is dimethylglyoxime which, because of its analytical applications, has been the subject of extensive investigations (1–3). Recently a few papers have appeared which were particularly concerned with oxime chelation. Murmann has calculated stability constants of chelates of 2-methyl-2-amino-3-butanone oxime and some of its derivatives (4). Proposed chelate structures demonstrated formation of hydrogen bonded species, similar to those observed for dimethylglyoxime chelates. Banerjea and Tripathi noted the intense colors of cuprous and ferrous chelates of methyl-2-pyridyl ketoxime and described the use of this oxime as an analytical reagent for these metals (5). During the course of the present investigation, a paper by Krause and Busch was published, which described in detail the isolation of and formulas for nickelous, palladium, and platinum chelates of pyridine-2-aldoxime (6).

The primary purpose of this investigation was to study the ability of pyridine-2-aldoxime to form chelates with selected metal ions. These metal complexes may be of value in the treatment of poisoning by organophosphate anticholinesterases. Wagner-Jauregg and associates (7) demonstrated that the hydrolysis rate of diisopropylphosphorofluoridate (DFP) is greatly accelerated in the presence of various cupric chelates; the α,α'-dipyridyl chelate, which is related structurally to pyridine-2-aldoxime, showed the strongest catalytic activity. A similar study by

Courtney and associates (8) described a number of metal chelate compounds which acted as catalysts in hydrolyzing DFP and isopropyl methylphosphonofluoridate (sarin). Although these complexes are efficient for decomposing organophosphate anticholinesterases, only a few appear to have been tested *in vivo* (9).

EXPERIMENTAL PROCEDURE

Reagents.—Pyridine-2-aldoxime, recrystallized from 50% ethanol, m.p. 113°; potassium nitrate, analytical reagent; sodium hydroxide solution (carbonate free) and hydrochloric acid, both standardized by conventional methods; ferric nitrate ferrous chloride, cobaltous nitrate, nickelous nitrate, cupric nitrate, mercuric chloride, cadmium nitrate, zinc nitrate, manganous nitrate, calcium chloride, and magnesium nitrate, all analytical reagent grade. Purities of the metal salts, with the exception of ferrous chloride, were checked by titrating with an 0.05 M solution of the disodium salt of EDTA, analytical reagent, according to methods suggested by Chaberek and Martell (10), using Eriochromeschwartz T and murexide as indicators. Ferrous chloride was analyzed by a conventional method.

Procedure.—The experimental method consisted of potentiometric titrations of the oxime alone and in the presence of various metal ions. The ratio of ligand to metal salt in solution was varied to determine both the qualitative and quantitative nature of the interaction (11). The ionic strength for all solutions was maintained at 0.1 M by the addition of potassium nitrate. To insure the exclusion of carbon dioxide, nitrogen was passed through the solutions during the course of the titrations. During each titration, enough time was allowed between addition of increments of base to make certain that equilibrium was attained. This precaution was especially critical in the cobaltous and ferrous systems, where in many instances a considerable period of time elapsed before the pH readings became constant. All measurements were made at $24 \pm 0.5°$ with a Beckman model G pH meter, equipped with extension electrodes. Spectrophotometric measurements were made with a Bausch and Lomb Spectronic 20 colorimeter.

THEORY

Chelate Formation.—Chelates of pyridine-2-aldoxime may take either of the two forms illustrated in Fig. 1. If equilibrium 2 is predominant it is possible that the resulting chelate may act as a relatively weak acid

$$C_5H_4N—CH\!\!=\!\!NOH + M \rightleftharpoons$$
$$[(C_5H_4N—CH\!\!=\!\!NOH)M] \rightleftharpoons$$
$$(C_5H_4N—CH\!\!=\!\!NO^-)M + H^+$$
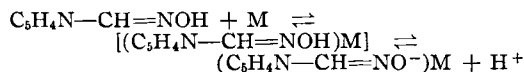
However, analysis of titration data on the basis of complete dissociation of the aldoxime hydrogen yielded constant values of chelate stability constants. This observation suggests that the intermediate, undissociated form represented above (bracketed) is either absent or present in only negligible amounts in these systems. Therefore, it is impossible to distinguish between the two equilibria represented in Fig. 1 by means of potentiometric titrations.
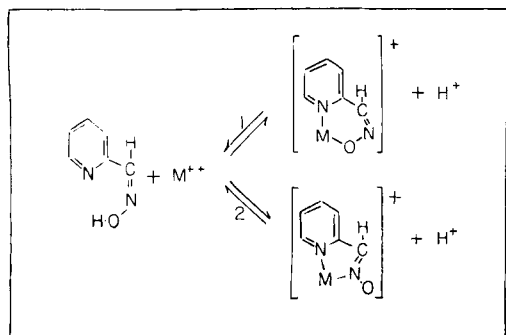

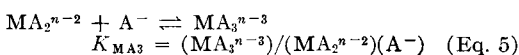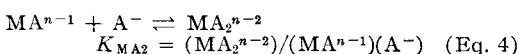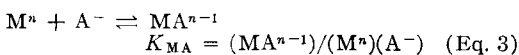Fig. 1.—Chelates of pyridine-2-aldoxime.

