THE UNIVERSITY OF MICHIGAN

COLLEGE OF LITERATURE, SCIENCE, AND THE ARTS
Department of Chemistry

Technical Report

THE THERMODYNAMICS OF CHELATION
OF 2,2'-BIPYRIDINE

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ORA Project 04448

under contract with:

U.S. ARMY RESEARCH OFFICE
DURHAM, NORTH CAROLINA

administered through:

OFFICE OF RESEARCH ADMINISTRATION   ANN ARBOR

August 1961

JMR0137

PREFACE

In the investigation of equilibria in electrolyte solutions, a single experimental technique rarely gives an unequivocal answer. Therefore, we have undertaken a multiple experimental approach to the problem of the investigation of such equilibria.

One such type of equilibria of great importance as it applies to both applied chemistry and biology is the chelation equilibrium. As a preliminary step to the investigation of such systems by ultrasonic and other relaxation techniques, we have studied them by conventional thermodynamic methods. This work is the result of this investigation and lays a firm groundwork for the study of such systems by more exotic methods.

We would like to express our gratitude to the sponsors of this work for their generous support.

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I. INTRODUCTION

The recent interest in the study of metal binding in biological systems has promoted an increase in fundamental research in solution coordination chemistry. Coordination compounds are classified as metal ions bonded to surrounding groups called ligands. The bonding sites on the ligands are usually restricted to the electronegative elements, in particular oxygen, nitrogen, and sulfur. The bonding of heterocyclic nitrogen with transition metal ions is the subject of this study.

One may consider the metal ion with its surrounding ligands as a complex ion. There are various classes of complex ions. If the ligand attaches itself to the metal ion at a single site, we have simple co-ordination by a so-called mono-dentate ligand. If, on the other hand, two or more sites are available on the ligand for attachment to the metal ion, we have a chelate structure. Such ligands are called biden-tate, tridentate, and so forth, as the case may be. In all chelates there is the presence of a ring structure as is illustrated below.

$$(1) \quad M \ + \ 4B \ \underset{\longleftarrow}{\overset{\beta_4}{\longrightarrow}} \quad \begin{array}{c} B \diagdown \quad \diagup B \\ M \\ B \diagup \quad \diagdown B \end{array}$$

M = metal ion   Simple coordination
B = ligand

$$(2) \quad M \ + \ 2B\text{-}B \ \underset{\longleftarrow}{\overset{\beta_2'}{\longrightarrow}} \quad \begin{array}{c} B \diagdown \quad \diagup B \\ | \ M \ | \\ B \diagup \quad \diagdown B \end{array}$$

Chelate structure

1
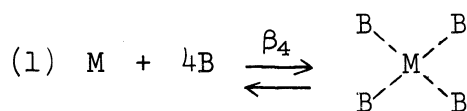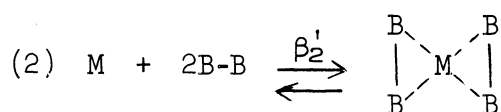
The stability of complex ions has been defined conventionally as the tendency for the above reactions to go to the right. If the systems of complex ions represent an equilibrium situation then the size of the equilibrium constant, as the above reactions are written, will be directly correlated with the stability of the complex.

$$\beta_4 = \frac{[MB_4]}{[M][B]^4}$$

This constant is called the formation constant or the stability constant of the complex. One may discuss individual stability constants, designated k_1, k_2 ... k_n or overall stability constants β_n where $\beta_n = k_1 \cdot k_2 \cdot k_3 \cdots k_n$, the product of the individual constants. It should be noted that this definition of stability says nothing about the resistance of the complex to oxidation, hydrolysis, or thermal decomposition, nor is there any indication of the kinetics of the complex-ion formation. In solution this definition of stability refers principally to the tendency of the complex to hold together, that is for the metal ion to associate itself with ligands other than solvent molecules in its inner sphere.

It has been known for many years by preparative inorganic chemists that chelated complexes are more stable than non-chelates. Since the precise thermodynamic work of Bjerrum,[1] Schwarzenbach,[2] Spike and Parry,[3] Martell and Calvin[4] and many others it has been known that chelated complexes are thermodynamically more stable than non-chelates. That is, for the two reactions depicted above: β_4(non-chelate) $< \beta_2'$(chelate).

Since the formation constants may be directly related to free energies

of formation by

$$\Delta F = -RT\ln K$$

one can say that for the reaction:

$$(3) \quad MB_4 + 2(B\text{-}B) \rightleftharpoons M(B\text{-}B)_2 + 4B$$
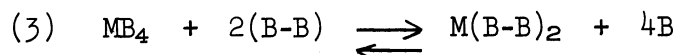
the free energy term will be negative. Now we may write

$$\Delta F = \Delta H - T\Delta S.$$

This permits a discussion of two factors contributing to the negative

free energy term - an enthalpy effect and an entropy effect. Together

they make up the chelate effect as defined by Schwarzenbach[2] in his studies

on ethylene-diaminetetraacetate versus the corresponding iminodiacetate.

He concluded that a favorable entropy change stabilized the chelated spe-

cies. That this is true may be observed quickly on comparing the number

of particles involved in reaction (3). Three particles on the left side

become five on the right. Thus we would always expect a positive con-

tribution to the translational entropy in such a process.

Adamson[3] has pointed out that the chelate effect is largely due to

asymmetry in the choice of standard thermodynamic states. For example

one uses the pure substance for the solvent standard state and a one

molal solution for the solute standard state. The choice of standard

state is primarily one of varying the translational entropy contributions.

For reactions of a similar charge type the use of the hypothetical mole-

fraction standard state tends to minimize the translational entropy effect. For a typical case of the chelate effect, ethylene diamine versus amnonia, the use of a mole-fraction standard state casues the chelate effect to substantially vanish.

Spike and Parry[3] studied the chelate effect with primary amines and found that enthalpy effects were present with metal ions such as Cu(II) which could be stabilized by a crystal field. Such enthalpy effects would be expected to show up in the spectra as well.

The chelate effect was defined by Schwarzenbach[2] as the added stability conferred upon a complex containing bidentate or higher order ligands as compared with that from unidentate ligands. The effect can be studied if a suitable coordinating ligand and its corresponding dimer are found. Thus far heterocyclic nitrogen complexes have not been studied with respect to the chelate effect. In this regard pyridine and 2,2'-bipyridine provide a suitable pair for a study of chelation.

pyridine   2,2'-bipyridine
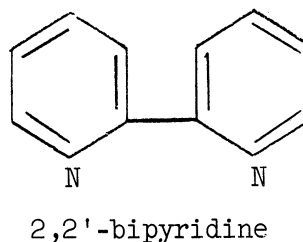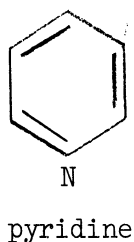
Bipyridine has been known to form brilliantly colored compounds with transition metal ions since the pioneering work of Blau in the 1880's. The crystal structure and stoichiometry of many of these compounds have been elucidated by such workers as Burstall, Dwyer, Jaeger and Van Dijk,

Tartarini, and Pfeiffer. However a study of the thermodynamics of the
formation of these complexes has not been systematically undertaken for
several reasons. Among the more important are the low base strength of
bipyridine as compared with primary amines, the low solubility of bipyri-
dine in water (1×10^{-2} moles/liter) and the one-sided equilibria of
some of its complexes, Fe(II) and Ni(II) having formation constants of
approximately 10^{20}. The low base strength of bipyridine renders the
potentiometric determination of stability constants by way of the conven-
tional pH meter more difficult than with the primary amines. The low
solubility of bipyridine causes troubles with calorimetry experiments
since one is forced to work with very dilute solutions containing on the
order of 1×10^{-4} moles of reagents and thus leading to measured tempera-
tures of reaction of only 1×10^{-4} degrees.

Aside from the interest in studying the thermodynamics of the bi-
pyridine system of complexes in order to look at the chelate effect, one
is also interested in studying the bonding of these compounds. Depart-
ing briefly from our above definition of stability, one finds bipyridine
stabilizing low oxidation states of transition metal ions. For example
the tris bipyridine Ni(II) complex is resistant to boiling in nitric
acid solutions. It is also valuable to look more closely at the type of
bonding which leads to such highly colored species as the tris complex
of Fe(II). Bipyridine is also a simple analog of many other heterocy-
clic nitrogen ligands, some of which have considerable biological inter-
est.

Such compounds as 1-2 bis(2-pyridyl)ethane (BPE) and bis(2-pyridyl)

methane (BPM) can be studied with the transition metals to note the ef-

fect of ring size on chelation.
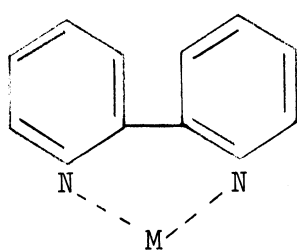
Bipyridine
5-membered ring
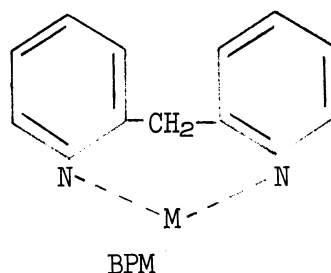
BPM

6-membered ring
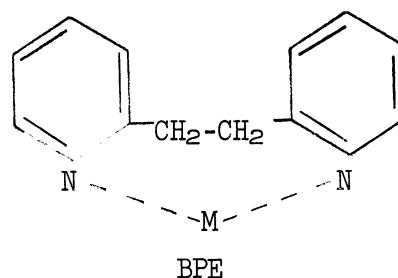
BPE

7-membered ring

Bipyridine complexes may be compared with those of orthophenanthroline.
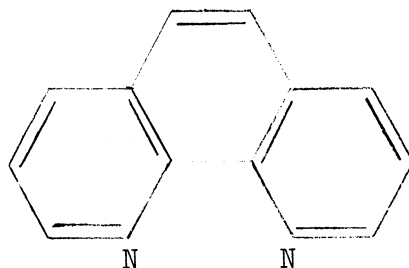
The porphyrins and phthalocyanines provide good examples of heterocyclic

nitrogen chelates of very great biological interest. They consist of

four coplanar heterocyclic nitrogens surrounding a transition metal.

This is very similar to two bipyridine molecules offering four nitrogens

for complexation. The very stable phthalocyanines are simple extensions

of the porphyrins.
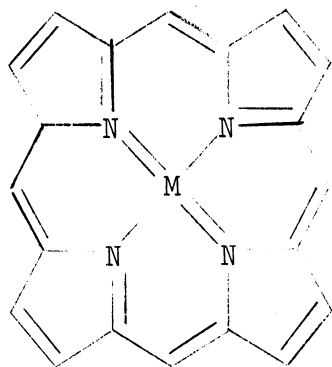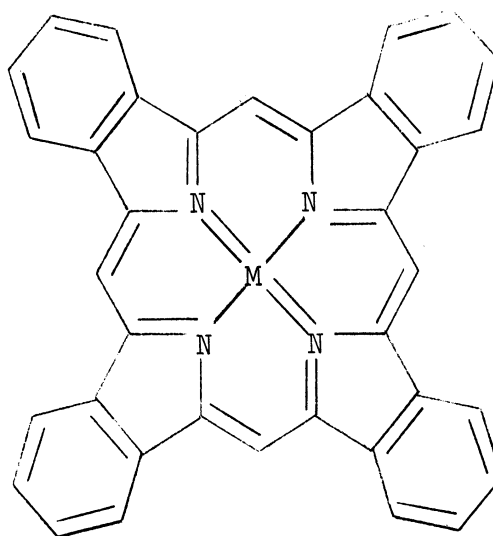
Porphyrin   Phthalocyanine

Furthermore the purines which act as prosthetic groups in many enzymes

and proteins also consist of a conjugated heterocyclic nitrogen system.
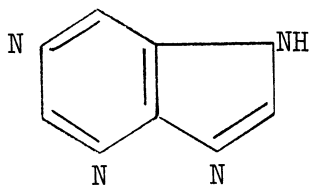
Bipyridine chelates also serve as catalysts in biological systems.

Wagner[6] reports that the hydrolysis of diisopropyl fluorophosphate is

accelerated by Cu(II) and especially by the bipyridine chelate. The

role of the chelate here appears to be that of keeping the copper in

solution above its usual precipitating pH.
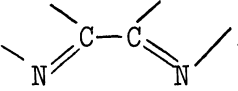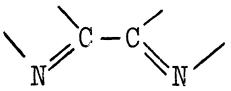
II. HISTORY OF WORK ON BIPYRIDINE COMPLEXES

The history of bipyridine complexes can be divided into three categories: the work of preparing and characterizing the complexes, spectral studies and other structural determinations on the complexes, such as magnetic properties, and the relatively recent measurements of equililibrium constants by a variety of methods.

