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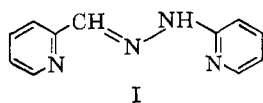
## Multidentate Ligand Equilibria. I. Pyridine-2-aldehyde-2-pyridylhydrazone

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In dilute aqueous solution pyridine-2-aldehyde-2-pyridylhydrazone (PAPHY) is a diacid base with acid dissociation constants  $pK_1 = 2.87$  and  $pK_2 = 5.71$ . Stability constants have been measured for complexes of this base with Mn, Fe, Ni, Cu, Zn, and Cd, all in the +2 oxidation state. The Fe(II) complex is exceptionally stable. In strongly alkaline solution the neutral PAPHY molecule undergoes a third, very feebly acid dissociation with  $pK_3$  between 14 and 15. The marked effect of metal coordination upon this third dissociation has been quantitatively examined.

The tridentate ligand 1,3-bis(2'-pyridyl)-1,2-diazaprop-2-ene (pyridine-2-aldehyde-2-pyridylhydrazone; "PAPHY"; I) and its complexes with a metal co-



ordinated to the three tertiary nitrogen atoms were first described by Lions and Martin.<sup>2</sup> More recently PAPHY has been shown<sup>3,4</sup> to belong to an extensive group of compounds forming complexes with transition metal ions and possessing, at another point in the molecule, a hydrogen atom whose acidic character is strongly enhanced by the presence of the coordinated metal. A bis complex of PAPHY with a divalent metal is thus cationic, but has two acidic protons which can dissociate, leaving a new, uncharged complex as a conjugate base. This paper describes the measurement in aqueous solution of the formation and acid dissociation constants of the cationic complexes.

## Experimental

**Materials.**—The ligand was prepared by interaction of redistilled pyridine-2-aldehyde and 2-pyridylhydrazine in stoichiometric amounts and recrystallized to constant melting point from ethanol.

A solution ( $10^{-2} M$ ) in previously boiled water, containing a slight excess of perchloric acid, was freshly prepared daily and stored under nitrogen.

Solutions of carbonate-free sodium hydroxide, perchloric acid, and metal perchlorates were all prepared in boiled water, standardized by conventional methods, and stored under purified nitrogen. Iron(II) solutions were freshly prepared, made acid with perchloric acid, and used on the same day.

**Methods.**—Titrations were carried out in a glass cell under an atmosphere of nitrogen at  $25.00 \pm 0.05^\circ$ . A Radiometer 4 pH meter standardized against  $0.05 M$  potassium tetroxalate (pH 1.681),  $0.05 M$  potassium hydrogen phthalate (pH 4.005), and  $0.01 M$  sodium borate (pH 9.177)<sup>5</sup> was used. Titrant was delivered below the surface of the solution from a fine capillary connected to a piston buret, and the cell contents were stirred magnetically.

Spectrophotometric measurements on solutions previously equilibrated at  $25^\circ$  were made in thermostated 1-cm. silica cells with a Uvispek spectrophotometer. The blank cell contained

water or, when necessary, an aqueous solution of metal perchlorate equal in concentration to the total metal in the test cell.

## Results

**Acid Dissociation of PAPHY.**—pH titration of a solution  $10^{-3} M$  in ligand and  $3 \times 10^{-3} M$  in perchloric acid followed the curve shown in Fig. 1: the first equivalent of acid was indistinguishable from excess perchloric acid itself, and the next two protons were titrated in two well-defined steps. The conjugate acid of PAPHY at this concentration is therefore dibasic with the corrected<sup>6</sup>  $pK$  values shown in Table I.

TABLE I  
EQUILIBRIUM CONSTANTS OF PAPHY AND ITS METAL COMPLEXES  
AT  $25^\circ$   
Acid dissociation of PAPHY:  $pK_1 = 2.87$ ;  $pK_2 = 5.71$ ;  $pK_3 \approx 14.5$ .

	Metal complexes					
	Mn	Fe	Ni	Cu	Zn	Cd
$\log \beta_1$	3.3	...	8.3	11.6	5.7	4.8
$\log \beta_2$	6.9	16.7	18.5	...	11.2	10.1
$pK_1'$	...	5.68	7.37 <sup>a</sup>	5.96	7.94	8.93
$pK_2'$	...	6.57	8.50 <sup>a</sup>	8.74	8.85	10.22
$\log \beta_2'$	...	33	32	(20) <sup>b</sup>	23	20

<sup>a</sup> By spectrophotometry  $pK_1' = 7.42$ ,  $pK_2' = 8.61$ . <sup>b</sup>  $\log \beta_1'$  calculated for  $CuL^+$ .