Acid Dissociation Constants.—A method suggested by Chaberek and Martell (12) was used to determine the acid dissociation constants of pyridine-2-aldoxime (pa) from titration data (Fig. 2). The relevant constants are

$$K_{a1} = (HA)(H^+)/(H_2A^+) = 2.05 \times 10^{-4} \quad (Eq. 1)$$

$$K_{a2} = (A^-)(H^+)/(HA) = 9.50 \times 10^{-11} \quad (Eq. 2)$$

where $(H_2A^+) = C_5H_4NH^+—CH\!\!=\!\!NOH$, $(HA) = C_5H_4N—CH\!\!=\!\!NOH$, and $(A^-) = C_5H_4N—CH\!\!=\!\!NO^-$. The first dissociation constant (K_{a1}) is of significance in solutions of pH less than 6. When calculating chelate stability constants at higher pH's this equilibrium may be neglected.

Chelate Stability Constants.—The applicable equilibria involved in chelate formation may be expressed as follows

$$M^n + A^- \rightleftharpoons MA^{n-1}$$
$$K_{MA} = (MA^{n-1})/(M^n)(A^-) \quad (Eq. 3)$$

$$MA^{n-1} + A^- \rightleftharpoons MA_2^{n-2}$$
$$K_{MA2} = (MA_2^{n-2})/(MA^{n-1})(A^-) \quad (Eq. 4)$$

$$MA_2^{n-2} + A^- \rightleftharpoons MA_3^{n-3}$$
$$K_{MA3} = (MA_3^{n-3})/(MA_2^{n-2})(A^-) \quad (Eq. 5)$$

where M^n = metal ion of charge n and A^- is defined above. The stability constants were calculated from potentiometric data by an adaptation of Bjerrum's method (13). Derivations of the equations involved have been reported elsewhere (12).
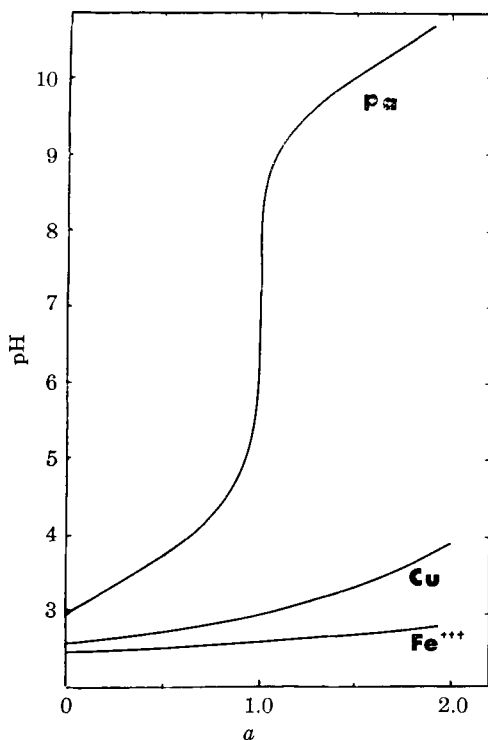

Fig. 2.—Titration curves of pyridine-2-aldoxime (pa) plus one equivalent of HCl. $C_{pa} = 0.008 \ M$. $C_{pa}/C_M = 0.004/0.004 \ M = 1$. a, Moles of base per mole of metal ion.

The value of (A^-) may be determined from titration data as follows

$$(A^-) = \frac{(C_A) - a(C_A) - (H^+) + (OH^-)}{\dfrac{(H^+)}{K_{a2}} + \dfrac{2(H^+)^2}{K_{a1}K_{a2}}} \quad (Eq. 6)$$

where C_A = total molar concentration of ligand in the system and a = moles of base added per mole of ligand.

