more s-character, which should be more suitable for better overlap with the bonding π-orbital of the olefin.

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Multidentate Ligand Equilibria. II. Complex Formation between Iron(II) and Some Hydrazones of Pyridine-2-aldehyde

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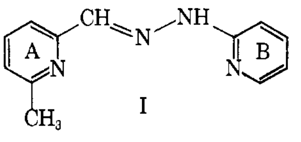
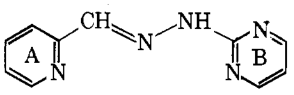
Formation and deprotonation equilibria have been studied for iron(II) complexes of the three tridentate chelates, 6-methylpyridine-2-aldehyde-2′-pyridylhydrazone, pyridine-2-aldehyde-2′-pyrimidylhydrazone, and pyridine-2-aldehyde-3′-methyl-2′-pyrazinylhydrazone. The respective measured stability constants were log β_1: 6.3, 6.0, 7.9; log β_2: 12.6, 14.0, 15.6; and the acid dissociation constants of the respective cationic bis complexes were pK_1: 6.28, 4.56, 4.12; pK_2: 7.95, 6.09, 5.61. A method is described for calculating stability constants and deprotonation constants from pH titration data when the buffer regions of the two equilibria overlap.

Introduction

A class of multidentate ligands has been reported[2] in which each ligand is capable of forming cationic and neutral complexes with bivalent transition metal ions. Addition of alkali to the cationic complexes deprotonates imino groups not involved in coordination to the metal, forming stable uncharged species. The previous paper of this series[3] discussed the equilibria of metal complex formation and deprotonation for the tridentate ligand pyridine-2-aldehyde-2′-pyridylhydrazone (PAPHY). Three related ligands, 6-methylpyridine-2-aldehyde-2′-pyridylhydrazone (I), pyridine-2-aldehyde-2′-pyrimidylhydrazone (II), and pyridine-2-aldehyde-3′-methyl-2′-pyrazinylhydrazone (III) have now been studied in coordination with iron(II).



I



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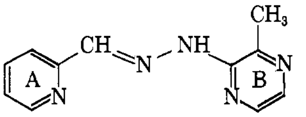

III

Experimental

The three ligands were taken from the same specimens prepared by Geldard and Lions.[2] Experimental methods of studying the equilibria have also been described previously.[3]

Results

Acid Dissociation Equilibria of the Free Ligands.—Solutions of each ligand in perchloric acid (4 moles), alone and in the presence of iron(II) (0.5 mole), were titrated with sodium hydroxide solution (10^{-2} *M*). Detailed experimental results are given in the Appendix.[4] In discussing the titrations, in view of the potentially acidic character of the NH group, we shall refer to species I–III as HL. The equilibrium constants are defined in Table I, and for purposes of computation we further define three quantities, L_T, the total ligand concentration in all its forms, *b*, the number of moles alkali added in the titration, and

$$g = (\Sigma i[\mathrm{H}_i\mathrm{L}] + \Sigma j[\mathrm{MH}_j\mathrm{L}_m])/L_\mathrm{T} \qquad (1)$$

easily calculable from the titration data. This last quantity, the average number of protons attached to L^-, falls below 1 only when deprotonation of the imino group occurs.

In spite of the presence of four nitrogen atoms in ligand I, its *g* values were found not to exceed 2.9 even at the beginning of the titration, and there was no spectrophotometric evidence for heavier protonation at lower pH. It could therefore be treated as a diacid base and the first two dissociation constants of the conjugate acid, $\mathrm{H_3L^{2+}}$, could be calculated from the titration in the usual way, with small activity corrections estimated from the Güntelberg formula.[5] They appear in Table I as pK_1 and pK_2.

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(1) Petroleum Research Fund Fellow, Sydney University.

(2) J. F. Geldard and F. Lions, *Inorg. Chem.*, **2**, 270 (1963).

(3) R. W. Green, P. S. Hallman, and F. Lions, *ibid.*, **3**, 376 (1964).

(4) For Appendix, order Document No. 8059 from the Chief, Photoduplication Service, Library of Congress, Washington 25, D. C., Auxiliary Publications Project, remitting $1.25 for microfilm (35-mm.) or $1.25 for photocopies.