In view of the tendency of PAPHY when complexed with a metal to lose a further proton, the free ligand was examined in alkaline solution also. The titration curve at high pH gave no indication of another dissociation stage, which must therefore be quite weak if it exists at all in free PAPHY. Spectroscopic examination of alkaline solutions showed no changes in the ultraviolet region. However, above pH 12.5 the hitherto very pale yellow ligand became deeper in color, with an absorption maximum developing at 4100 Å. That this color was a pure pH effect and did not originate in a sodium complex was established by repeating some of the measurements with tetramethylammonium hydroxide as the alkali. The intensity of the color with either alkali increased steadily with pH, and at pH 13.8 the molar extinction had reached 5400 without showing any sign of approaching a maximum. As well as the difficulties inherent in all measurements in such alkaline solutions,

(6) E. Güntelberg, *Z. Physik. Chem.*, **123**, 199 (1926).

(1) Petroleum Research Fund Fellow, University of Sydney.

(2) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

(3) J. F. Geldard and F. Lions, *ibid.*, **84**, 2262 (1962).

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

(5) V. E. Bower and R. G. Bates, *J. Res. Natl. Bur. Std.*, **69**, 261 (1957).

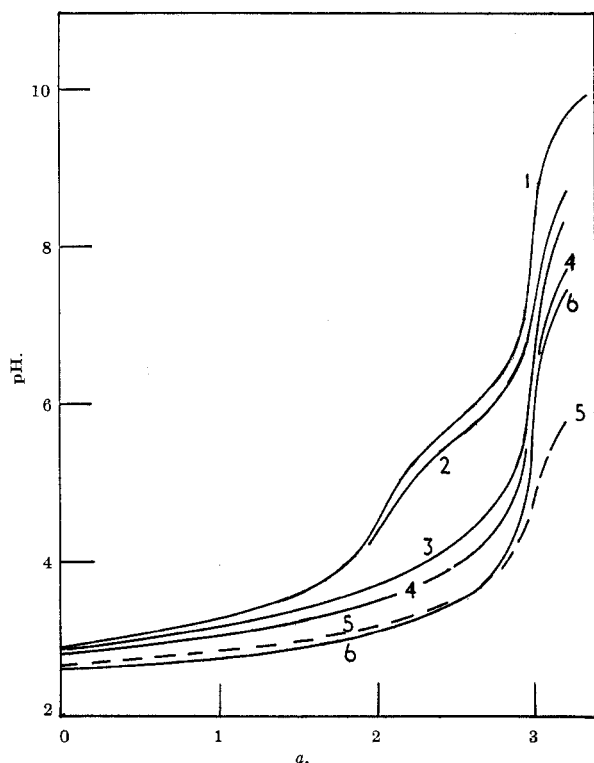


Fig. 1.—pH titration of PAPHY ( $10^{-3} M$ ) in perchloric acid ( $3 \times 10^{-3} M$ ): 1, alone; 2-6, with  $0.5 \times 10^{-3} M$  Mn, Cd, Zn, Fe, Ni, respectively;  $a$  = moles of NaOH/mole of ligand.

evidence of decomposition of the solute began to appear at this high pH, so that the expected constant molar extinction coefficient indicative of complete dissociation could not be reached. However a rather precarious extrapolation suggests that the development of the absorption band at  $4100 \text{ \AA}$ . may be due to a third dissociation with  $pK_3$  near 14.5.

**Stability Constants of Cationic Complexes.**—Although the dissociation of a hydrogen atom from the neutral PAPHY molecule is weak and ill defined, the enhancement of its acidity after metal complex formation compels its treatment as a replaceable hydrogen atom. For consistency, therefore, we shall consider the protonated form of the ligand as  $H_3L^{2+}$ , the cationic complexes as  $M(HL)^{2+}$  and  $M(HL)_2^{2+}$  and the uncharged bis complex as  $ML_2$ .