The number of moles of ligand bound per mole of metal ion, $\bar{n}$, has been called the "formation function" by Bjerrum (13).

$$\bar{n} = \frac{(C_A) - (A_{free})}{(C_M)} =$$
$$\frac{(C_A) - (A^-)[1 + (H^+)/K_{a2} + (H^+)^2/K_{a1}K_{a2}]}{(C_M)}$$
$$(Eq. 7)$$

where (A_{free}) = total concentration of all free ligand species and (C_M) = total concentration of metal ion in the system; $\bar{n}$ may be calculated from Eqs. 6 and 7.

Bjerrum has shown that log K_{MA}, log K_{MA2}, and log K_{MA3} may be determined from a plot of $\bar{n}$ vs. pA, where $pA = -\log (A^-)$, if the successive K values are sufficiently different

$$\log K_{MAn} = pA, \text{ when } \bar{n} = n - 0.5 \quad (Eq. 8)$$

$$\log (K_{MAn}K_{MAn-1}) = 2pA, \text{ when } \bar{n} = n - 1$$
$$(Eq. 9)$$

If the K values, as obtained by this method, do not

differ greatly in magnitude, a method of successive approximations may be used to determine more exact values of the stability constants (13). In the present investigation, K_{MA} and K_{MA2} for the mercuric, zinc, and cadmium chelates were determined by the latter method.

Spectrophotometric measurements may be employed to determine stability constants if the absorption of all pertinent species is known. In the present work, K_{MA} for the ferric chelate was determined by this method. The extinction coefficient for the 1:1 chelate was determined by measuring the absorption of a solution containing ferric ion and oxime, in which the ferric ion was present in large excess to insure complete formation of the 1:1 chelate. The concentration of chelate formed in solutions where chelation was not complete could then be determined from spectrophotometric measurements and K_{MA} calculated according to the following relationship

$$K_{MA} = [(x)/(C_M - x)(C_A - x)] \times$$
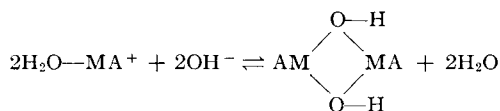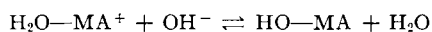$$[(1 + (H^+)/K_{a2} + (H^+)^2/K_{a1}K_{a2}] \quad (Eq.\ 10)$$

where x = molar concentration of chelate.

RESULTS AND DISCUSSION

Titration Curves.—The formulas and stability constants of the metal chelates were determined from potentiometric titration curves illustrated in Figs. 2–7. Although manganous ion showed evidence of a weak interaction, precipitation occurred early in the titration, and stability constants could not be calculated. Calcium and magnesium ions showed no evidence of chelate formation. Therefore, the results for the manganous, calcium, and magnesium ions have been omitted from the data.

Figure 2 shows the titration curves for pyridine-2-aldoxime alone and in the presence of equimolar concentrations of ferric and cupric ions. One equivalent of hydrochloric acid was added to the titration mixtures in order to determine the first dissociation constant for the oxime (K_{a1}). Since more than half of the oxime was bound to both ferric and cupric ions before the addition of the acid, the titrations illustrated in Fig. 2 were necessary to determine values of (A^-) at lower values of $\bar{n}$.

Titration curves for a 1:1 ratio of reactants are shown in Fig. 3. Precipitation is indicated by the letter x. In all cases where precipitation did not occur before the completion of the titration, a definite inflection was observed at some point after the addition of one equivalent of base. Such results indicate hydrolysis and/or polymerization of the chelate species (14). In the cases of the cadmium, zinc, and nickelous ions, the end point observed at two equivalents of base suggests one of the following reactions

$$H_2O—MA^+ + OH^- \rightleftharpoons HO—MA + H_2O$$

$$2H_2O—MA^+ + 2OH^- \rightleftharpoons AM\underset{\diagdown\;\diagup}{\overset{\diagup\;\diagdown}{\underset{O—H}{\overset{O—H}{}}}}MA + 2H_2O$$