(5) E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

TABLE I

EQUILIBRIUM CONSTANTS AT 25°

Equilibrium	Constants	Ligand I	Ligand II	Ligand III	PAPHY[a]
$H_3L^{2+} \rightleftharpoons H_2L^+ + H^+$	pK_1	3.65 ± 0.01^b	1.1 ± 0.06^c	1.4 ± 0.05^c	2.87 ± 0.01^b
$H_2L^+ \rightleftharpoons HL + H^+$	pK_2	6.06 ± 0.003^b	4.48 ± 0.003^b	4.52 ± 0.005^b	5.71 ± 0.005^b
$HL \rightleftharpoons L^- + H^+$	pK_3	$>14^c$	13.3 ± 0.01^c	12.9 ± 0.01^c	$>14^c$
$M^{2+} + HL \rightleftharpoons M(HL)^{2+}$	$\log \beta_1$	6.3 ± 0.06^b	6.0 ± 0.3^c	7.9 ± 0.06^c	...
$M^{2+} + 2HL \rightleftharpoons M(HL)_2^{2+}$	$\log \beta_2$	12.6 ± 0.05^b	14.0 ± 0.01^c	15.6 ± 0.05^c	16.7 ± 0.02^c
$M(HL)_2^{2+} \rightleftharpoons MHL_2^+ + H^+$	pK_1'	6.28 ± 0.02^b	4.56 ± 0.02^b	4.12 ± 0.003^b	6.27 ± 0.01^b
$MHL_2^+ \rightleftharpoons ML_2 + H^+$	pK_2'	7.95 ± 0.02^b	6.09 ± 0.02^b	5.61 ± 0.003^b	7.63 ± 0.01^b
$M^{2+} + 2L^- \rightleftharpoons ML_2$	$\log \beta_2'$	26	30	32	31

[a] From ref. 3 for comparison. [b] By pH titration. [c] By spectrophotometry.

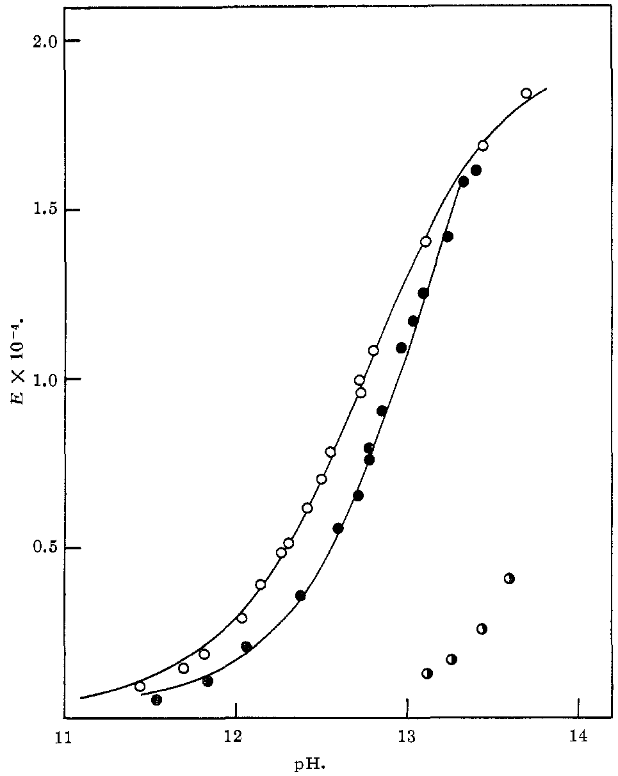

Fig. 1.—Variation of molar extinction coefficient, E, of free ligands with pH. Experimental points: ◑, ligand I at 410 mμ; ●, ligand II at 385 mμ; ○, ligand III at 425 mμ. Continuous curves are calculated from the constants of Table I.

The other two ligands behaved in the titration as monoacid bases with maximum values of g very near 2.0 in that pH range. Table I shows calculated values of pK_2, representing the dissociation of H_2L^+. However, changes in absorption spectra indicated the formation of H_3L^{2+} in more strongly acid solution, and pK_1 values for II and III were determined by spectrophotometry at 312 and 335 mμ, respectively. They are given in Table I to only one decimal place because of the uncertainty of the activity corrections in such strongly acid solution.