Further, because of the uncertainty in the value of  $pK_3$ , it is necessary to depart slightly from convention and determine the stability constants in terms of the activity,  $a$ , of HL rather than of  $L^-$ . Thus

$$\beta_1 = \frac{a_{MHL}}{a_M a} \quad \beta_2 = \frac{a_{M(HL)_2}}{a_M a^2}$$

These constants were derived by the application of least-squares curve-fitting procedures to the expression

$$\bar{n} = \frac{\beta_1 a + 2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2} \quad (1)$$

where  $\bar{n}$  is the degree of complex formation of the system,<sup>7</sup> and  $a$  is calculated from  $pK_1$  and  $pK_2$  and the con-

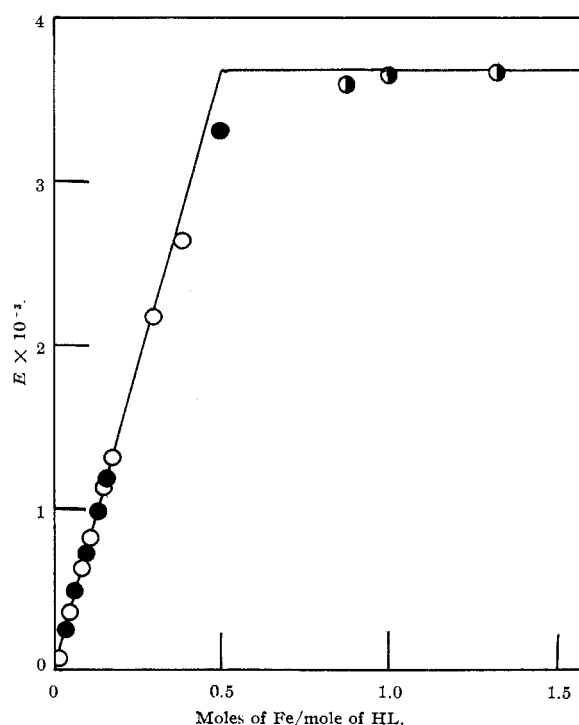


Fig. 2.—Effect of added  $Fe^{2+}$  on molar extinction coefficient of PAPHY at  $5100 \text{ \AA}$ .: O, pH 2.5; ●, pH 3.0; ◐, pH 4.0.

centration of free ligand. Activity corrections were estimated as before.<sup>6</sup>

When a pH titration similar to that of the previous section was performed in the presence of  $0.5 \times 10^{-3} M$  metal ion, the curve was so strongly depressed (Fig. 1) that useful ( $\bar{n}$ ,  $a$ ) data could be derived only for manganese, zinc, and cadmium. Stability constants for complexes of these metals are presented in Table I. pH titration gave no evidence of complex formation in dilute aqueous solutions of magnesium or calcium.

As the combination of high complex stability with low basic strength of the ligand rendered the pH method ineffective for iron, nickel, and copper, spectrophotometric methods were used. The iron(II) complex, the only one to be more strongly colored in acid solution than the ligand itself, exhibited a strong absorption band at  $5100 \text{ \AA}$ . In the presence of excess iron(II) the ligand had a constant molar extinction,  $E$ , of  $3.68 \times 10^3$  (Fig. 2). The figure also shows that small additions of iron(II) to excess of the initially almost colorless ligand produced a linear increase in  $E$ , independent of pH above pH 2.5. If, as seems justified in the light of earlier preparative work<sup>3,4</sup> and the evidence of pH titration, it is assumed that the iron(II) was here forming a bis complex, then the slope of the graph gives the same value,  $3.68 \times 10^3$ , for combined ligand. This means that at  $5100 \text{ \AA}$ . free ligand has  $E$  0 and combined ligand has  $E$   $3.68 \times 10^3$  without reference to whether it is present as the mono or bis complex. This is a not uncommon situation<sup>8</sup> and permits the immediate determination of  $\bar{n}$  of any solution from an optical density measurement.

(7) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Company, New York, N. Y., 1961, Chapter 5.

(8) R. W. Green and G. K. S. Ooi, *Australian J. Chem.*, **15**, 786 (1962).