The titration curve for the nickelous ion is also characterized by the appearance of a break at one and one-half equivalents of base. Possible explana-
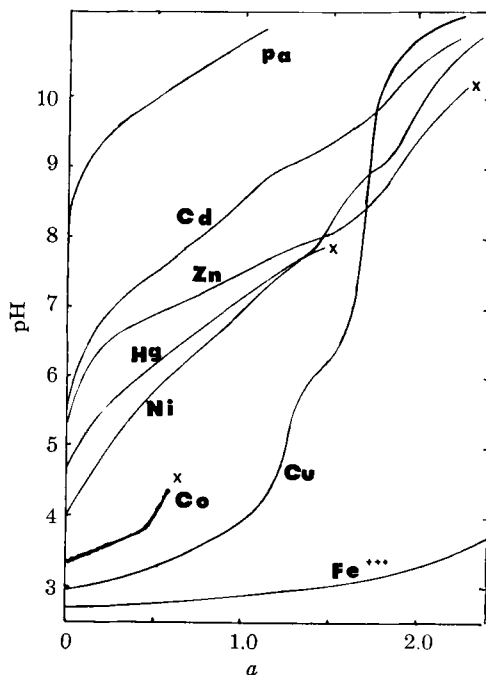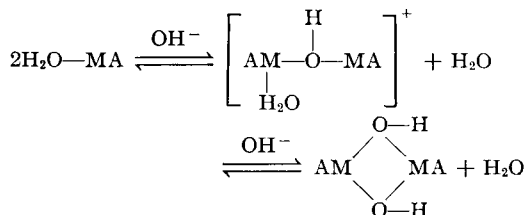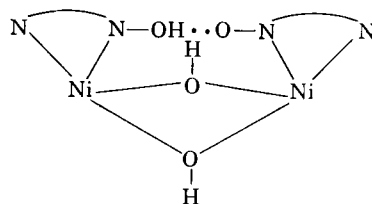

Fig. 3.—Titration curves of pyridine-2-aldoxime (pa). $C_{pa} = C_M = 0.004\ M$. a, Moles of base per mole of metal ion; x, precipitation.

tions of this phenomenon are: (a) dimerization is occurring stepwise

$$2H_2O—MA \overset{OH^-}{\rightleftharpoons} \left[AM\underset{H_2O}{\overset{H}{\underset{|}{\overset{|}{—O—}}}}MA \right]^+ + H_2O$$

$$\overset{OH^-}{\rightleftharpoons} AM\underset{\diagdown}{\overset{\diagup}{\underset{O—H}{\overset{O—H}{}}}}MA + H_2O$$

and (b) a stable, dimeric, hydrogen-bonded species is formed

The breaks at approximately one and one-quarter and one and two-thirds equivalents of base for copper are very difficult to rationalize. It would appear that formation of a complex polymeric species is occurring in these solutions. Titration of the ferric chelate was complete upon addition of three equivalents of base, and this fact suggested that a stable dihydroxo-ferric chelate was formed.

When the reactants were present in a molar ratio of two aldoximes to one metal ion, an end point was observed at two equivalents of base (Fig. 4). These
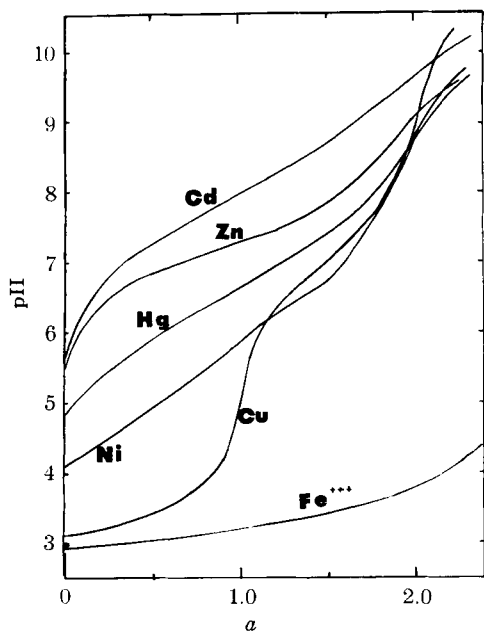
Fig. 4.—Titration curves of pyridine-2-aldoxime. C_{pa} = 0.004 M. C_{pa}/C_M = 2. a, Moles of base per mole of metal ion.
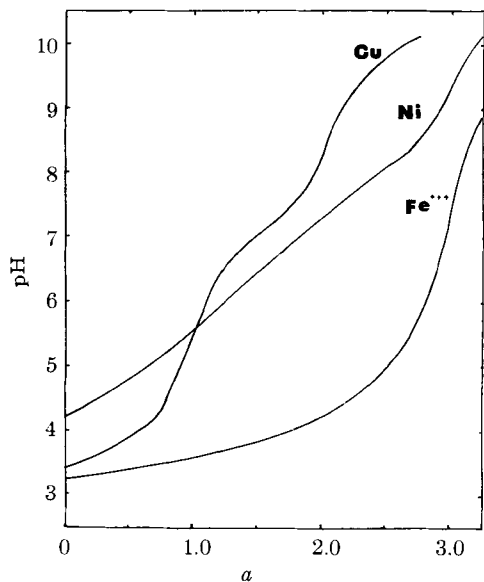

Fig. 5.—Titration curves of pyridine-2-aldoxime. C_{pa} = 0.004 M. C_{pa}/C_M = 3. a, Moles of base per mole of metal ion.