A. PREPARATION OF COMPLEXES

The work prior to 1954 is described by Brandt and Dwyer[7] in a review article. The classical work on solid derivatives dates to Blau[8] who reported the brilliant red Fe(II) complex. This comples was resolved into optical isomers by Werner[9] in 1912, using tartrate. Further studies by Smirnoff[10] determined that neither 2(2'-pyridyl)quinoline nor 2,2'-biquinoline gave a color with Fe(II). Bipyridine was promoted as a colorimetric reagent for Fe(II). Bipyridine was promoted as a colorimetric reagent for Fe(II). During the 1930's, Morgan and Burstall[11] synthesized many derivatives of bipyridine and the corresponding transition metal complexes. Burstall[12] noted that 6,6'-dimethyl bipyridine did not react with Fe(II). He also synthesized the series of ter-, tetra-, penta-, and hexapyridines. Crystal studies and careful synthesis of many of the complexes were reported by Jaeger and Van Dijk.[13] Bipyridine and Cu(II) were studied by Tartarini.[14] The Cu(II) salts were described by Pfeiffer,[15] and a tris complex verified polarographically by Onstott and Laitinen.[16]

In more recent times, Baker, Basolo, and Neumann[17] have studied the Co(II)

derivatives, and Inskeep and Bjerrum[18] have prepared several Cr(II) com-

pounds. Sandwich compounds have been reported for bipyridine with Cr(0).

Several points should be mentioned regarding peculiarities of these

chelates. Most noted is the bright red Fe(II) complex which appears in

systems containing the $\ce{>C-C<}$ (with N) linkage. Speculation regarding

the nature of this bond with metals has been indulged in by Busch and

Bailar[19] as well as by Irving and Krumholz.[20] The tris-bipyridine Mn(II)

comples is bright yellow and yet it is spin-free. The closely related

Cr(II) complex is spin-paired with a magnetic moment of 3.27 B.M. Fur-

thermore, while the Cr(III) complex can be easily prepared by oxidizing

the Cr(II) form, there is no evidence that the Mn(II) complex can be oxi-

dized to Mn(III). There appears to be a further complication to solu-

tion studies of the Fe(II) and Cu(II) complexes at pH values greater

than 7. Dimers of Fe(II) are shown to exist in solution by Gaines and

co-workers.[21] Leussing[40] and Gustafson[42] have studied the dimerization

of Cu(II) pyridine and bipyridine complexes. Some workers have indicated

steric problems could be expected from the rigid geometry of the bipyri-

dine molecule as compared with ethylenediamine. This is especially true

if one assumes that the two rings must be co-planar with the resonating

$\ce{>C-C<}$ (with N) structure for complex formation. Of further interest to

coordination chemists is the apparent capacity of bipyridine to stabilize

low valence states of transition metals as reported by Herzog.[22]

Magnetic moments for the complexes are reported by Burstall and

Nyholm[23] as well as Perthol[24] and presented in Table I.

TABLE I

Magnetic Moments of Tris Bipyridine Complexes

Metal	Magnetic Moment Bohr Magnetons	Color
Ti(0)	0	
Ti(-I)	1.7	
V(II)	3.75	Green
V(I)	2.8	Red
V(0)	1.7-2.0	Blue
V(-I)	0	Red
Cr(III)	3.76	Yellow
Cr(II)	3.27	Black
Cr(I)	2.0	Blue
Cr(0)	0	Red
Mn(II)	5.98	Yellow
Fe(III)	2.35	Blue
Fe(II)	0	Red
Co(III)	0	Yellow
Co(II)	4.85	Brown
Ni(II)	0	Pink
Cu(II)	1.8	Blue
Cu(I)	0	Red

B. SPECTRA OF BIPYRIDINE AND COMPLEXES

Spectral studies were made in the 1930's by Yamasaki.[25] There appeared to be no direct relationship between the bathochromic shift in the bipyridine ultraviolet spectrum and the stabilities of the complexes. However Sone[26] reported that a study of the two ultraviolet bands of bipyridine showed that while both are shifted to longer wavelengths, the A-band is split in complex formation. With protons this band is shifted but is not split. The relative heights of the two absorption peaks appear

to follow the general order of stabilities Ni > Cu > Zn > Cd > Co > Mn.

More recently Nakamoto[27] has reported the shift in the spectra can be

explained by designating one species as the mono-cation which is appar-

ently cis, and the other as a trans species which exists in basic solu-

tion. The spectrum of bipyridine in basic solutions is very similar to

that in organic solvents such as ethanol where bipyridine is known to be

trans. The splitting of the A-band in the metal chelate is thought to

be due to vibrational fine structures, while the blurring of the fine

structure would indicate non-planarity. The red shift is ascribed to

resonance. The di-cation as reported by Krumholz[28] has a blue shift be-

cause of no resonance. One might expect hydrogen bonding due to the

similarity of the spectra with chelates, but the nitrogen-hydrogen dis-

tance of 2.60 Å seems long for hydrogen bonding.

Recently Schläfer[29] has studied the visible spectra of the complexes

and presents a good valence bond treatment after analyzing the absorption

spectra in solution as well as the reflection spectra of the solids.

C. STRUCTURAL STUDIES ON BIPYRIDINE

Dipole moment studies performed by Fielding[30] indicate bipyridine

exists in solution in the trans form. The measured dipole moment of 0.91

Debye is attributed to the two rings being at an angle of 28°. Since the

rings of biphenyl are said to be at a 45° angle, he did not consider the

interaction between the rings to be as great with bipyridine as with bi-

phenyl. The molecule becomes cis in the presence of H^+ but is trans in

the solid state or in organic solvents.

The crystal structure of solid bipyridine was determined by Merritt and Shroeder[31] using x-rays. The molecule is trans and planar, with the following dimensions.
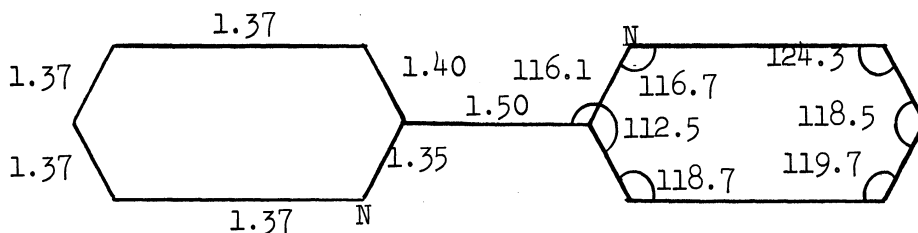
In biphenyl the C_1-C_1' distance is 1.48 Å. The observed length of this band indicates that rotation is easily possible in solution. In addition the closest approach between atoms of adjacent molecules shows that only weak Van der Waal's forces are operating. This explains the low melting point and ease of sublimation.

D. ELECTRON SPIN RESONANCE SPECTRA

Malmstrom and Vänngård[32] have reported a study of many heterocyclic nitrogen complexes of Cu(II) as studied by ESR. Using solid samples or frozen solutions they measured three parameters, $g_{||}$, $g_{\perp}$, and $\underline{A}$, the hyperfine splitting. They report on the extent of covalency of the Cu(II) unpaired electron. From a fraction .86 for hexaquo copper nitrate to .79 for the bipyridine complex (where 1.00 indicates the ionic case) they claim that the difference in the bond must not lie with the in-plane-sigma-bonding. However in arriving at this conclusion they have assumed

tetragonal symmetry for the Cu(II); neglected some of the terms for $g_{||}$, $g_{\perp}$, and $\underline{A}$; and assumed that λ_{max} is the same at room temperature as at 100°K.

McGarvey[33] has used ESR to determine stability constants for Mn(II) pyridine complexes. When Mn(II) is in solution, a decrease in the symmetry of the surroundings of the ion causes the resonance to disappear. The magnetic susceptibility of the pyridine complex of Mn(II) is 5.97, which indicates there would be no broadening of the signal due to a change to a ground state of lower multiplicity. Thus the concentration of uncomplexed Mn(II) can be found by measuring the intensity of the hyperfine resonance. This intensity is proportional to the amount of non-complexed Mn(II). Knowing the total Mn(II) in solution, one can write the following expression for the complexity constant:

$$K \; = \; \frac{[Mn(py)_n^{+2}]}{[Mn^{+2}]} \; \frac{1}{X_{py}^n}$$

where X is the mole fraction of pyridine. A plot of $\log \dfrac{[Mn(py)_n^{+2}]}{[Mn^{+2}]}$ vs $\log X_{py}$ gives a straight line of slope n. From this he gets n = 1.06, K = 130. However chloride which was used as the anion in this work can confound the interpretation of the complexing data by forming ion-pairs with the manganese.

III. PROPOSED RESEARCH

In an attempt to study the chelate effect further and also to examine closely the nature of the bonding involved in bipyridine complexes, it is necessary to obtain precise data on the thermodynamics of these complexes. Previous work of this nature has been done under a variety of conditions using a variety of techniques such as potentiometry, polarography, and spectroscopy. Enthalpies have been determined by varying the temperature of these log K measurements or occasionally by calorimetry. various ionic strengths have been used. Thus it is desirable to perform the thermodynamic measurements under identical conditions of ionic strength in a systematic manner. Standard techniques of glass electrode potentiometry and adiabatic calorimetry should be used to determine ΔF and ΔH.

Since the activities of the complex ions are related in a complicated way to the concentrations, and can only be roughly approximated, it is proposed that all of the work be done in solutions of high constant ionic strength (1 molar $NaClO_4$). A one molar neutral salt background has been used by many workers, for example Bjerrum, Verhoek and Leussing. With reagent concentrations at millimolar levels, the activities of the various species should remain constant and in direct proportion to the concentrations. Since several complex ions are to be studied for purposes of comparison, it is not thought profitable to attempt to extrapolate the concentration constants to infinite dilution by running experi-

ments at other ionic strengths.

The ligands chosen for investigation in this work will be pyridine and bipyridine. Since both are weak bases, the concentration of the several species involved in complex ion formation can be found by measuring the pH of the solution at various concentrations of metal ion, acid and ligand. The acid-ligand equilibrium constant must be measured to permit this calculation. The study of the complextion equilibria for several metals will proceed according to the scheme outlined by Bjerrum.[1] Stepwise equilibria are postulated and an attempt to calculate individual equilibrium constants for each stage of the complex ion formation will be made. Graphical methods, successive approximations, and finally a least squares fit of the potentiometric data to that calculated from equilibrium constants will be tried. The computations will be facilitated by using the IBM 704 computer.

Previous work on nitrogen complexes has shown that the determination of the enthalpies of formation by varying the temperature of the equilibrium constant determination leads to widely scattered results.[35] With a current revival in solution calorimetry by coordination chemists, several good models of workable calorimeters are in the literature. Thus we will construct an adiabatic calorimeter capable of giving 1 or 2% accuracy. Since stepwise equilibria are involved, an enthalpy titration will be run at the same concentrations as the potentiometric titration.

The metals chosen for the study are the divalent ions of manganese,

nickel, copper and zinc. Mn(II) and Zn(II) having half-filled and filled

d-electron shells respectively are chosen to establish the trend across

the latter half of the transition metal series, Cu(II) and Ni(II) com-

plexes provide good examples of crystal field stabilization energy (CFSE).

Due to the tetragonal nature of copper complexes and the apparently more

rigid steric requirements for bidentate ligands, it is desirable to in-

clude both metals in the study. None of these metals can be expected to

hydrolyze significantly in the pH range to be used. The experience of

Fernelius and others has shown that the hydrolysis of trivalent cations

creates very serious experimental problems, to say nothing of computa-

tional difficulties. Cu(II), Ni(II), and Mn(II) have the further advan-

tage of being paramagnetic thus opening another area for fruitful in-

vestigation. All of the metals give spectral information in the ultra-

violet and visible region which can aid in understanding the bonding of

these complexes.

Outline of Proposed Experiments

1. Determine free energies of complexes formed by pyridine and bipyri-

dine with Mn(II), Ni(II), Cu(II) and Zn(II).

    a. Determine the ligand-acid equilibrium constant.

    b. Perform titrations to obtain the complex-ion formation constants

2. Determine the enthalpies of the above systems.

    a. Build an adiabatic calorimeter suitable for an enthalpy titra-

       tion.

3. Record the electron spin resonance spectra of the complexes with the aim of obtaining quantitative data.

4. Compare all of these data with reference to the chelate effect, ligand field theory, existing spectral data, the entropy contribution and similar pertinent parameters.