As in PAPHY, the last dissociation (of HL) was weak in all three ligands in the absence of coordinated metal and had to be determined spectrophotometrically. The normal pale yellow color of the ligands deepened under alkaline conditions with appearance of absorption maxima at 410, 385, and 425 mμ, respectively. The rise in E, the molar extinction coefficient, with pH si shown in Fig. 1. As with PAPHY, the rise in E for ligand I associated with the formation of L^- was perceptible only above pH 13 and remained incomplete in the most alkaline solutions examined. We conclude therefore that the development of the absorption band at 410 mμ was due to a dissociation with pK between 14 and 15.

The corresponding proton in II and III was a little more acidic and the intensification of the color became apparent at pH 11.5. Even so, E was still increasing at pH 13.5, so that a value could not be directly assigned to E_L. The data of Fig. 1 were therefore treated by rearranging the expression

$$E = (E_{HL}[HL] + E_L[L])/([HL] + [L])$$

in the form

$$a_H(E - E_{HL}) = K_3E_L - K_3E$$

and plotting the left-hand side against E. This gave an approximately straight line of slope $-K_3$ and intercept K_3E_L. The values of pK_3 so obtained are shown in Table I and were used together with E_L to calculate the continuous curves of Fig. 1.

Complex Formation and Deprotonation. Ligand I.—The titration curve of ligand I in the presence of perchloric acid (4 moles) and iron(II) (0.5 mole) differed from that followed by the parent compound PAPHY in being less strongly depressed when $b < 4$, so that it could be used for stability constant determinations. However, although an inflection appeared at $b = 4$ the last stage of the titration (b = 4–5) was depressed far enough to suggest that deprotonation of the cationic bis complex to the uncharged form might have already begun before the inflection. Precipitation of the neutral complex was observed at 5×10^{-4} M at pH 6, but it could be kept in solution by titrating at a ligand concentration of 10^{-4} M. The possible overlap between complex formation and deprotonation equilibria necessitated a more elaborate computation than usual.

As a first approximation deprotonation was ignored when $b < 4$, so that (1) reduced to

$$g = \Sigma(i - 1)[H_iL]/L_T + 1$$

That is

$$[HL] = (g - 1)L_T/\beta$$

and the formation function

$$\bar{n} = (L_T - \alpha[HL])/M_T$$

where M_T = total metal concentration

$$\alpha = 1 + a_H/K_2 + a_H^2/K_1K_2$$

$$\beta = a_H/K_2 + 2a_H^2/K_1K_2$$

Stability constants, β_1 and β_2, of MHL and $M(HL)_2$ were then derived by least-squares curve fitting of the expression

$$\bar{n} + (\bar{n} - 1)\beta_1[HL] + (\bar{n} - 2)\beta_2[HL]^2 = 0$$

Similarly, assuming bis complex formation to be complete when $b > 4$, free ligand and mono complexes were ignored, so that (1) became

$$g = \frac{2[M(HL_2)] + [MHL_2]}{2[M(HL)_2] + 2[MHL_2] + 2[ML_2]} = \frac{2a_H^2 + K_1'a_H}{2(a_H^2 + K_1'a_H + K_1'K_2')} \quad (2)$$

or

$$2gK_1'K_2' + (2g - 1)K_1'a_H + (2g - 2)a_H^2 = 0 \quad (3)$$

Least-squaring then gave K_1' and K_2', the acid dissociation constants of $M(HL)_2$.

Successive cycles of the calculation were required to take cognizance of the possibility of overlap by estimating and subtracting the small quantities in (1) ignored in the first cycle. This was done as follows.

$$M_T = [M^{2+}] + [MHL] + [M(HL)_2] + [MHL_2] + [ML_2] \quad (4)$$

$$L_T = 2M_T = \alpha[HL] + [MHL] + 2[M(HL)_2] + 2[MHL_2] + 2[ML_2]$$

Expressing concentrations of individual species in terms of equilibrium constants gave

$$[M^{2+}] = \alpha[HL]/(2 + \beta_1[HL]) \quad (5)$$

which could be substituted in (4) to give

$$\alpha P[HL]^3 + \alpha\beta_1[HL]^2 + (\alpha - \beta_1 M_T)[HL] - 2M_T = 0 \quad (6)$$