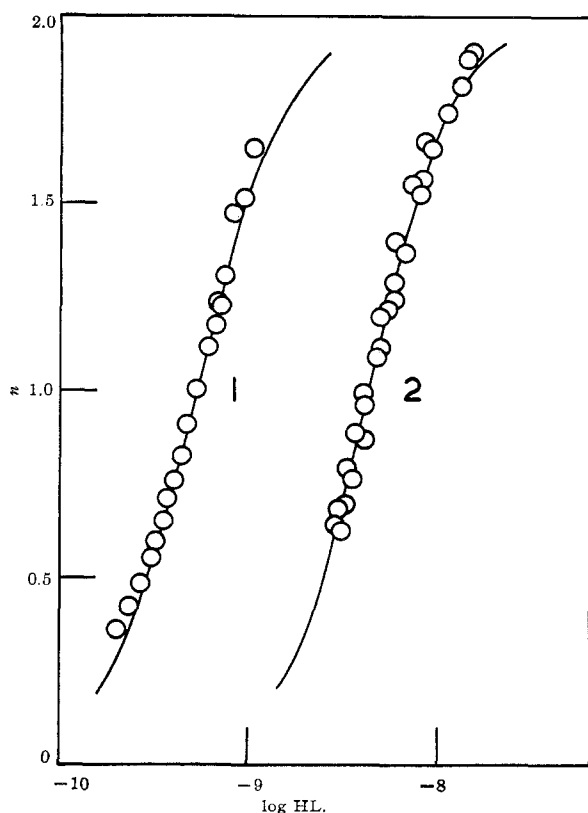


Fig. 3.—Degree of complex formation between PAPHY and: 1, Ni; 2, Fe. Continuous curves calculated from constants of Table I.

When this method was applied to solutions of iron(II) and PAPHY below pH 3, it was found that full development of the color took 2 hr. after mixing. The color then remained unchanged for 12 hr. In the pH range 1.9–2.4 optical density measurements at equilibrium led to  $\bar{n}$  values from 0.6 to 1.95 as shown in Fig. 3. Application of eq. 1 to these experimental results, with the usual corrections for activity, yielded the value of  $\beta_2$  shown in Table I, but a value of  $\beta_1$  too small to be significant. Reversal of the calculations showed that the optical density of any individual solution could be fully accounted for in terms of  $\beta_2$  and the above figure of  $E$  for the bis complex.

This absence or insignificance of a lower complex, while unusual, has parallels among similarly constituted ligands. PAPHY resembles dipyriddy and 1,10-phenanthroline in forming a highly colored, diamagnetic iron(II) complex<sup>2</sup> whose stability in solution is unusually high by comparison with its neighbors in the Irving–Williams series.<sup>9</sup> It seems probable that the gain in stability accompanying spin pairing occurs only under the influence of the full ligand field in the bis complex,<sup>10</sup> with the result that the mono complex is not detectable in solution.

The cationic copper(II) complex of PAPHY was not sufficiently strongly colored to permit application of the above method, but its ultraviolet absorption spectrum did differ from that of the free ligand at wave lengths below 2500 Å. In this region the ligand of

course absorbed quite strongly and to a degree that varied with pH. Measurements of the effect of added copper(II) on the optical density of PAPHY at 2220 and 2380 Å. showed the familiar initial linear increase and ultimate constancy. At 2380 Å. plots of  $E$  against  $r$ , the copper–ligand ratio, at pH 2.5 and 3.4 were linear up to  $r = 0.9$  and on extrapolation intersected at  $r = 1.0$ . At this point of intersection  $E$  was equal to that observed for solutions containing a large excess of copper. At 2220 Å. the plots at the two pH values coincided throughout, were linear to  $r = 0.9$ , and again gave a value of  $E$  at  $r = 1.0$  unaffected by excess copper. There was no discontinuity at  $r = 0.5$  and no evidence for anything higher than a mono complex. Spectrophotometry could therefore be used to determine the concentrations of free and combined ligand in any solution where complex formation was incomplete. The stability constant of the mono complex reported in Table I was evaluated in this way from measurements between pH 1.0 and 1.5. This low pH, which was necessitated by the great stability of the complex, was unavoidably associated with large activity corrections. These were estimated in the same way as before but must introduce some uncertainty, so that this constant is less accurate than the others in the table.

Although nickel(II) formed a strong cationic complex with PAPHY, its visible and ultraviolet spectra were almost identical with those of the free ligand. Neither pH titration nor the direct spectrophotometric method was applicable. The more elaborate titration methods employing competition with a second ligand were also ineffective through lack of a suitable ligand. However, it was found that the nickel(II) and iron(II) complexes were sufficiently similar in stability to make possible a competitive spectrophotometric method.

Mixed solutions of iron(II) ( $3 \times 10^{-4}$ – $6 \times 10^{-3}$  M), nickel(II) ( $1$ – $6 \times 10^{-4}$  M), and PAPHY ( $1$ – $6 \times 10^{-4}$  M) were prepared under nitrogen in the pH range 2.2–3.0. In the thermostat at 25° equilibrium was reached only after 2 days, but the state of the solution was then independent of the order of mixing the reagents and remained stable in the absence of air for a further 5 days. Under these conditions the ligand was found to be distributed between the two metals, the optical density at 5100 Å., where the nickel complex did not absorb, giving the degree of formation,  $\bar{n}$ , of the iron(II) complex. This and the known stability constant of the iron complex could be substituted in eq. 1 to give  $a$  and  $[HL]$ , from which the total concentration of uncomplexed ligand could be found at any pH. By subtracting the free ligand and the ligand combined with iron(II) from the total ligand, the concentration combined with nickel could be derived. In this way a set of ( $\bar{n}$ ,  $a$ ) was obtained for nickel, with  $\bar{n}$  ranging from 0.3 to 1.7 as shown in Fig. 3. Substitution in eq. 1 then gave the stability constants reported in Table I. The continuous line in Fig. 3 is derived from them.