IV. EXPERIMENTAL

A. ΔF DETERMINATIONS

1. Previous Work with Bipyridine

Since Bjerrum's work on reversible step reactions, the process of complex-ion formation has been considered to consist of a series of sequential additions of ligand molecules to a single metal ion. Each addition represents a true equilibrium situation and thus is capable of being described by an equilibrium constant, k, known as the formation constant.

$$M^{++} + B \underset{\longleftarrow}{\longrightarrow} MB^{++}$$
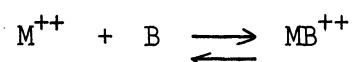
$$k = \frac{a_{MB^{++}}}{a_{M^{++}} a_B}$$

where a represents the activity of the various species. Thus any method which permits a knowledge of $a_{M^{++}}$, $a_{MB^{++}}$, and a_B will lead to a value of the formation constant. However, even the most optimistic use of the Debye-Hückel theory does not permit one to ascribe activity coefficients to such bulky species as protonated heterocyclic amines. Therefore concentration constants must be resorted to. In this case:

$$k_c = \frac{[MB^{++}]}{[M^{++}][B]} \approx k_a$$

at constant high ionic strength (1M) and dilute reagents (1×10^{-3} M). Since the stoichiometry and initial concentration of metal ion and ligand are known, the formation constant may be evaluated by measuring the con-

centrations of either free ligand or free metal-ion.

There are four basic methods of measuring either of these concentrations which have been attempted with pyridine or bipyridine and the transition metal ions: distribution methods, spectrophotometry, metal electrodes, and electron spin resonance.

Irving[43,44] has used the distribution or partition method to obtain successive formation constants for all of the divalent transition metal ions of the first row with bipyridine. The difficulties associated with the measurement are mainly analytical problems, the effect of the organic liquid on the equilibrium between metal ion and aqueous ligand, and most important, the size and linearity of the distribution coefficient with concentration. With bipyridine the analytical problem is minimized by the highly colored Fe(II)-bipyridine complex which permits colorimetric determination of the concentration of the complexed ligand. The choice of the organic liquid would involve considerable experimentation.

Miller and Brandt[46] used spectrophotometry to determine the overall complexity constant for Mn(II) with bipyridine. They found no sharp absorbance peak in the visible or near ultraviolet due to the complex. Also, the absorbance increased with pH, only remaining constant in the range 6-8. Thus they chose a wavelength of 370 mμ, a pH of 6.2-6.4, and a 10-1 ratio of bipyridine to Mn(II) (which gave the maximum color formation). They measured the concentration of the complex by the absorbance of light under these conditions. At this wavelength the non-complexed Mn(II) was found not to interfere. The degree of complexation of the

measured species was determined by a Job plot of absorbance versus mole

ratio of the total Mn(II) to Mn(II) plus bipyridine. This peaked at a

ratio of 0.25 indicating $Mn(bipy)_3^{+2}$. The major limitation of the method

is that only one constant can be determined (in this case the overall

constant β_3) and any intermediate species formed are required not to in-

terfere at the wavelength of the measurement.

Bjerrum[38] has used a copper-amalgam electrode to measure the free

metal ion directly in terms of activities in the case of pyridine com-

plexes. Cabani and Scrocco[51] have measured the emf of a concentration

cell to determine the stability constants of silver and bipyridine. The

cell is of the type:

| Ag | $AgNO_3$ c_1
 KNO_3 c_2
 bipy - varying conc.
 alcohol - 50% | 50% alcohol <br> saturated with
 KNO_3 | $AgNO_3$ c_1
 KNO_3 c_2
 alcohol - 50% | Ag |
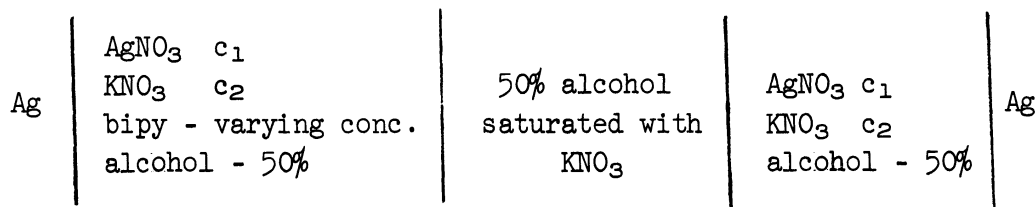
The second major class of methods which has been used to obtain

thermodynamic data on bipyridine and pyridine complexes involves compet-

ing reactions. The first type perfected by Bjerrum[1] involves the protona-

tion reaction of the ligand.

$$BH^+ \underset{\longleftarrow}{\overset{k_a}{\longrightarrow}} B + H^+$$
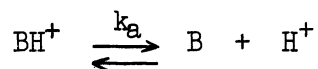
When k_a is determined by measurement of the hydrogen ion via the glass

electrode, the corresponding equilibria of metal ions and the ligand can

be evaluated. Other similar methods involve the competition between two

metal ions for the ligand.

$$M' \; + \; B \; \underset{\longleftarrow}{\overset{k_{M'}}{\longrightarrow}} \; M'B$$

$$M \; + \; B \; \underset{\longleftarrow}{\overset{k_M}{\longrightarrow}} \; MB$$
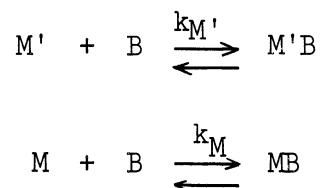
In this case the concentration of M' could be measured and $k_{M'}$ would be known.

Experiments involving the glass electrode have been used by many persons including Bjerrum,[1] Verhoek,[39] and Yamasaki[45] in their studies on pyridine and bipyridine complexes. Bruehlman and Verhoek[39] made up a standard series of solution which were 0.5 molar in KNO_3 and .1 M in HNO_3, with varying amounts of pyridine. From roughly ten such solutions, a value of pK_a could be calculated. When a solution of metal nitrate of 0.02 molar concentration was used with the above series, the formation constants could be calculated. The Ag(I) and Cu(II) pyridine constants were determined in this way.

Edsall[52] determined the stability constants for imidazole with transition metals by forming the protonated ligand at a concentration of 0.1 M, the metal nitrate at 0.01 M and titrating with 0.05 N NaOH. This method was used by Gustafsen and Martell[42] on bipyridine complexes of Cu(II). One disadvantage of the method is that bipyridine complexes with the Cu(II) ion even at a pH of 3 before the NaOH titration begins. This requires work in the very acid regions of the pH scale where readings become rather ill-defined. It also involves the standardization of a third

solution, the NaOH. A ligand as weakly basic as bipyridine may still be

used directly as a titrant if one does not wish to study the more (> pH 6)

basic areas of the metal-ligand equilibrium. Yamasaki and Yasuda[45] meas-

ured the formation constants of bipyridine with Zn(II), titrating bipy-

ridine and Zn(II) at 10^{-4} molar concentrations with standard nitric acid.

Onstott and Laitenen[16] used polarography to measure the overall sta-

bility constant of the Cu(II)-bipyridine system. They found the reduc-

tion of the Cu(II) bipyridine complex to be diffusion controlled and re-

versible. By plotting the log of the concentration of the complexing

agent against the half-wave potential of the complex ion they determined

the number of groups coordinated to Cu(II) and Cu(I) as three and two

respectively. Maximum coordination was achieved with a 50 to 200 fold

excess of bipyridine in .1 N KNO_3. At these concentrations one has a

supersaturated solution of bipyridine.

The method of a competitive known metal-bipyridine reaction is best

illustrated by the work of Cabani and Scrocco mentioned above. By intro-

ducing varying concentrations of divalent transition metals into their

silver concentration cell, they have been able to measure successive

formation constants for a few of the transition metals. Another possi-

bility for studying reactions is spectrophotometry by using the red Fe(II)

bipyridine complex as an indicator of the "free" ligand concentration.

A similar approach is possible with electron spin resonance. Since Mn(II)

has the capacity to complex with bipyridine, and the amount of non-com-

plexed Mn(II) ion can be calculated from the intensity of the ESR spectra,

changes in the non-complexed Mn(II) can be observed when a more strongly

competing metal ion such as Zn(II) is introduced.

2. Materials Used in the Research

Metal perchlorates were obtained as hexahydrates from the G. F. Smith

Company. They were used without further purification. All solutions

used in the studies were made up to be 1 molar in $NaClO_4$. For this pur-

pose anhydrous $NaClO_4$ was purchased from G. F. Smith and the required

amount of solid salt was weighed in. The Cu(II), Ni(II), Mn(II), and

Zn(II) solutions were first made up at 0.01 molar with boiled distilled

water adding no $NaClO_4$. Each solution was analyzed for the respective

metal ion. Approximately 100/1 dilutions of these stock solutions were

then made to get the metal ions at the proper concentrations for titra-

tions. Details of the analysis of the stock solutions follow.[53,54]

(a) $Cu(ClO_4)_2 \cdot 6H_2O$

After a 0.01 molar solution was made up, a brown precipitate

formed. This was filtered off and the solution analyzed by

electrodeposition onto platinum electrodes. (ref. 53; pg 415)

(b) $Ni(ClO_4)_2 \cdot 6H_2O$

The analysis proceeded as with copper. (ref. 53; pg 498)

(c) $Zn(ClO_4)_2 \cdot 6H_2O$

Zinc was determined gravimetrically as the pyrophosphate.
(ref. 54, 52)

(c) $Mn(ClO_4)_2 \cdot 6H_2O$

Mn(II) was oxidized by sodium bismuthate to the permanganate

and the resulting solution was then used to titrate a standard

ferrous ammonium sulfate solution. (ref. 53; pg 479)

In all cases the concentration of the reagents was considered known to

one part per thousand.

Pyridine was obtained from the Baker Chemical Company. It was re-

fluxed two hours with KOH and distilled. The criterion of purity was a

boiling range of 0.5 degree. A dilute solution (.06 M) was made up by

weighing a quantity of reagent pyridine into freshly boiled distilled

water. Solid $NaClO_4$ was added and the resulting solution was titrated

against standard $HClO_4$ to determine the concentration of pyridine.

Bipyridine was purchased from the G. F. Smith Company. It was puri-

fied by recrystallizing from petroleum ether (40-60°C) or ethanol. The

resultant product gave a melting point of 69.0 to 70.0°C which was iden-

tical with that of the commercial material. A further check on the purity

of the amine was made by dissolving it in ethanol (.05 molar) and titrat-

ing with standard $HClO_4$. It is such a weak base and so insoluble in

water that an acid titration of an aqueous bipyridine solution gives no

precise endpoint. For the titration of metal ions, bipyridine was used

at approximately two millimolar concentration. The exact concentration

of the bipyridine was determined by weighing out a given quantity of the

purified solid.

3. Determination of Stability Constants

A Beckman Model GS pH meter was used to measure the hydrogen ion

concentration. A circulating water bath kept a titration vessel at

25.00 ± 0.05°C. The sensitive scale of the pH meter was used. A stan-

dard glass electrode (Beckmann number 4990-80) and a calomel reference

electrode (Beckmann 40451) were used. Since an ionic strength of one

molar concentration was being maintained with $NaClO_4$ it was found that

the KCl salt bridge of the calomel cell did not function due to a pre-

cipitate of $KClO_4$. Thus a saturated NaCl solution was used as a salt

bridge.

In order to insure the measurement of hydrogen ion concentration

rather than an activity expression, the pH meter was calibrated with

standard $HClO_4$ solutions which were one molar in $NaClO_4$. The region of

interest between pH values of 3 and 6 was examined many times with such

solutions of known hydrogen ion concentration. The term "pH' then will

refer to the negative log of the hydrogen ion concentration in all that

follows.

To insure a strictly comparable measurement of each metal-ligand

equilibrium, identical titrations were performed with each metal. The

ligand was the titrant in every case. A solution containing $HClO_4$ and

the metal perchlorate at a pH of approximately 3 served as the starting

point of a titration. Since none of the metals in this study hydrolyze

measureably at this pH, the stoichiometric amount of $HClO_4$ determined the

"zero point" of the pH meter. Each increment of ligand was recorded; as

well as a reading on the millivolt scale. These values were converted

to apparent pH units, and the concentration of hydrogen ions was found

by reference to the calibration curve for the pH meter. In order to isolate the metal-ligand equilibrium form the proton-ligand equilibrium, a separate titration was necessary involving the titration of $HClO_4$ with the ligand. Details of the calculation of the stability constants are in Appendix A. A computer program was used to reduce the rough data to concentration constants.

Each titration included from 10 to 50 points and was completed in approximately 1/2 hour. Runs were made several times on each system to become convinced of the consistency of each equilibrium. The formation curves for all eight of the systems are shown in Figures 1 through 8. In these cases $\bar{n}_m$, the average number of ligands per metal ion, is shown as a function of pB, the negative logarithm of the free ligand concentration. Data for these curves are given in Appendix B.