Fig. 6.—Titration curves of pyridine-2-aldoxime. C_{pa} = 0.0032 M. C_M = 0.00048 M. a, Moles of base per mole of metal ion; x, precipitation.

Fig. 7.—Titration curves of pyridine-2-aldoxime. 1, C_{pa} = C_M = 0.00032 M. 2, C_{pa} = 0.00032 M. C_{pa}/C_M = 2. 3, C_{pa} = 0.00032 M. C_{pa}/C_M = 3. a, Moles of base per mole of metal ion.

curves are indicative of the formation of stable 2:1 chelates. The ferric ion again showed a break at three equivalents of base, an indication of formation of a hydroxo-2:1 chelate. The sharp breaks at one and two equivalents of base for the copper chelate is indicative of a large "spreading factor" (13) between the first and second chelate stability constants.

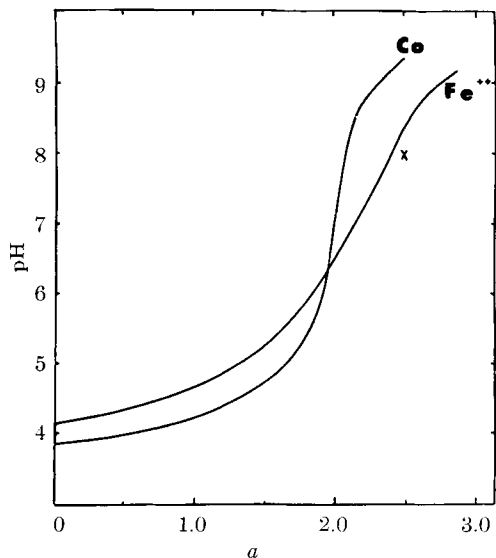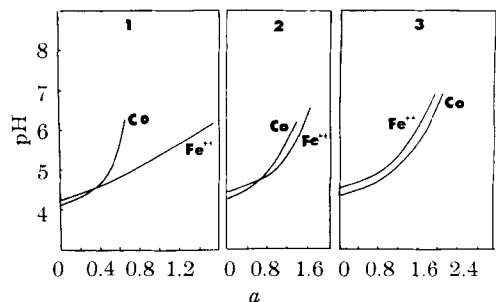Figure 5 illustrates titration of the nickelous,

cupric, and ferric systems, containing the reactants in a ratio of three ligand to one metal ion. The single break at three equivalents for the nickelous and ferric ions indicates formation of 3:1 chelates. The curve for the cupric ion shows that stable chelates of an order higher than 2:1 are not being formed. Because zinc, cadmium, and mercuric ions showed no evidence of forming 3:1 chelates under similar conditions, the results are not shown here.

The ferrous and cobaltous interactions (Figs. 6 and 7) have been treated separately for several reasons. Precipitation of a chelate species occurred before completion of the titration in solutions comparable in strength to those illustrated in Figs. 3–5. Further, equilibrium occurred very slowly and it was extremely difficult to determine the point at which the pH of these solutions remained steady. To overcome these difficulties, studies were made at a larger ratio of ligand to metal ion (Fig. 6). These results show the formation of a 2:1 cobaltous and a 3:1 ferrous chelate. In the ferrous system, the

fact that after the addition of two equivalents of base the buffer region occurred at lower pH values was indicative of formation of a 3:1 species. An end point at three equivalents of base was not observed because precipitation occurred before this point was reached. Although equilibrium occurred rather quickly in these systems, cobaltous chelation was virtually complete before the addition of base and stability constants could not be determined. Therefore, studies were made at lower concentrations of reactants (Fig. 7). Again, precipitation occurred in some cases and the equilibrium pH could not be determined at elevated pH readings (pH 5–6) but enough values were obtained at lower pH values to yield reproducible stability constants.

Analysis of Colored Species.—The above discussion does not take into account the possibility that the end points observed in the 2:1 and 3:1 systems could also be due to titration of hydroxo-chelates. The method of Job (15) was used to demonstrate that 2:1 and 3:1 chelates were indeed forming in these systems. This method was applicable to those chelates which formed colored solutions (Table I.)