where

$$P = \beta_2(1 + K_1'/a_H + K_1'K_2'/a_H^2)$$

Solution of (6) for each experimental point gave a value of [HL] which, with $[M^{2+}]$ from (5) and the first estimates of the equilibrium constants, was then used to estimate the several terms in (1). When $b < 4$ the small term $[MHL_2]$ was evaluated and used to derive improved values of [HL] and $\bar{n}$, and hence of β_1 and β_2. When $b > 4$, the small concentrations of free ligand and of MHL were evaluated and subtracted appropriately from the numerator and/or denominator of (1). Application of (3) then gave improved values of K_1' and K_2'. The cycle could then be repeated by returning to (6) with revised coefficients and continuing as long as any significant change occurred in the equilibrium constants. This procedure was followed with a program written in Algol 60 for an English Electric KDF 9 computer, with the results reported in Table I.

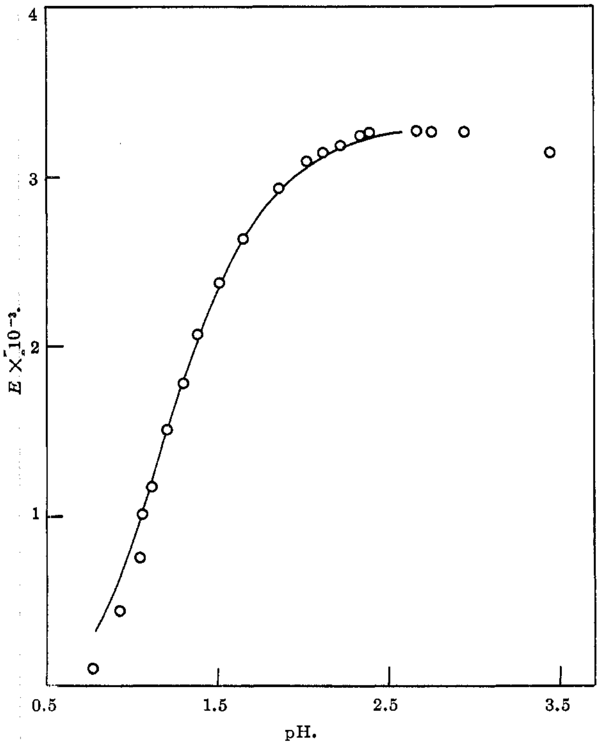

Fig. 2.—Effect of pH on molar extinction coefficient of iron(II) complex of ligand III at 515 mμ. Continuous curve is calculated from constants of Table I.

Ligands II and III.—In the presence of iron(II) and perchloric acid the pH titration curves of ligands II and III below $b = 3$ both resembled that of a strong acid, complex formation being virtually complete before the titration had begun. Deprotonation also set in earlier, as shown by a steady deepening of the red color of the solution from the beginning and by the absence of inflection at $b = 4$. Stability constants were therefore measured by the spectrophotometric method previously described[3] at wave lengths where the cationic and neutral complexes differed most widely in absorption, *viz.*, 505 mμ for II and 515 mμ for III. By the same method the molar extinction coefficient of ligand II in the cationic complexes was found to be 3.84×10^3; for ligand III, E_{HL} in MHL was 3.30×10^3 and in $M(HL)_2$ it was 3.59×10^3. Figure 2 illustrates the variation of E with pH for a 2:1 solution of III with iron(II), the continuous curve having been calculated from the above molar extinction coefficients and the values of β_1 and β_2 shown in Table I.

The slight fall in E above pH 2.8 (Fig. 2) marks the onset of deprotonation but also shows that complex formation and deprotonation did not overlap here. It was therefore legitimate to calculate K_1' and K_2' in the conventional way from the upper part of the pH titration curve, and the values reported in Table I were so derived.

Discussion

The estimates of error in Table I call for comment. The buffer solutions used for calibration give the true value of $-\log a_H$[6] and standardization of the pH meter

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[6] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959, p. 367.

against several solutions provided a check on the slope of the e.m.f.–pH straight line. Standardization before and after a titration showed reproducibility better than 0.01 pH unit, and the method of titration with a piston buret[3] was equally reliable. We have therefore estimated random errors in the equilibrium constants by applying the usual statistical tests to our calculations.