Table II contains the formation constants for each system. A discussion of the independent determination of the formation constants for Mn(II) by electron spin resonance is found in Appendix D.

B. CALORIMETRY

1. <u>Review of Solution Calorimetry</u>

There are two common methods for getting enthalpy data on complex-ion formation equilibrium. The most common method in the past has been the measurement of the variation of the stability constants with temperature. For two temperatures T_1 and T_2, with corresponding log k_1 and log k_2
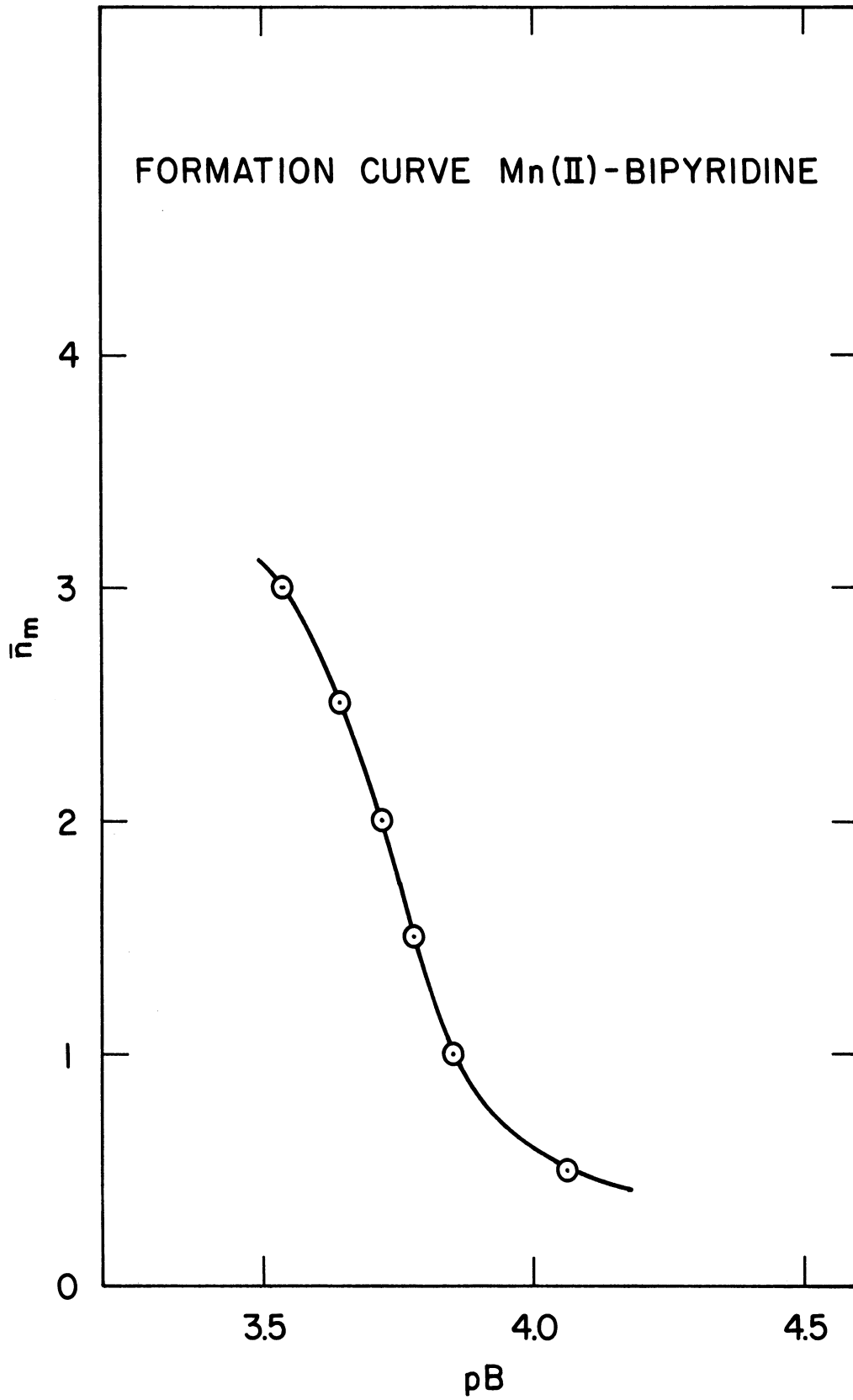