TABLE I.—COLORS OF CHELATE SOLUTIONS

Chelate	Color Low pH	High pH
Ferric	Deep orange	Brown-red
Cupric	Light green	Deep green
Cobaltous	Yellow	Yellow orange
Ferrous	Red	Deep red
Nickelous	Yellow	Orange
Mercuric	Colorless	
Cadmium	Colorless	
Zinc	Colorless	

Among these solutions only the ferrous chelate showed an absorbance peak in the visible spectrum (515 mμ). [The ferrous chelate formed an intense red solution under alkaline conditions. In dilute, alkaline (pH 10–11) solutions of ferrous ion containing excess oxime, no precipitation occurred and the color was stable for approximately 12 hours. These facts suggest possible use of the oxime as an analytical reagent for ferrous ion.] For the other solutions, a convenient wavelength was selected for analysis as indicated in Fig. 8. Although the data are not included here, the nickelous ion showed evidence of 2:1 chelate formation at high pH values, according to the method of Job. This fact seems to suggest that under these conditions the 3:1 species dissociates to the 2:1 chelate. Otherwise, the results shown in Fig. 8 are completely compatible with the previous discussion.

Isolation of Chelate Species.—A mixture of 0.02 M mercuric chloride and 0.02 M pyridine-2-aldoxime yielded a white, crystalline precipitate.

Anal.—Calcd. for $(C_5H_4N—CH=NOH)HgCl_2$: N, 7.15; O, 4.07; Hg, 51.0, Cl, 18.0. Found: N, 7.3; O, 4.2; Hg, 50.4; Cl, 17.8.

It is interesting to note that this insoluble species probably contains the oxime in an undissociated form, since insoluble chelates usually have a zero net charge. However, as mentioned previously, this undissociated form is probably present in negligible amounts in more dilute solutions in which the chelate is soluble.

Attempts to isolate pure chelates formed by cobaltous and ferrous ions failed because the insoluble species precipitated in a colloidal form. Extreme conditions of pH and temperature applied to more concentrated solutions (0.02 M) of these chelates resulted in appreciable precipitation. However, analysis showed that these precipitates probably were either mixtures of chelate and metal hydroxides or complicated polymeric forms. Analysis of precipitates obtained by adding excess base to 0.02 M solutions of the zinc and cupric chelates also showed no correspondence to a single, simple species. No insoluble chelates could be isolated from the other systems.

Formation Functions.—The formation functions illustrated in Fig. 9, were calculated according to Eq. 7 from data derived from Figs. 2–7. This plot clearly shows the relationship of the stability constants of the various chelates. With one exception, $\bar{n}$ vs. pA values calculated from titration curves of different ligand:metal ratios were in good agreement. In the nickelous system, results obtained from the 1:1 curve, which described K_{MA}, were different from corresponding results derived from the 2:1 and 3:1 curves. Since the 2:1 and 3:1 titration curves yielded data which were in good agreement, the nickelous chelate formation curve in Fig. 9 was constructed from these data.

The large breaks for the ferrous chelate at $\bar{n} = 2$ and for the cupric chelate at $\bar{n} = 1$ indicate a large value for the "spreading factor" between successive stability constants. The other curves show no such inflections, indicating relatively small differences between successive stability constants.

Stability Constants.—Table II lists the Stability constants determined in this study. Previously reported values for dimethylglyoxime are included for purposes of comparison. The constants were determined from the formation functions by methods previously described. Values of $\bar{n}$ greater than 2.3 could not be determined for the ferrous system. Therefore, the value of log K_{MA3} reported in Table II is an approximation, determined from the value of (A^-) at $\bar{n} = 2$ (Eq. 9). K_{MA} for the ferric chelate was also determined at pH 2 by a spectrophotometric method outlined in the calculations section (Eq. 10) and was in good agreement with the value determined potentiometrically (Table III). The fact that formation of a 1:1 chelate is the predominant equilibrium in solutions of pH 2 was demonstrated by Job's method (Fig. 8). This check was

TABLE II.—STABILITY CONSTANTS

Metal Ion	Pyridine-2-aldoxime Log K_{MA}	Log K_{MA2}	Log K_{MA3}	Dimethyl-glyoxime[a,b] Log K_{MA}	Log K_{MA2}
Ferric	11.4	10.3	8.4	..	..
Cupric	10.8	6.0	..	11.9	11.4
Cobaltous	9.6	8.7	..	9.8	9.1
Ferrous	9.4	8.0	5.1[c]	..	..
Nickelous	8.1[d]	6.1	5.0	11.2	10.5
Mercuric	6.5	5.7	..	..	..
Zinc	5.5	5.3	..	7.7	6.2
Cadmium	5.2	4.4	..	5.7	5.0