No constants could be measured for cobalt(II). The initially pale yellow solution turned brown at an

(9) H. M. N. H. Irving and R. J. P. Williams, *Nature*, **162**, 746 (1948).

(10) F. Basolo and F. P. Dwyer, *J. Am. Chem. Soc.*, **76**, 1454 (1954).

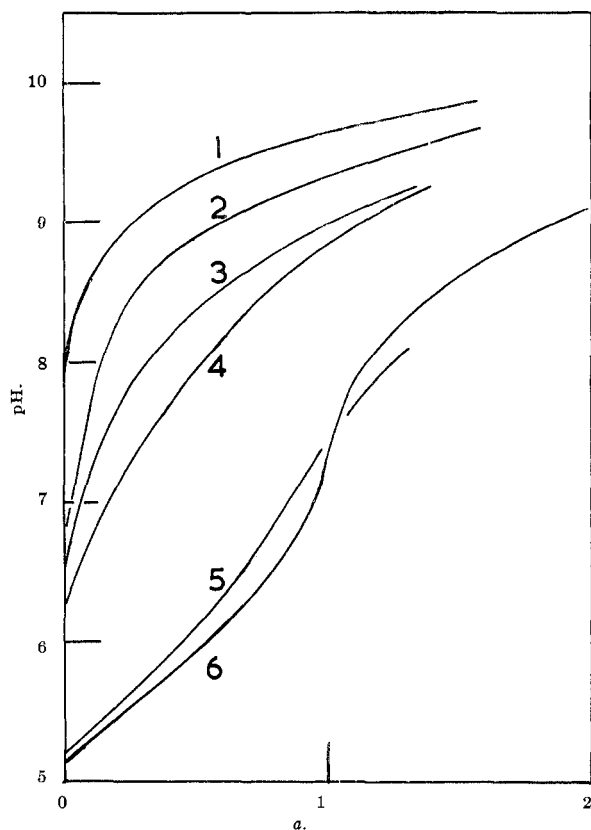


Fig. 4.—pH titration of cationic bis complexes ( $6 \times 10^{-5} M$  in water): 1, ligand alone; 2, Cd; 3, Zn; 4, Ni; 5, Fe; 6, Cu;  $a$  = moles of NaOH/mole of ligand.

early stage of the titration, and the end point required more alkali than the equivalent of the perchloric acid present. If oxygen was bubbled through the solution for increasing periods, the brown color appeared before the titration was begun and the end point was displaced further, ultimately reaching a value of 1.0 equivalent of excess alkali per mole of cobalt. This can be explained in the light of two observations<sup>2,4</sup>: the cobalt(II)-PAPHY complex is very readily oxidized to the cobalt(III) complex,<sup>2</sup> and the cobalt(III) complex loses a proton from the secondary nitrogen of each ligand even more easily than do complexes of metals in the +2 oxidation state.<sup>4</sup> The displacement of the end point observed here is the resultant of these two effects: the reduction of one hydrogen ion by each cobalt(II) atom and the liberation of two hydrogen ions by the two coordinated ligand molecules. Since this reaction occurs even in the absence of oxygen, no constants are reported for the cobalt complex.

**Acid Dissociation Constants of the Cationic Complexes.**—It was shown by Geldard and Lions<sup>3</sup> that the cationic bis complexes of PAPHY with transition metals in the +2 oxidation state could easily be converted by the loss of two protons to highly colored uncharged bis complexes, soluble in organic solvents but almost insoluble in water. From what has been said above of the third acid dissociation of PAPHY itself, it is clear that these uncharged complexes can be formally represented as coordination compounds of the metal ion with two  $L^-$  ions. Experimentally, however,