Fig. 1. Formation curve Mn(II)-bipyridine.
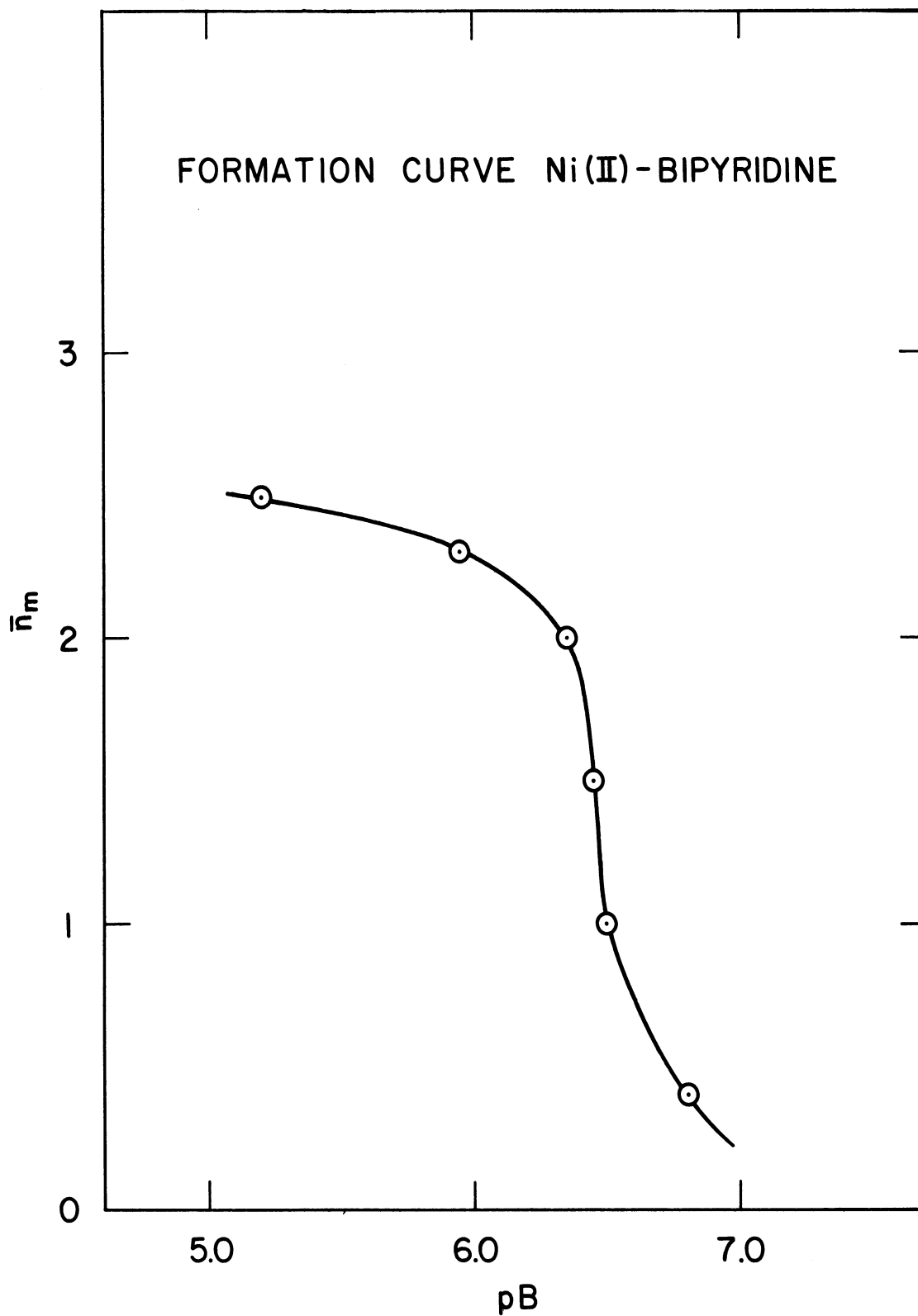
Fig. 2. Formation curve Ni(II)-bipyridine.
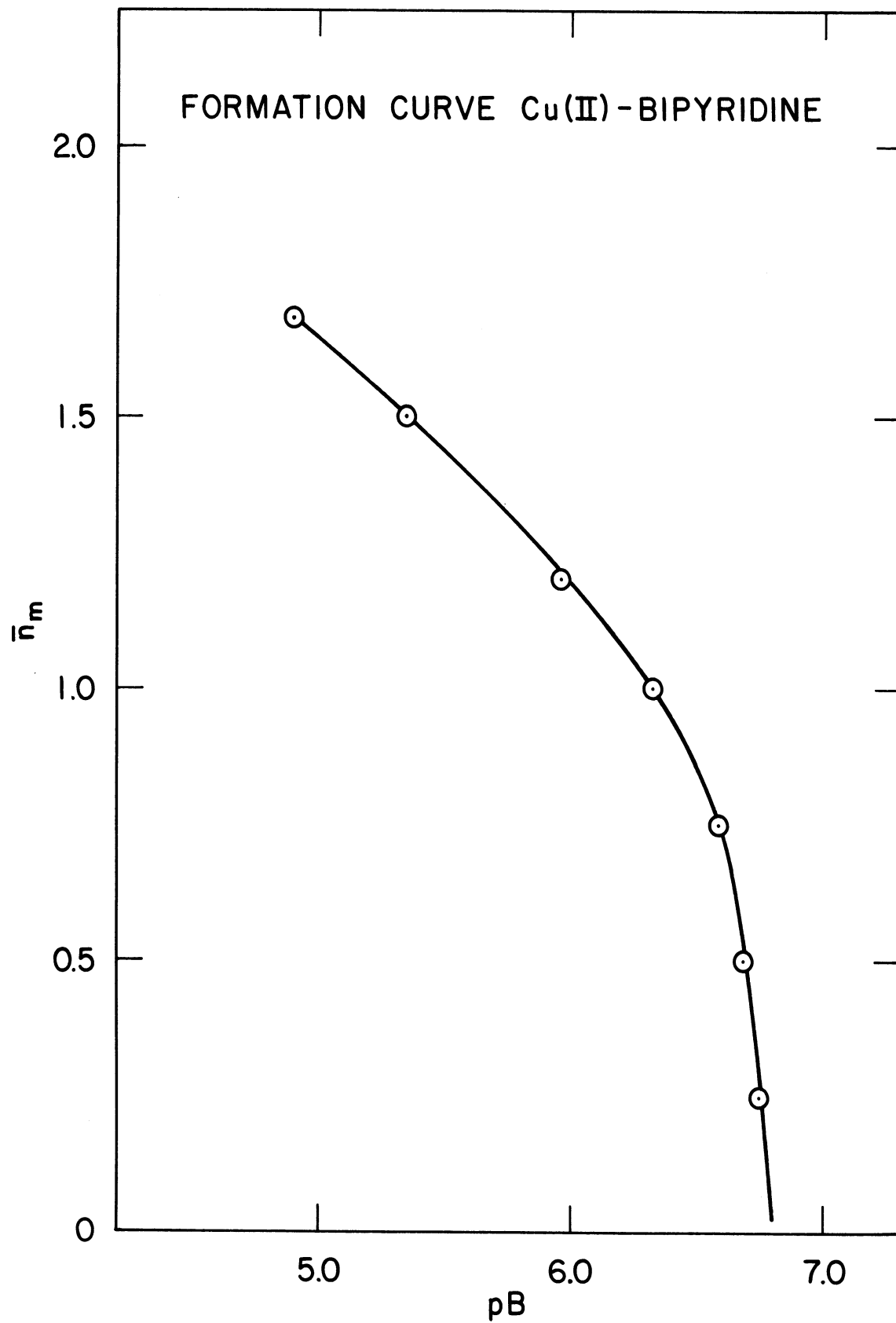
Fig. 3. Formation curve Cu(II)-bipyridine.
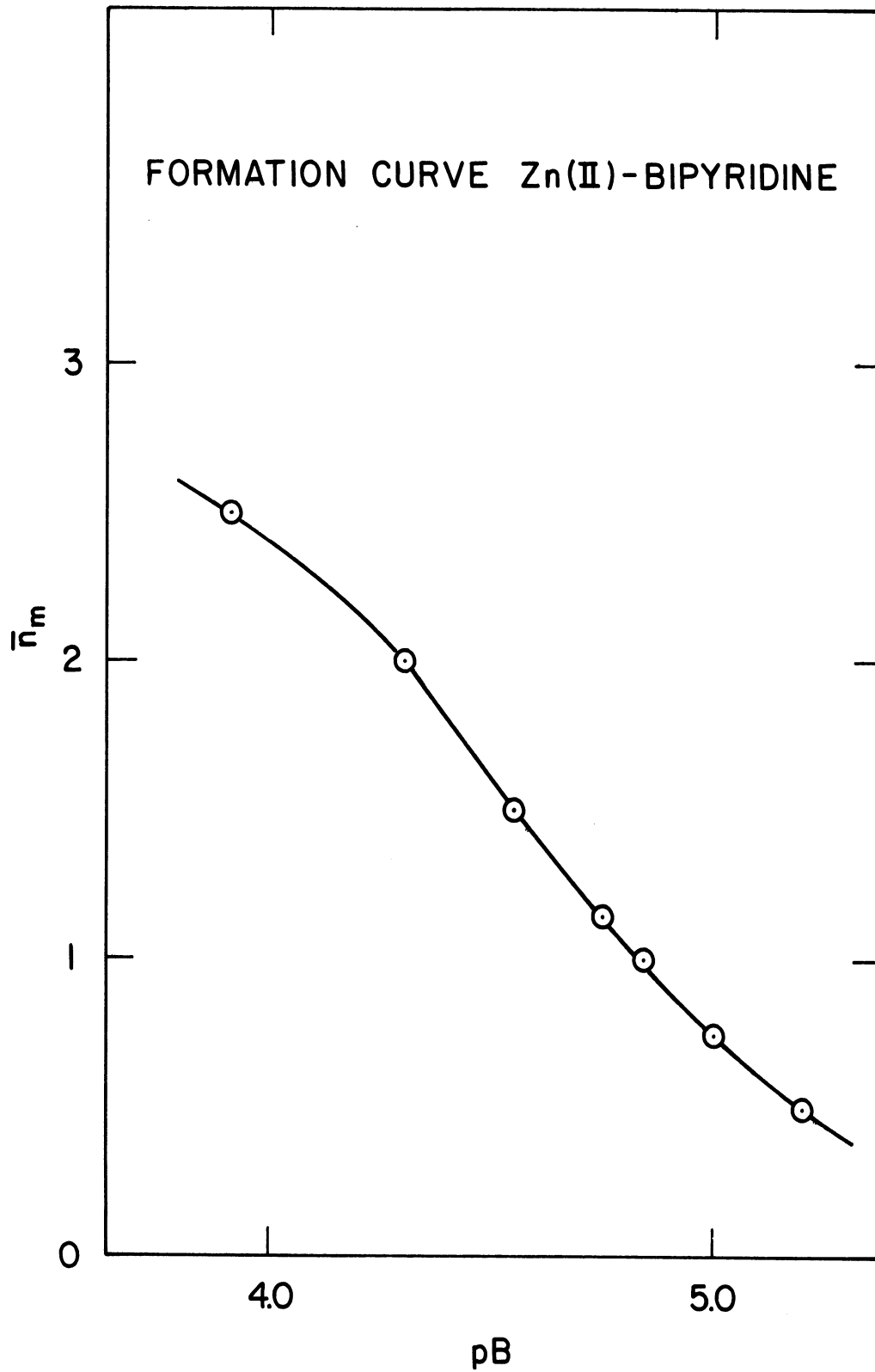
Fig. 4. Formation curve Zn(II)-bipyridine.
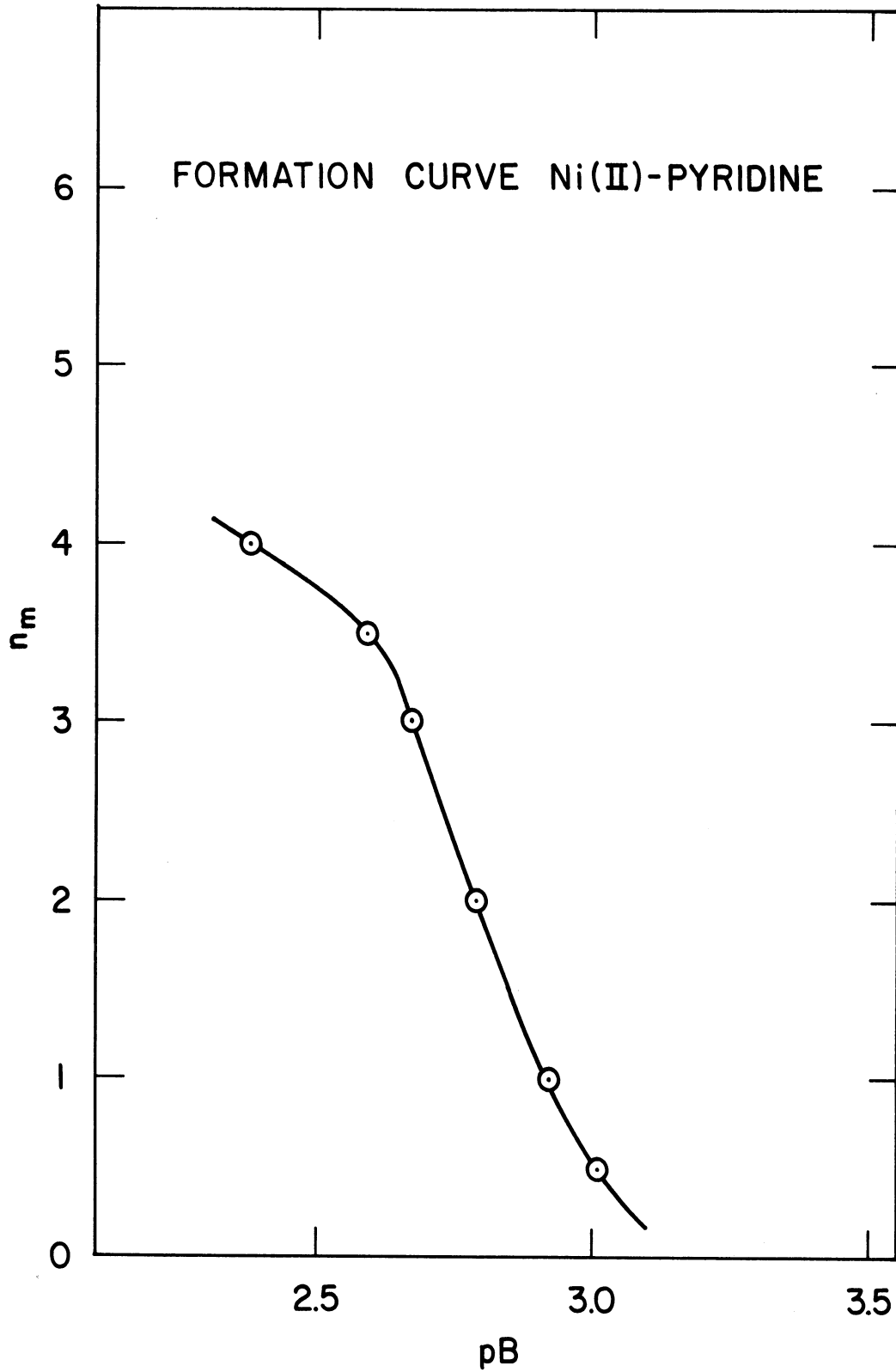
Fig. 5. Formation curve Mn(II)-pyridine.
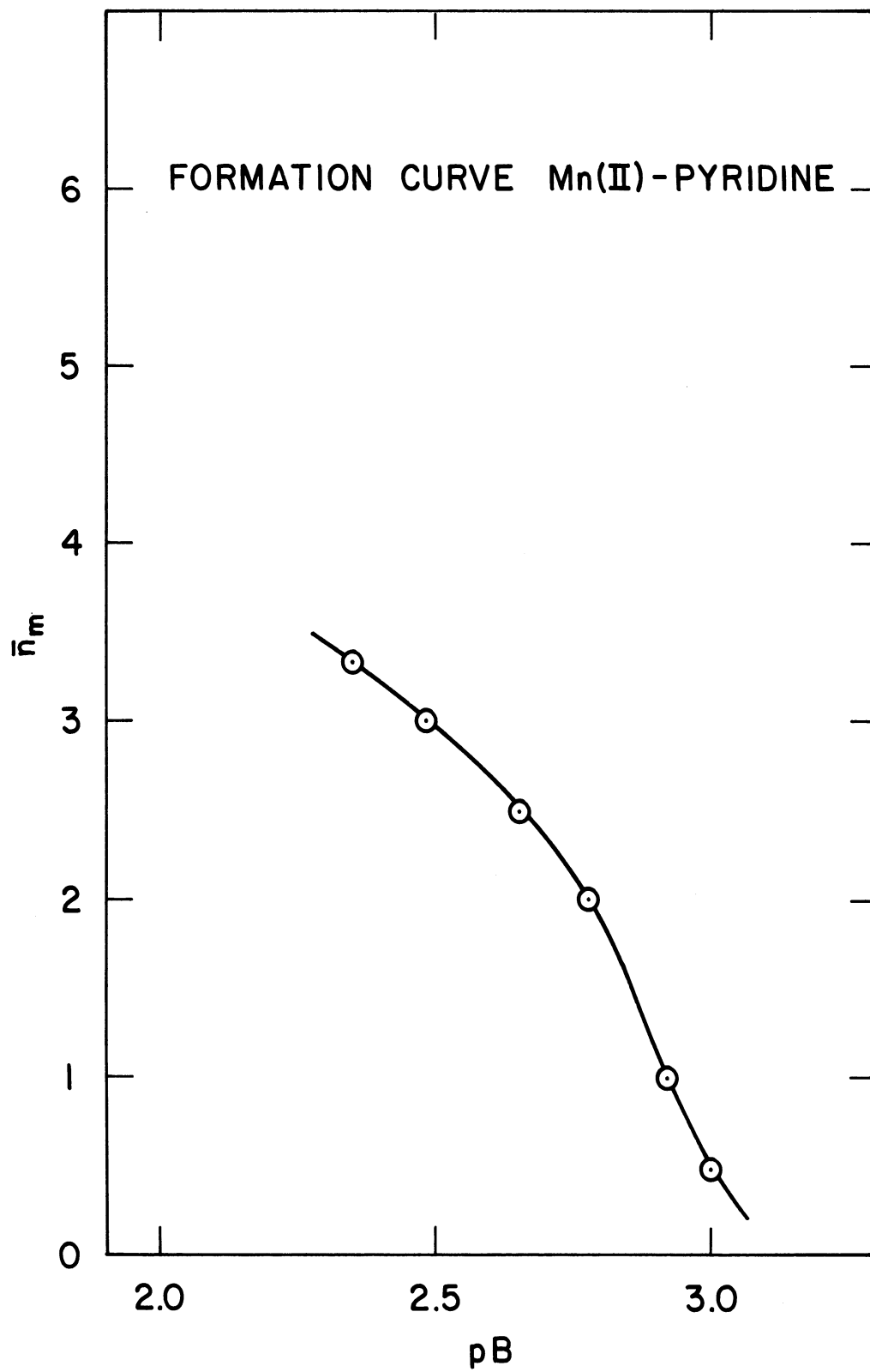
Fig. 6. Formation curve Ni(II)-pyridine.
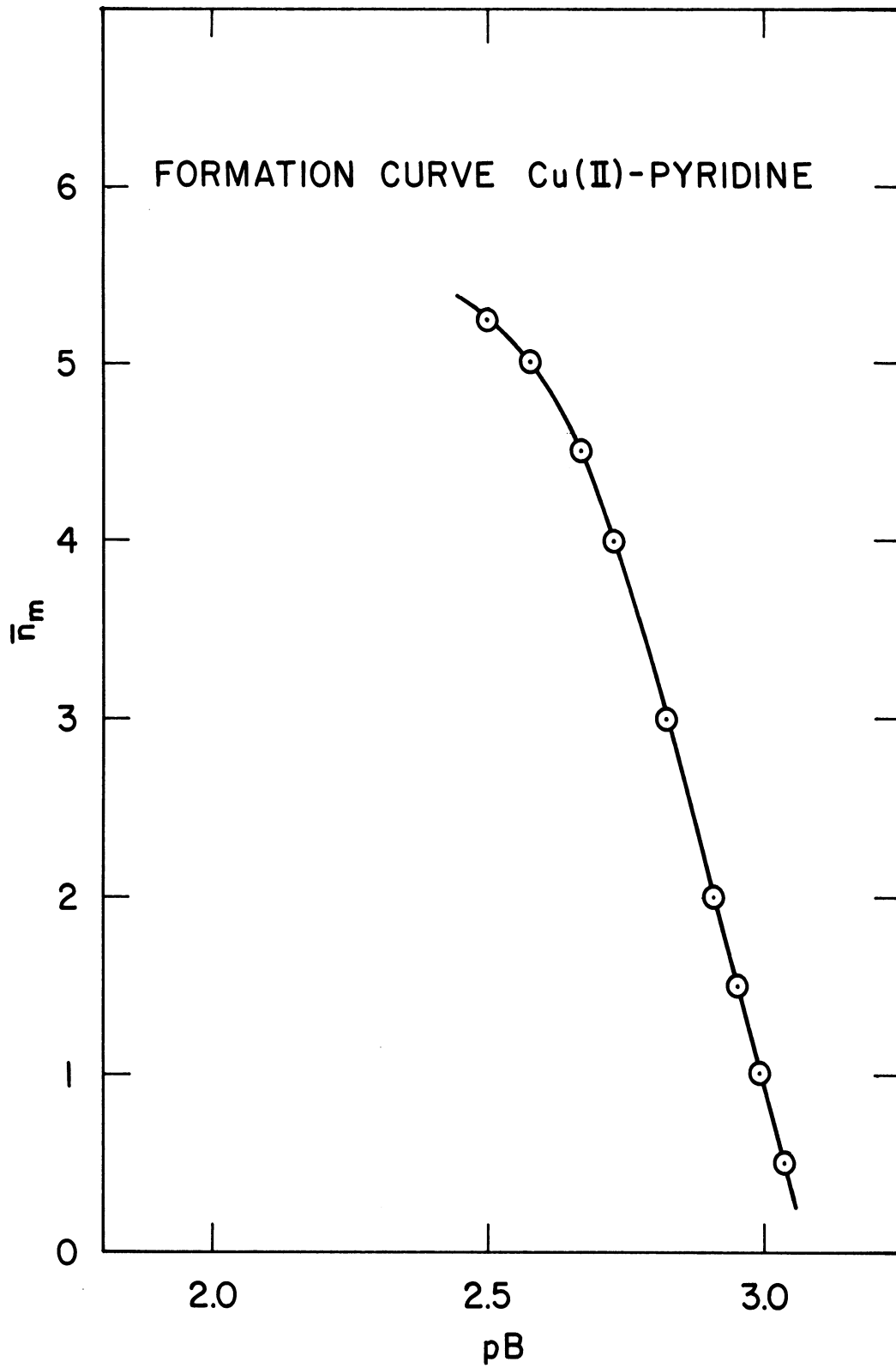
Fig. 7. Formation curve Cu(II)-pyridine.
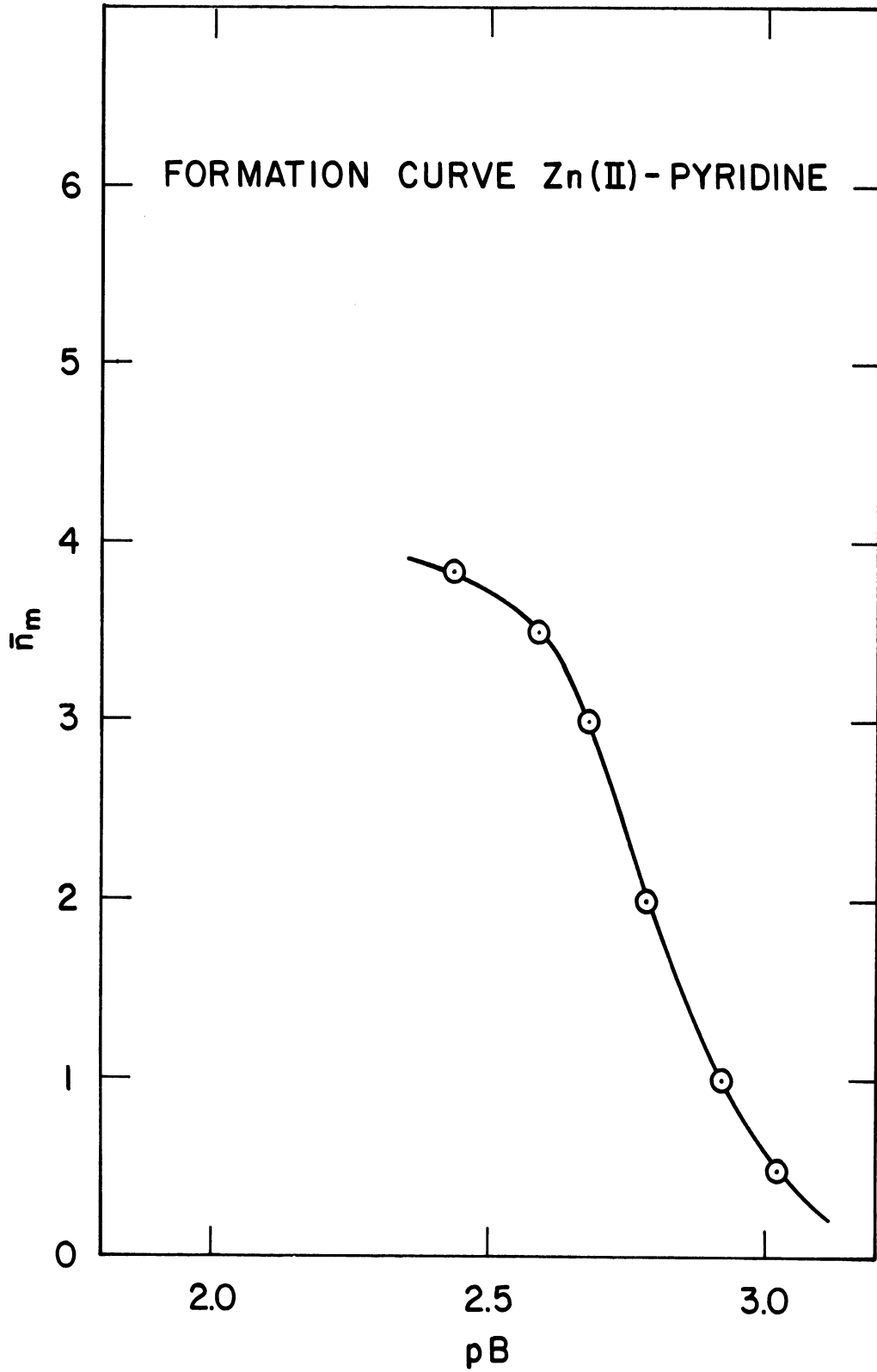
Fig. 8. Formation curve Zn(II)-pyridine.