[a] In 50% dioxane. [b] From Bjerrum, J., *et al.,* "Stability Constants," Part 1; Organic Ligands, The Chemical Society, London, 1957. [c] Estimated value. [d] Determined from 2:1 and 3:1 titration curves.
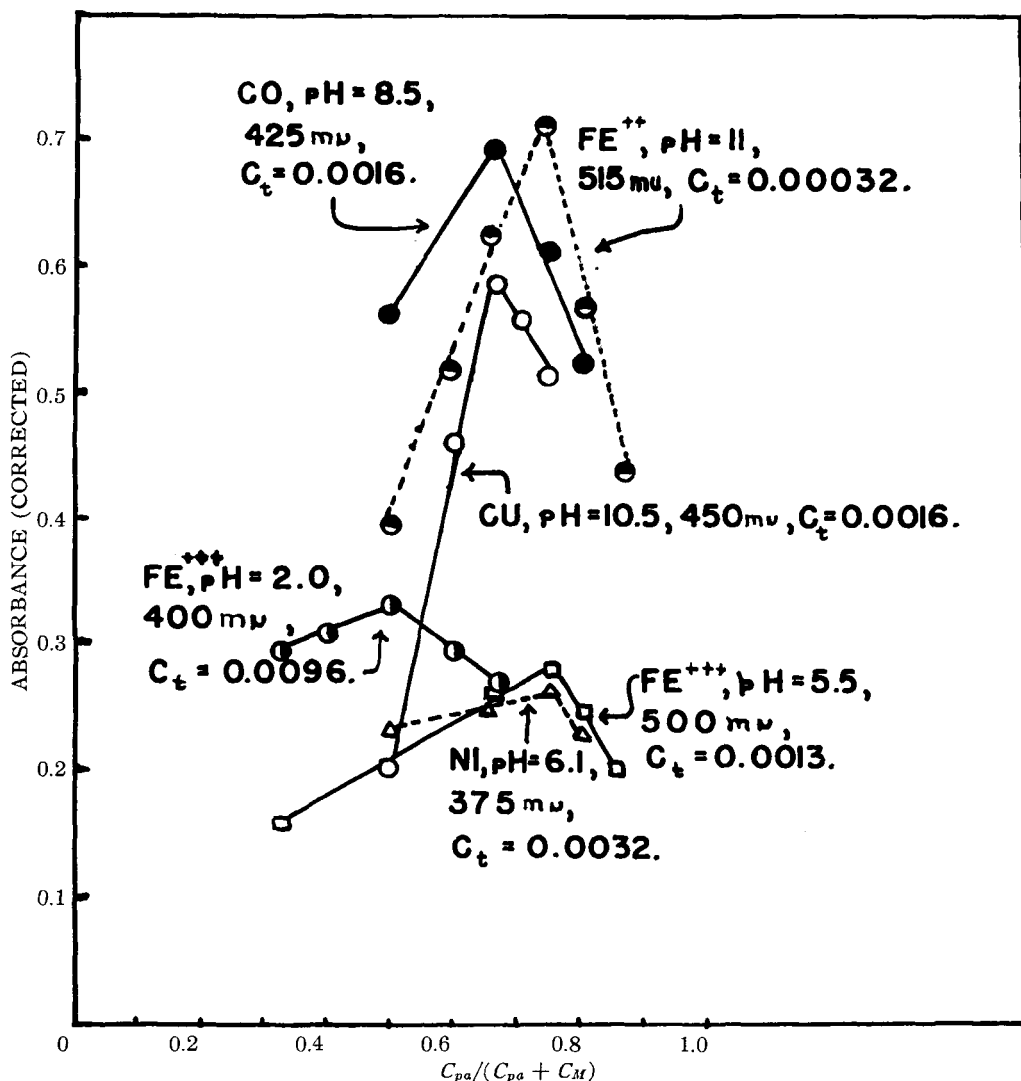
Fig. 8.—Composition curves (method of Job). $C_t = C_{pa} + C_M$.

TABLE III.—STABILITY CONSTANT OF 1:1
FERRIC CHELATE DETERMINED
SPECTROPHOTOMETRICALLY[a]

$(C_A)/$ $[(C_{pa}) + (Fe^{+++})]$	Absorbance, 400 mμ (Corrected)	Log K_{MA}
0.33	0.295	11.27
0.40	0.306	11.23
0.50	0.326	11.25
0.60	0.291	11.21
0.67	0.264	11.20

[a] pH = 2.   Molar absorbance of chelate (400 mμ) = 556.
$(Fe^{+++}) + (C_{pa}) = 0.0096\ M$.

made because large errors may be introduced in the
determination of a very large stability constant when
a relatively small amount of (A^-) is in equilibrium
with the chelate.