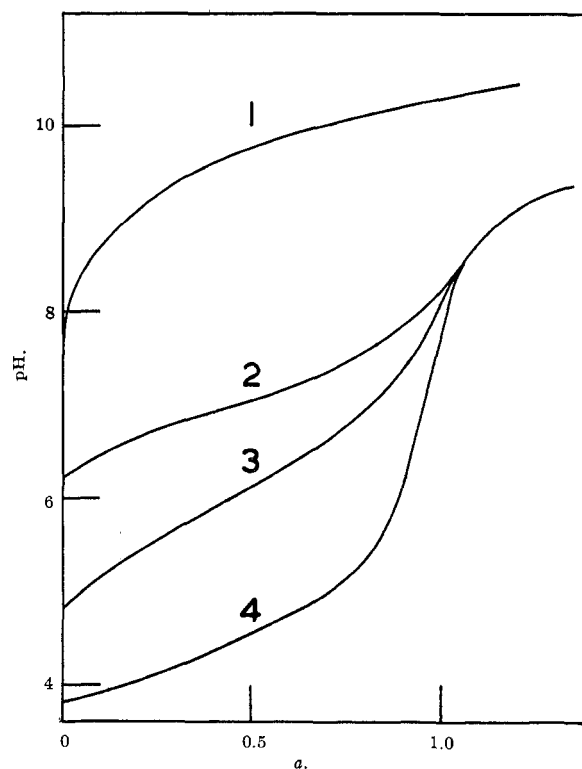


Fig. 5.—pH titration of cationic bis complexes ( $5 \times 10^{-4} M$  in water) in the presence of a layer of chloroform: 1, ligand alone; 2, Zn; 3, Ni; 4, Fe;  $a$  = moles of NaOH/mole of ligand.

it is more convenient to treat the cationic bis complexes  $M(HL)_2^{2+}$  as dibasic acids, whose acid dissociation constants  $pK_1'$  and  $pK_2'$  are measured in the usual way. At the pH where this acid dissociation begins, the several cationic complexes can be seen from the results of the previous section to be fully formed, so that the results of a pH titration could be treated like those for any ordinary dibasic acid, without the need to take the formation equilibria into consideration.

The pH titration curves are shown in Fig. 4. The very low water solubility of the complex conjugate bases  $ML_2$  made it necessary to perform these titrations at a metal concentration of  $6 \times 10^{-5} M$ . This low concentration combined with the rather weak dissociation of the protons to make the end points of most titrations imperceptible. To demonstrate that under the conditions of our experiment two hydrogen ions from each molecule of complex were in fact dissociable, a two-phase titration was also performed.

An aqueous solution of the cationic complex was added to a layer of previously washed chloroform in the titration vessel, and the aqueous layer was then stirred and slowly titrated in the manner described above. As the uncharged complex was formed by titration it passed into the organic phase, which became strongly colored. This extraction of the water-insoluble conjugate base as it was formed permitted the use of more concentrated solutions ( $5 \times 10^{-4} M$ ) and served to enhance the acid dissociation, so that distinct end points could be observed. Figure 5 shows that the end points fell at exactly one mole of alkali per mole of ligand.

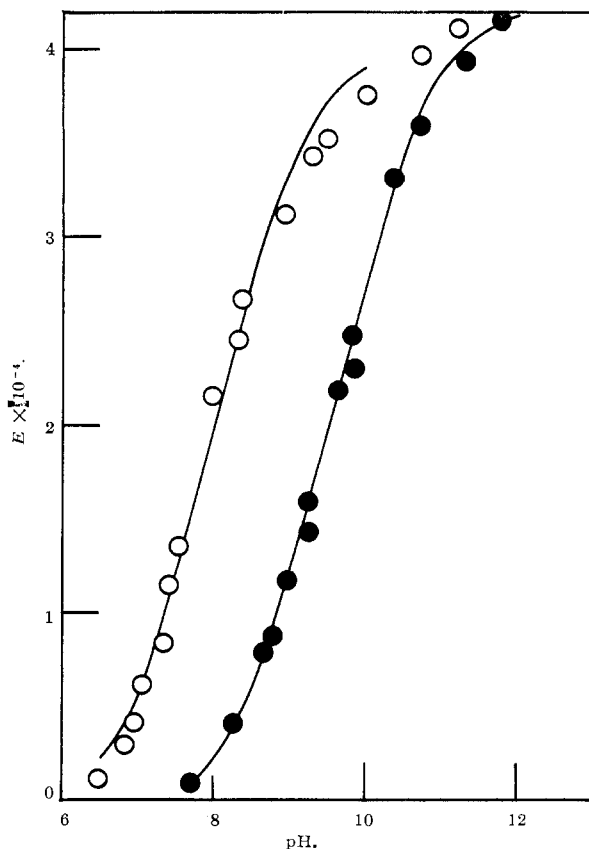


Fig. 6.—Effect of pH on molar extinction coefficients of bis complexes at 4300 Å.: ○, Ni; ●, Cd. Continuous curves calculated from  $pK'$  values of Table I and from  $E_0$   $4.0 \times 10^4$  for Ni and  $4.2 \times 10^4$  for Cd.