TABLE II

Formation Constants for the Complexes

at 25°C in 1 Molar $NaClO_4$

Bipyridine

	$\log k_1$	$\log k_2$	$\log \beta_2$	$\log k_3$	$\log \beta_3$
Mn(II)	4.06	3.78	7.84	3.63	11.47
Ni(II)	6.80	6.46	13.26	5.20	18.46
Cu(II)	6.94	5.74	12.68	--	--
Zn(II)	4.89	4.58	9.47	4.27	13.74

Pyridine

	$\log k_1$	$\log k_2$	$\log \beta_2$	$\log k_3$	$\log k_4$	$\log \beta_4$
Mn(II)	1.86	1.59	3.45	.90	.60	4.95
Ni(II)	2.13	1.66	3.79	1.12	.65	5.56
Cu(II)	2.46	1.95	4.41	1.27	.84	6.52
Zn(II)	2.08	1.69	3.77	1.03	.64	5.44

Acid Dissociation Constants of Protonated Ligands

Bipyridine   pKa = 4.334

Pyridine   pKa = 5.151

$$\Delta H = \frac{2.303 \, RT_1T_2(\log k_2 - \log k_1)}{T_2 - T_1}$$

Such a procedure has been followed by Fernelius[55] for many amine complexes, by Spike and Parry[3] for ethylenediamine complexes, by Krumholz[49,50] for pyridine and bipyridine pk_a values, and by Cabani and Scrocco[51] for cadmium and silver bipyridine complexes. Basolo and Murmann[56] have used both the temperature variation method and direct calorimetry to measure the heats of formation of several amine complexes. They have found, as many others such as Rossotti and Sillen[35,57] have maintained, that calorimetry is the better method and justifies the added experimentation. Values for the heat of reaction of copper with ethylenediamine as tabulated by Rossotti[35] vary from -8.6 to -18.9 kcals/mole. This gives entropy variations of from +21 to -15 eu.

A simple calorimeter has been described by Bjerrum.[58] This has been used successfully with ethylenediamine complexes. It consists basically of a Dewar with a Beckmann thermometer and stirrer. Various amounts of amine solution can be pipetted into the device, which contains some 400 ml. of dilute metal solution. Knowing the heat capacities of the calorimeter, the metal solution, and the added amine, the temperature rise associated with the combination of amine with metal ion can be converted into calories. On correction for the heat of dilution of the amine, the molar heat of complexation can be readily obtained. Similar calorimeters have been used successfully by Fyfe,[61] Davies,[62] Charles,[63] Basolo and

Murmann,[56] and Laidler.[64] For rather high concentrations of reagents

(.02 molar metal salts) the heat produced is on the order of 1°C and can

be measured adequately with a Beckmann thermometer.

A more precise calorimeter was described by Pitzer[59] which could be

used satisfactorily in heat of dilution experiments. He used a copper

resistance thermometer and a well-built Wheatstone bridge to obtain a

temperature sensitivity of approximately 1×10^{-5} degrees. Sturtevant[65]

used a dual calorimeter successfully to measure very small heats of so-

lution. Schug and King[60] have used a similar resistance thermometer to

study the formation of $CrCl_x$ complexes. The classic work on calorimeters

capable of specific heat measurements was done by Richards and Gucker;[66]

Gucker, Ayres, and Rubin;[67] and Randall and Rossini.[68] Leussing and

Gallagher[47] have used calorimetry to study copper pyridine complexes.

A more spectacular calorimeter was described by Jordan and Alleman.[69]

Using a Dewar at room temperature and an automatic burette they were able

to record temperature changes with a thermistor bridge circuit on the

order of 2×10^{-4} degree. They determined the heat of EDTA complexation

with a variety of transition metals to approximately 3% accuracy.

A very comprehensive treatment of calorimetry from the standpoint

of precise enthalpy titrations has been presented by Schlyter.[70,71] The

calorimeter features a resistance thermometer, a thermostated buret, a

cooler and an electric heater. Before each addition from the buret, the

temperature of the calorimeter can be adjusted to be as close as possi-

ble to the buret solution. An electrical calibration can be made on the

calorimeter and contents between each addition of titrant in order to

determine the heat capacity as a function of total volume. Temperature

changes are associated with errors of $\pm 6 \times 10^{-5}$ degrees which corresponds

to ± 0.02 calories. This corresponds to 1 or 2% accuracy in the heats of

formation of complexes.

2. Design of Calorimeter and Experimental Procedure

The idea of employing a titrimetric procedure instead of the single

reaction technique deminated the design of this calorimeter. Since step-

wise equilibria were being studied and several successive measurements

of enthalpies were desirable, a system was used which would permit the

same titration which had been run in the stability constant determinations

to be run in the calorimeter vessel. The similarity of this problem to

that of heat of dilution experiments prompted consultation with Hepler.[72]