Where a constant was evaluated singly, so that one value was derived from each experimental point, we quote the mean pK or log K and its standard error. Overlapping acid dissociation constants were evaluated by least-squaring the linear regression equation. The table quotes standard errors of pK derived in the usual way from the standard errors of intercept and slope. Errors in stability constants were considered from two points of view; the statistical errors of the regression lines were evaluated as before, and the propagation of errors of pK or molar extinction coefficient into log β_2 was also estimated. The figures quoted in the table represent approximate standard errors from a combination of these several sources. The values of the constants for PAPHY are reproduced from the earlier paper, but with revised figures for pK_1' and pK_2'.

It has previously[3] been concluded from spectrophotometric evidence and from comparison with other pyridine compounds that pK_1 (2.87) and pK_2 (5.71) for PAPHY refer to the acid–base equilibria of the two heterocyclic nitrogen atoms. While tautomerism is common in polyfunctional pyridine derivatives, so that pK values measured by titration cannot be assigned unequivocally to given groups in the molecule, nevertheless the greater susceptibility of pK_1 to the influence of the methyl group in I suggests that it is concerned principally with ring A.

When B is a pyrimidyl or methylpyrazinyl ring, whose basic properties are known[7] to be weak, the low observed values of pK_1 indicate that it is now principally measuring the equilibrium at ring B. In ligands II and III, pK_2 is now a characteristic chiefly of ring A and is to be compared with pK_1 of PAPHY (2.87) and of ligand I (3.65). Its comparatively high values no doubt stem from the lower net positive charge on the dissociating species.

All the ligands considered here resemble PAPHY and *o*-phenanthroline in forming strongly colored cationic iron(II) complexes and in favoring the bis complex in solution. Only for III is log $\beta_1 > {}^1/_2$ log β_2, and for PAPHY itself β_1 could not be detected spectrophotometrically, suggesting that log β_1 was probably less than $^1/_2$ log $\beta_2 - 1$. Ligand I provides an example of the familiar influence of a methyl group adjacent to the pyridine donor nitrogen in reducing complex stability by steric hindrance in spite of its base-strengthening effect.

The acid-strengthening effect of coordinated metal on the imino group has already[3] been shown to depend on the nature of the metal. Comparison of the iron(II) complexes of the four ligands now shows the effect to be almost independent of modifications to the periphery of the ligand. It may be measured by $\Delta pK_3 = pK_3 - {}^1/_2(pK_1' + pK_2')$ and then appears for ligand I, as for PAPHY, to be about 8 pK units but cannot be determined more precisely because of the uncertainty in pK_3. However, in II and III, where the imino group is initially more acidic and pK_3 is better defined, ΔpK_3 has the value 8.0. We therefore conclude that the electron-withdrawing influence of a coordinated metal, transmitted through the conjugated system of the ligand, is not affected by changes in the ligand outside the chelate rings.

Acknowledgment.—The authors gratefully acknowledge a grant from the Petroleum Research Fund of the American Chemical Society which has made this work possible.

[7] A. Albert, "Heterocyclic Chemistry," Athlone Press, London, 1959, p. 344.

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Five-Coordinate Nickel(II) Complexes with Tris(3-dimethylarsinopropyl)phosphine[1]

By Gereld S. Benner, William E. Hatfield, and Devon W. Meek

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Chemical analyses, magnetic moments, electronic absorption spectra, and molar conductance values indicate that tris(3-dimethylarsinopropyl)phosphine (TAP) reacts with nickel(II) salts to form the five-coordinate cations $[Ni(TAP)X]^+$ (where X is a monodentate anion). The aquo complex $[Ni(TAP)H_2O]^{2+}$ is analogous. The absorption spectra suggest that the cation has a trigonal-bipyramidal structure in which the organic molecule functions as a tetradentate ligand. The electronic absorption spectra and the chemical reactions of the complexes are discussed.

Introduction

Although many complexes have been reported with mono-, bi-, and tridentate arsenic and phosphorus ligands, relatively little work has been done with tetradentate arsenic or phosphorus ligands. The complexes of tetradentate molecules of the type $D[(CH_2)_nDR_2]_3$ (where n = 2 and 3) reported thus far contain ligands in which all four donor atoms are alike. Thus the

[1] Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.