The existence of two dissociable hydrogen atoms having been established for aqueous solution, the more dilute titrations of Fig. 4 were then examined. The ionization was shown to be reversible by back-titrating, when the same curve was followed. Near the calculated end point of the direct titration the pH readings were found to drift downward, and this was traced to slow precipitation of the uncharged complex. There were, however, enough stable pH readings in the earlier part of each titration to ensure reliable calculation, which was done by the usual methods for overlapping equilibrium constants. The results for iron, nickel, copper, and zinc are shown in Table I. The titration curve for the mono complex of copper indicated the liberation of two hydrogen ions, but in steps much more widely separated than the two hydrogens from the bis complexes of other metals. The color change during the titration showed the first of these two hydrogen ions to come from the ligand, so that the second must come from the ionization of a water molecule in the fourth coordination position. The  $pK$  values for cadmium and manganese were too high to be measured by titration, and so a spectrophotometric method was applied.

When a dibasic acid changes color upon dissociating, it is easily shown that the molar extinction coefficient of an ideal solution

$$E = \frac{E_2 a_{H^2}^2 + E_1 k_1' a_{H^2} + E_0 k_1' k_2'}{a_{H^2}^2 + k_1' a_{H^2} + k_1' k_2'} \quad (2)$$

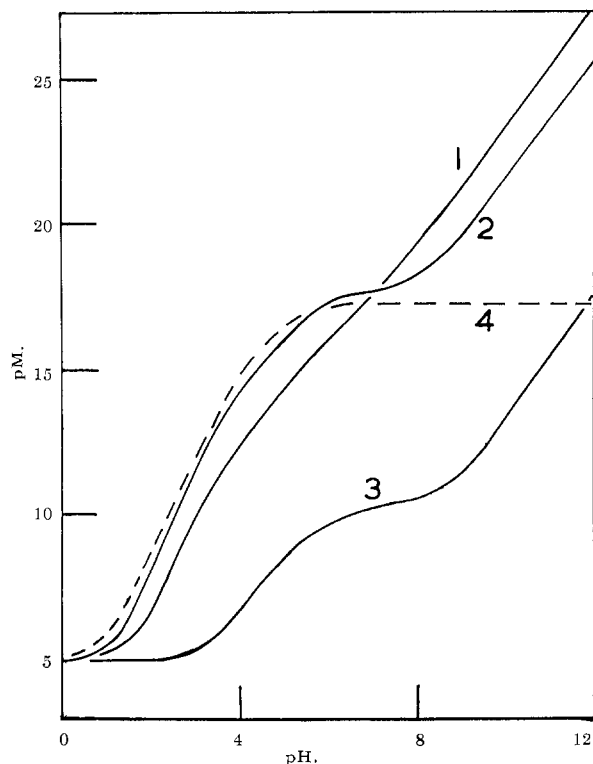


Fig. 7.—Calculated variation of pM with pH in solutions of ligand ( $10^{-8} M$ ) and metal ( $10^{-5} M$ ): 1–3, PAPHY with Fe, Ni, and Zn, respectively; 4, 1,10-phenanthroline with Fe, from results of T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Am. Chem. Soc.*, **70**, 2348 (1948).

where  $E_2$ ,  $E_1$ , and  $E_0$  are, respectively, the molar extinction coefficients of the acid and its first and second conjugate bases. The cationic complexes were generally almost colorless ( $E_2$  0 at 4300 Å.) but the uncharged species absorbed strongly near 4300 Å. Figure 6 shows that  $E$  rose to a maximum near pH 12, when it could be equated to  $E_0$ . With the close overlap between  $k_1'$  and  $k_2'$ , it was not possible to determine  $E_1$  directly, and a method of successive approximation was adopted. As a first estimate  $E_1$  was taken as  $1/2 E_0$  and expression 2 was fitted to the experimental points of Fig. 6 by the usual procedures. From the first estimates of  $pK_1'$  and  $pK_2'$ , the relative proportions of the three forms of the complex at any pH could then be calculated, and a refined value of  $E_1$  could be found. In practice, no improvement resulted from this refinement; the agreement between the calculated curve and the experimental points of Fig. 6 was best when  $E_1$  was assumed to be  $1/2 E_0$ . The poor fit for high pH values of the nickel solution was again traced to slow precipitation of the uncharged complex even at these low concentrations ( $1.6 \times 10^{-5} M$ ). When these highest points were excluded from the calculations, the spectrophotometric method gave values of  $pK_1'$  and  $pK_2'$  of the nickel complex, agreeing well with those from pH titration. We conclude, then, that the spectrophotometric method is valid and we record in Table I the constants obtained in this way for the cadmium complex. When the method was applied to manganese, this complex suffered base hydrolysis at

the high pH, so that its constants have no significance.