Out of this came the idea of using thermistors in a Maier bridge arrange-

ment[73] to measure the temperature rise associated with complexation. A

circuit diagram of the thermometer circuit is shown in Figure 9. A 6

volt storage battery supplies the bridge with a current of 2 ma, after

passing through a 2700 ohm slide wire resistor. The bridge consists of

four arms of 300 ohms each. Two arms are fixed with 300 ohm precision

wire wound resistors. The other two arms each consist of three 1000 ohm

bead thermistors (Veco number 31A18) connected in parallel. To balance

the bridge at a given temperature 10,000 ohm micropots are used in paral-

lel with the thermistors. The voltage across the bridge is measured on

THERMOMETER CIRCUIT
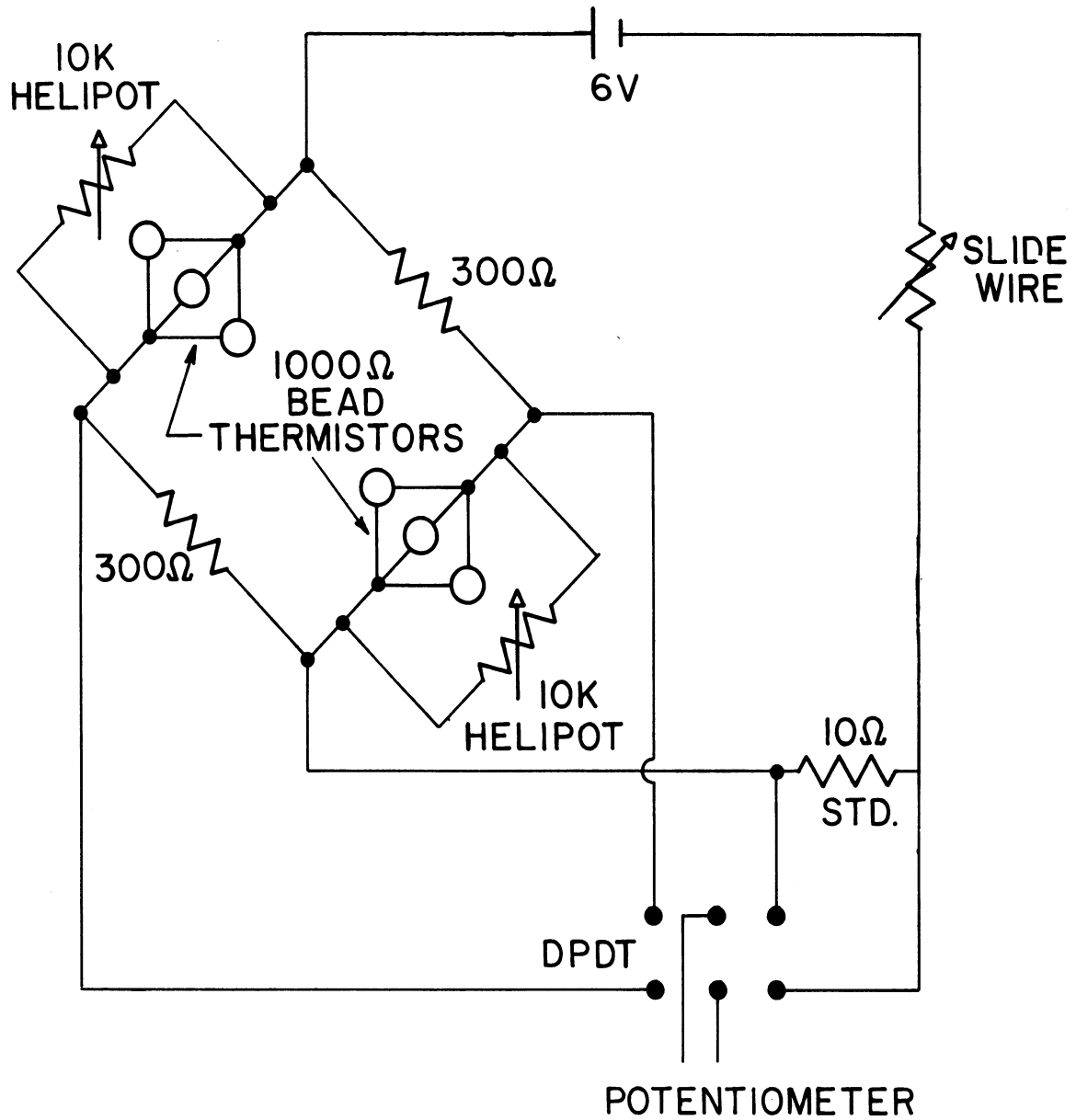
Fig. 9. Thermometer circuit for calorimeter.

a Queen-Gray potentiometer connected by a DPDT switch to both the bridge

and a 10 ohm standard resistor. This latter element is in the circuit

to provide a measure of the current thru the bridge.

The potentiometer is balanced by means of a coarse microgalvanometer.

Final measurements are made with a Rubicon precision galvanometer with

a sensitivity of 1.5 x 10^{-9} $\mu a/mm$. The illuminated scale of this instru-

ment is divided into 100 divisions, each corresponding to 1 x 10^{-4} degrees

in operation of the bridge.

The thermistors were calibrated against a Beckmann thermometer for

which the reading at 25.00°C had been checked by comparison with a cali-

brated mercury thermometer with 0.02 degree divisions. Over the range

of temperatures between 24 to 26°C the voltage output of the bridge was

a linear function of temperature. Thus an equation of the following form

can be written:

$$T = T_0 + \frac{E_T}{A} + \beta(R-50)$$

where:

T_0 represents a temperature at which the bridge is balanced with

the potentiometer set at zero.

E_T represents the reading in millivolts found by balancing the

bridge at a different temperature, T.

A is the sensitivity of the bridge in terms of millivolts per

degree. It has a value of about 10 m.v./deg. and is carefully

determined during each series of experiments by comparison with

a Beckmann thermometer.

β is the sensitivity of the fine scale of the galvanometer in terms of degrees per millimeter deflection. It has a value of 1×10^{-4} degree/m.m.

R   represents the reading of the galvanometer scale in terms of 0 - 100 mm where 50 is the midpoint or balance. R is measured in millimeters.

Thus the thermistor bridge can measure temperature differences down to $\pm 1 \times 10^{-4}$ degree. To prevent stray currents from interfering with the temperature measurement, the leads to the thermistor were shielded. To prevent changes in ambient temperatures as much as possible during an experiment, the bridge elements can be submerged in oil.

A schematic diagram of the calorimeter and buret device is shown in Figure 10. The calorimeter consists of two parts - the top, containing the elements of the calorimeter, and a 250 ml Dewar vessel to which a bakelite collar has been cemented with Epoxy resin. This collar contains a grove (F) for a 1/8" o-ring and holes for 4 brass thumb-screws which can be tightened to provide a water-tight seal. A represents a heater used in the joule calibration of the calorimeter. Double glass wound Karma wire, number 40, of 125.81 ohms resistance was coiled in a thin glass tube after copper leads were soldered. To provide good contact with the solution, molten napthalene was poured into the tube.

A thin-walled glass cooling tube, represented by B, is used in the calorimeter to quickly bring the contents to bath temperature after a

CALORIMETER
WITH BURET DEVICE

WATER
LEVEL
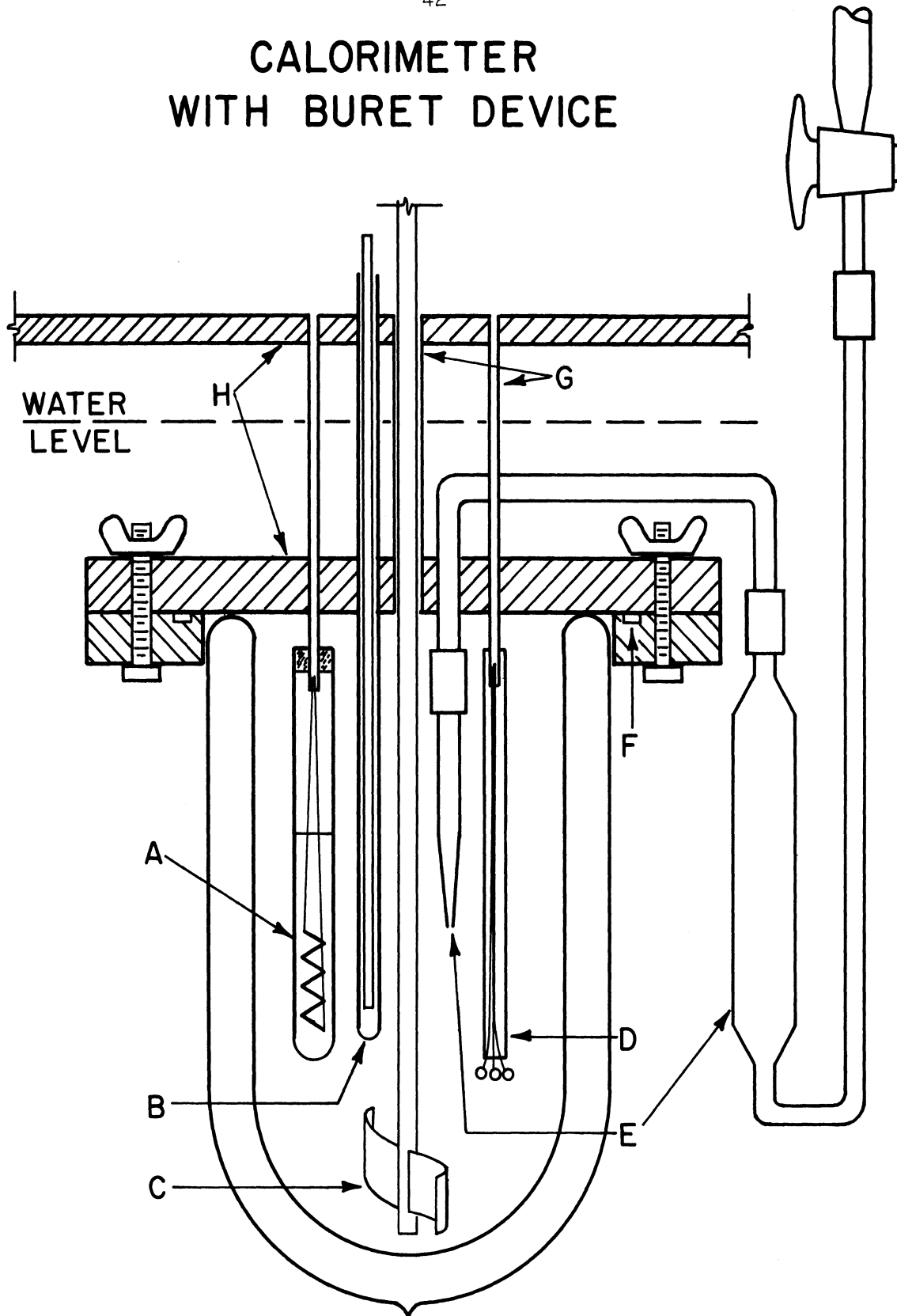
Fig. 10. Calorimeter with buret device.

A. heater   E. buret device
B. cooling coil   F. O-ring
C. glass stirrer   G. stainless steel tubing
D. thermistors (2 sets of 3) H. bakelite top

reaction. Cold air may be forced through the tube. It also serves a useful secondary purpose of bringing the calorimeter and contents very quickly to bath temperature at the start of an experiment.

The stirrer, respresented by C, is all glass. It enters the calorimeter through a thin steel tube G which is sealed into the bakelite top by Duco cement. A 180 rpm motor drives the stirrer. The motor is located about 5 inches above the surface Bakelite plate. Thus the direct transmission of heat from the motor to the calorimeter is minimized.

The two sets of glass bead thermistors, D, are mounted at the ends of glass tubes. The ends of the tubes are sealed with glyptal to prevent the solution from seeping into the lead conduits. The leads were soldered while suspending the heat sensitive thermistors in ice water. By using pliers to grasp the lead wires between the beads and the soldering operation one can prevent the thermistors from being seriously damaged by excessive heat during soldering.

The burette device is represented by E. A thermostated bulb of approximately 25 ml capacity was used in conjunction with a 10 ml burette at ambient temperatures. By confining additions of titrant to a few milliliters at a time, the temperature within the bulb remained at bath temperature.

To maintain the temperature of the bath, constant cooling water was added and a 125 ohm heater was turned on and off through a mercury relay regulated by a De Khotinsky thermal regulator. This gave approximately $\pm 1 \times 10^{-2}$ degree control when the ambient temperature remained constant

(± 0.5 degree). However a Philadelphiz microset control device provided

$\pm 1 \times 10^{-3}$ degree control at much wider variations in room temperature.

The heater circuit diagram is shown in Figure 11. A 12 volt storage

battery was adjusted by an 800 ohm slide wide resistor, R, to supply

about 20 milliamps to the heater. The current through the circuit was

measured by a 1 ohm standard resistor connected to the potentiometer. A

dummy heater D of the same resistance as the heater was used to equililib-

rate the battery. A 4 PDT switch activated an electric timer and the

heater simultaneously. The timer was a product of American Instrument

Company and could be read to the mearest 1/10 second.

A number of joule calibrations were made during enthalpy titrations

to determine the heat capacity in calories per degree of the calorimeter

and contents. The bridge was balanced and the galvanometer switched in

the circuit on its most sensitive scale. No external damping was used

in the course of the determinations. Readings in mm were taken at thirty

second intermals for about five minutes, or until a constant drift was

maintained. A typical drift rate was 2 mm/period. The heater was then

turned on. A lag of about 30 seconds always accompanied the heating.