As previously noted, analysis of the 1:1 titration
curve for the nickelous chelate resulted in values of
K_{MA} which differed from values obtained from the

2:1 and 3:1 curves.   Algebraic calculation of log
K_{MA} (12) from 1:1 data at low values of $\bar{n}$ (where
chelate hydrolysis does not interfere with the cal-
culations) yielded values which were not constant,
varying from approximately 7.5 to 7.0 at $\bar{n}$ equal to
0.21 and 0.36, respectively.   These low, inconsistent
results are difficult to explain; but they may possibly
be due to incomplete dissociation of the oxime
hydrogen from the chelate in these solutions.   For
example, the formation of a dimeric species of a
structure similar to that previously suggested
(see under discussion of the 1:1 titration curve of
the nickelous chelate) could account for the in-
consistency of these calculations.

The relative stabilities of transition metal chelates
have been correlated with the atomic number of
the metal ion (16).   This relationship is shown
graphically in Fig. 10 for chelates of EDTA, ethyl-
enediamine, and pyridine-2-aldoxime; for which
the maximum value of the stability constant occurs
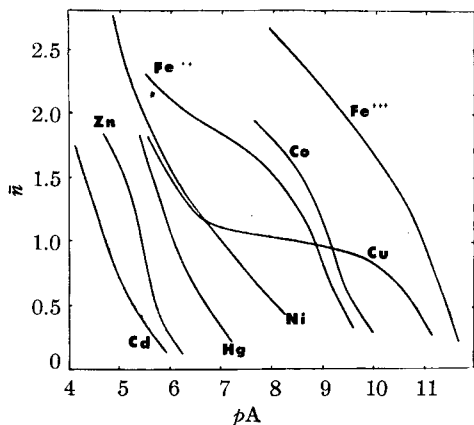for the copper system.   A further increase of the

Fig. 9.—Formation functions. $pA = \log [1/(A^-)]$.
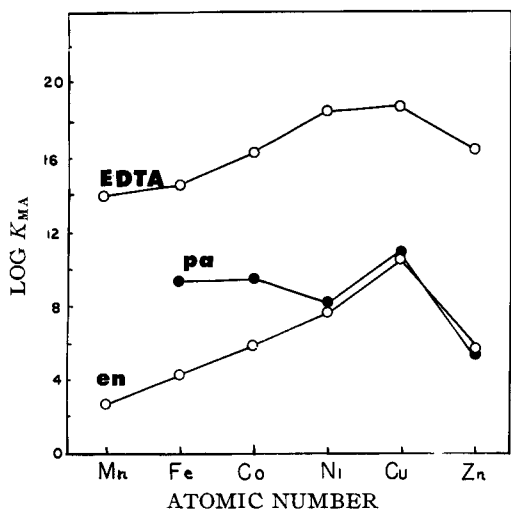$\bar{n} = (\text{Ligand}_{\text{bound}})/(C_M)$.

Fig. 10.—Correlation of log K_{MA} with atomic numbers of transition metals (and zinc). en, Ethylenediamine; pa, pyridine-2-aldoxime.

atomic number by one, going to zinc, results in a decrease of the stability constant. It should be noted that the ferrous and cobaltous chelates of pyridine-2-aldoxime show large deviations from the usual results; the affinity of the oxime for these ions is greater than that which would be expected from results observed in other chelate systems. It has been previously noted that complexation may occur through either the oxime nitrogen or oxygen (Fig. 1).

The actual configuration may depend on particular circumstances such as pH and the properties of the metal ion. The "specificity" observed for the ferrous and cobaltous chelates may be due to an optimum set of such conditions for the formation of a chelate ring.

SUMMARY

1. The acid dissociation constants of pyridine-2-aldoxime and its chelate stability constants with various metal ions have been determined by means of potentiometric titrations. The stabilities of the 1:1 chelates were in the following order: $Fe^{+++} > Cu^{++} > Co^{++} > Fe^{++} > Ni^{++} > Hg^{++} > Zn^{++} > Cd^{++} > Mn^{++}$. Ferrous and cobaltous ions appeared to have unusually high affinities for the oxime. Calcium and magnesium ions showed no evidence of complexations. Cu^{++}, Co^{++}, Hg^{++}, Zn^{++}, and Cd^{++} ions formed stable 2:1 complexes, while Fe^{+++}, Fe^{++}, and Ni^{++} ions formed 3:1 species.

2. One to one titration curves indicated that hydrolysis and/or polymerization of the 1:1 chelates was occurring at elevated pH values.

3. Colored species were formed in the Fe^{+++}, Cu^{++}, Co^{++}, Ni^{++}, and Fe^{++} systems. In particular, the ferrous chelate formed an intense stable red solution at high pH values.

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