### Discussion

The systems described above present the unusual phenomenon of two distinct bis complexes linked by a reversible deprotonation reaction. Protonated complexes whose acid dissociations have been reported previously fall into two classes. In one class are the products of incomplete functioning of a sexadentate ligand with the proton temporarily attached to a potential donor group.<sup>11,12</sup> In such instances the presence of the metal inductively enhances the acid strength of the particular proton by only 1–2  $pK$  units and the domains of stability of the protonated complex and its conjugate base closely overlap.

Complexes in the second class have a dissociable hydrogen atom remote from the site of metal coordination, and the acidity of this hydrogen atom is enhanced by the presence of the metal. Freiser and his co-workers have examined this effect in the phenolic hydrogen of chelidamic acid<sup>13</sup> and of 4-(2-pyridylazo)-resorcinol<sup>14</sup> and in the imino hydrogen of 2-(2-pyridyl)-benzimidazole.<sup>15</sup> In complexes of this kind the electron-withdrawing power of the metal ion appears to be readily transmitted through the conjugated system of the ligand to the site of dissociation. The magnitude of the effect is much greater than in the first class and is influenced by the nature of the metal.

Complexes of PAPHY fall into this second class. Here the ligand is tridentate, acid dissociation occurs at an atom not involved in bonding to the metal, the two regions overlap only slightly, and the effect is 5–8  $pK$  units, displaying a marked variation with the coordinated metal. The order of increasing acidity is  $Mn < Cd < Zn < Ni < Fe$ . There seems to be no simple explanation of this order, but, as far as reliable measurements are available, it appears to follow the order of acidity of a water molecule in simple hydrated ions of the same metals.

Although the dissociation constants vary thus from metal to metal, the pair for any one metal never differ by more than 1.3  $pK$  units. This behavior in dibasic acids is usually found when similar dissociating groups are widely separated in the molecule, so that there is little inductive interaction. If, as seems probable, the driving force behind the deprotonation of PAPHY complexes arises from resonance stabilization of the

conjugate bases, then the overlap of the two equilibria here may have a different cause. In a bis complex of PAPHY with a zero net charge, the negative charges from the sites of deprotonation will be delocalized by resonance across the whole ligand, so that interaction between the two will be reduced. Further, the two tridentate chelate ligands lie in mutually perpendicular planes, and loss of a proton from one should not modify the resonance or conjugation in the other.

From the several constants reported in Table I it is now possible to make a rough estimate of the stability constant of each uncharged complex

$$\beta_2' = \frac{\alpha_{ML_2}}{\alpha_M \alpha_L^{-2}} = \frac{k_1' k_2' \beta_2}{k_3^2}$$

The calculated logarithmic values are quoted in Table I only to the nearest integer, since they bear all the uncertainty of  $k_3$ , but they do demonstrate the very great stability of the uncharged complexes. The cationic stability constants follow the Irving–Williams series, although the iron(II) constant is abnormally near the nickel constant, as with the ligand 1,10-phenanthroline. In the uncharged complexes this displacement has gone so far as to reverse the normal order of iron and nickel. Doubtless this is a consequence of the spin pairing already mentioned.

The unusual nature of the equilibria investigated is perhaps best illustrated by the curves shown in Fig. 7. Here we have used the constants of Table I to calculate  $pM$  ( $-\log [M]$ ) as a function of pH for solutions  $10^{-5} M$  in metal and  $10^{-3} M$  in ligand. Below pH 12 the curves are independent of the value of  $pK_3$  and therefore have the full precision of the stability constant measurements. The effect of the deprotonation reaction is clearly seen in that the curves have a second rising portion, sometimes, as with iron(II), almost continuous with the first. A leveling-off of the  $pM$  curve as shown for 1,10-phenanthroline and iron(II) can be expected with PAPHY only as the pH begins to approach  $pK_3$  in very alkaline solution.

This very powerful sequestering action in mildly alkaline solutions, coupled with the preferential solubility of the uncharged complexes in organic solvents, suggests an effective means of almost completely removing certain metal ions from aqueous solution. It should also be applicable to separating divalent metals from metals in other oxidation states.

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