After a period of about 60 to 150 seconds, depending on the volume of

liquid in the calorimeter, the heater was cut and the drift of the galva-

nometer followed until a constant rate was observed. By extrapolation

both pre-heat-drift and post-heat-drift to the midpoint of the heating

cycle, the difference in the readings gave a measure of the temperature

change. Using the arbitrary sensitivity of 1×10^{-4} degrees per mm, the

HEATER CIRCUIT
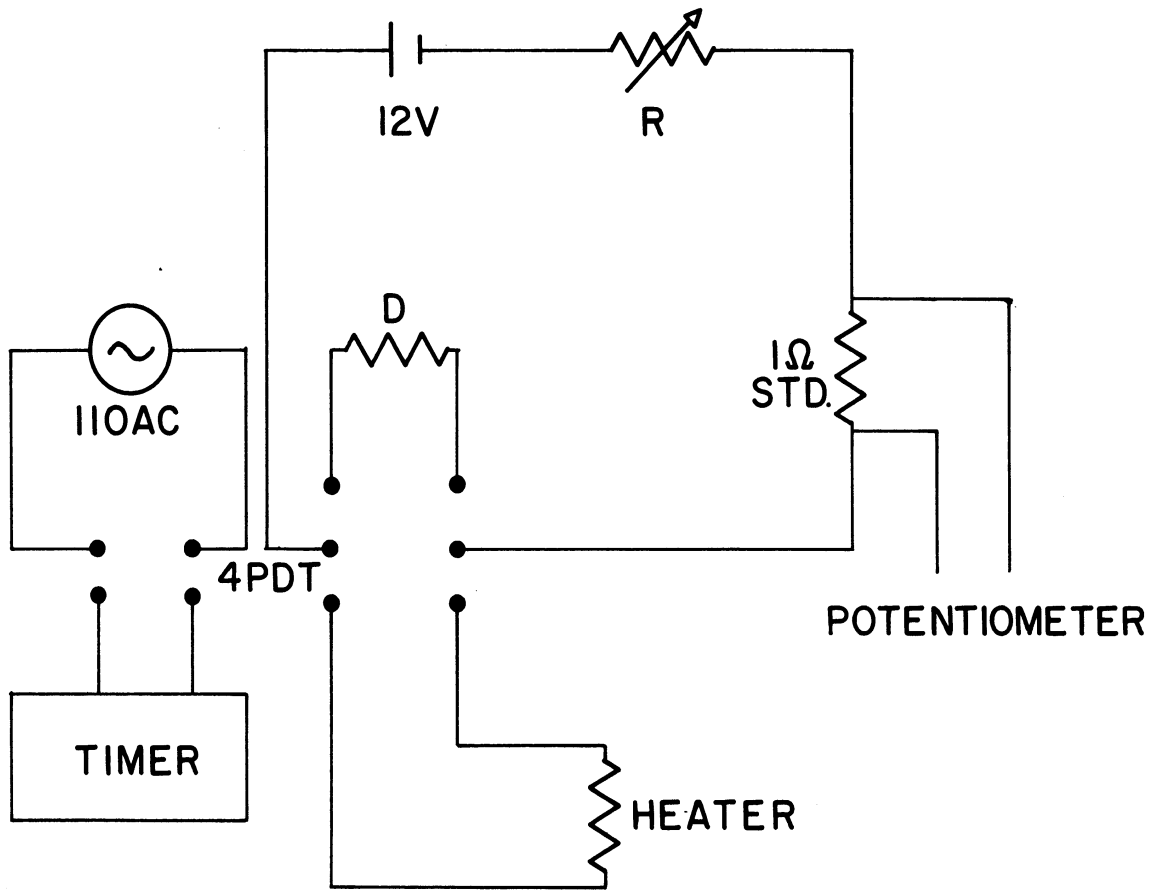
Fig. 11. Heater circuit for calorimeter.

heat capacity in calories per degree could be calculated by

$$C_p = \frac{(i^2)(R)t}{4.1840 \text{ joules/cal} \cdot \Delta mm \cdot 10^{-4}}$$

where i represents the heating current in amperes

     R represents the heater resistance, 125.81 ohms

     t represents the heating time in seconds

and Δmm represents the change in galvanometer reading.

For any heat of reaction, the same procedure was followed as with

the calibration. Before and after drift rates were obtained which were

extrapolated to the reaction time. The reading in millimeters was con-

verted to $\Delta T_{(reac)}$ by multiplying by 1×10^{-4}, and the calories computed

by

$$Q = C_{p(avg)} \Delta T_{(reac)}$$

The value of $C_{p\ (avg)}$ could be obtained by electrical calibrations

before and after an addition of titrant. Values of C_p averaged around

150 calories per degree for a typical experiment involving 100 ml of so-

lution. Since the temperature sensitivity of the thermistors was

$\pm 1 \times 10^{-4}$°C, this permitted heats to be measured to about ± 0.02 calorie.

Thus for quantities of heat involving 1 calorie or more, the calorimeter

could be expected to show about 2% accuracy.

To ascertain the reliability of the calorimeter, the heat of two

known reactions were measured. Approximately 0.01 molar HNO_3 was titrated

with 0.1 N NaOH. The heat capacity of the calorimeter was 165 ± 6 cal/degree.

The heat of neutralization was $1.42 \pm .05$ cal. This gave a heat of reaction of 12.6 ± 0.4 kcal/mole. Further experiments were done on the heat of dilution of HCl. Using Sturtevant's data[74] as a reference, 3.6 normal HCl was titrated into 125 ml of water in approximately one milliliter increments. Values of C_p were determined in a series of runs before and after the titration. A linear plot of C_p vs. ml added HCl permitted the heat capacity at any point to be read as

$$C_p = C_{pi} + (C_{pf} - C_{pi}) \left(\frac{V_o + 1/2 \ V_x}{V_f} \right)$$

where C_{pi} and C_{pf} represent the average heat capacity before and after the titration

V_f = total volume of titrant in ml.

V_o = volume of titrant before an addition in ml.

V_x = volume of individual addition.

This gave values in terms of calories per ml. which agreed within 2% with Sturtevant's data.

Heats of reaction of bipyridine or pyridine with the metal ions were found in much the same was as the above mentioned heat of dilution. Data on all of the systems can be found in Appendix C. The titrations were done in the same manner as the potentiometric determinations described above. Approximately 125 ml. of a solution which was one molar in $NaClO_4$ and 0.01 molar in $HClO_4$ and metal ion were titrated with a 0.06 molar solution of pyridine, also 1 molar in $NaClO_4$. Approximately five,

one milliliter additions of base were made, and the associated temperature rises calculated. With bipyridine, no $HClO_4$ was used since the low solubility of the bipyridine required the measurement of heats on the order of 0.3 calories. Also 5 milliliter additions of ligand were made. The individual values in calories per ml of ligand were easily converted to kcal per mole by dividing through by $\Delta\bar{n}_m \, C_m$, where $\Delta\bar{n}_m$ represents the change in the number of ligands per metal ion as determined by earlier potentiometric studies, and C_m represents the overall concentration of the metal ion in all of its forms. With pyridine, the presence of the proton-ligand equilibrium complicated the calculations and required that the observed heat be distributed between protonation and metal complexation. Since a constant ionic strength was maintained, no corrections were made for heats of dilution. Since the temperature of the titrant was not always exactly the temperature of the calorimeter and its contents, a correction had to be made to each observed heat to account for this difference. For this purpose, the heat capacity of one milliliter of a 1 molar $NaClO_4$ solution was taken as 0.918 cal per degree.[75] The temperature difference between the calorimeter and the titrant was recorded as the difference between the Beckmann Thermometer, placed in the bath, and the emf of the thermistor bridge, both values corrected to a standard of 25.00°C. Assuming a 0.01 degree uncertainty in temperature readings, this factor causes an error of 0.01 cal per ml of titrant.

The following information was recorded to calculate ΔH values for the titrations

(1) Concentrations and volumes of all reagents

(2) Temperature change on addition of the titrant

(3) Heat capacity

    (a) For pyridine these values were determined from individual electrical calibrations before and after each run. 1 calorie = 4.1840 joules

    (b) For bipyridine systems these values were determined from a plot of the heat capacity versus volume of one molar $NaClO_4$ solution in the calorimeter

(4) Temperature of both the bath and the calorimeter.

The principal difficulty associated with the determination of the bipyridine heats lies in the temperature difference between the titrant and the solution in the calorimeter. Since 10 ml of bipyridine (2 x 10^{-3} molar) is required to complex with .02 m moles of metal ion, the correction in calories for a temperature difference of 0.01°C can be calculated as follows:

$$(0.01 \text{ deg}) \left(.918 \frac{\text{cal}}{\text{ml-deg}} \right) (10 \text{ ml}) = .09 \text{ cal}$$

Since the overall heat of complexation would be on the order of 10 kcal/mole, a reaction heat of q = .25 cal would be expected. Therefore, even using the most accurate calibration of this effect, the bipyridine reaction enthalpies could not be determined to better than ±5%. The underlying problem with the bipyridine work is the low solubility of bipyridine in water. This demanded the use of a dilute titrating solution and

magnified the error. It is hoped that an improvement in the calorimeter design will mitigate this effect in future work.

Within the experimental error limits of this work it was not possible to distinguish between the enthalpies of successive complexation steps. Therefore, further discussion of the enthalpies will procede under the assumption that the ΔH's for the stepwise complexations of pyridine and bipyridine with these metals are equal. As is discussed in the results section this is not at all unreasonable in view of previous work on stepwise enthalpy determination.

Table III gives the measured enthalpies of complexation. Each value is the average of several runs on a given system. The figures are calculated on the basis of kilocalories/mole of complex formed. Thus, by dividing the bipyridine heats by 2 one can obtain the enthalpies per nitrogen-metal bond and, so, compare them with the pyridine values.

TABLE III

Enthalpies of Formation of Complex Ions

	Bipyridine	Pyridine
	(kcal/mole)	
H^+	-2.93	-5.04
Mn(II)	-4.30	-2.39
Ni(II)	-8.07	-2.65
Cu(II)	-8.33	-2.95
Zn(II)	-5.27	-2.58

V. DISCUSSION OF RESULTS

The values of stability constants for pyridine and bipyridine are presented in Table IV. The data reported by Irving[43] were obtained by a distribution method. The agreement with the bipyridine data in the present determination is good with the exception of log k_1 for Cu(II). This is a region in which the potentiometric method should yield better results than the distribution method, according to Leussing.[40] With the exception of Cu(II), pyridine data is not in agreement with the literature data. However existing data is quite scarce. Although the potentiometric Mn(II) bipyridine results of the present determinations do not agree too well with the existing data, it is notable that the electron spin resonance value does.

Source	Method	log k_3 for Mn(II)(bipy)$_3$
Miller and Brandt[46]	Spectrophotometry	6.3
Irving[44]	Distribution	5.8
This work (Appendix D)	E.S.R.	6.0

It is remarkable that three very different measurements have yielded similar results for the overall formation constant.

There has been very little research thus far on the ΔH values for this series of complexes. Leussing[47] has reported calorimeter data for Cu(II) pyridine complexes in 1 M KNO$_3$. He reports an average ΔH of -4.4 Kcal/mole for the Cu(II) pyridine system and -5.2 Kcal/mole for the heat

TABLE IV

Comparison of Literature Values of Formation Constants

Temperature 25°C

Bipyridine

Metal	pKa	log k_1	log k_2	log k_3	log β_3	Source
Mn(II)	--	--	--	--	6.3	Miller[46]
	--	2.62	2.0	1.1	5.8	Irving[43]
	4.33	4.06	3.78	3.63	11.47	This work
Cu(II)	--	--	--	--	17.85	Onstott[16]
	4.45	6.33	--	--	--	Gustafson[42]
	--	8.15	5.50	3.30	16.95	Irving[43]
	4.33	6.94	5.74	--	--	This work
Ni(II)	--	7.07	6.86	6.10	20.13	Irving[43]
	4.33	6.80	6.46	5.20	18.46	This work
Zn(II)	4.44	5.4	4.4	3.7	13.5	Yamasaki[45]
	--	5.04	4.35	3.57	12.96	Irving[43]
	4.33	4.89	4.58	4.27	13.74	This work

Pyridine

Metal	pKa	log k_1	log k_2	log k_3	log k_4	log β_4	Source
Mn(II)	--	2.11	--	--	--	--	McGarvey[33]
	5.15	1.86	1.59	.90	.60	4.95	This work
Cu(II)	5.21	2.41	1.88	1.14	.60	6.03	Bjerrum[37,38]
	5.45	2.52	1.86	1.31	.85	6.54	Bruehlmann[39]
	5.51	2.59	1.74	1.60	.61	6.54	Leussing[40]
	5.15	2.46	1.95	1.27	.84	6.52	This work
Ni(II)	5.21	1.78	1.05	.31	--	(3.14)	Bjerrum[37]
	5.15	2.13	1.66	1.12	.65	5.56	This work
Zn(II)	5.21	.95	.5	--	--	--	Bjerrum[37]
	--	1.41	.30	.50	.32	1.93	Nyman[41]
	5.15	2.08	1.69	1.03	.64	5.44	This work

of neutralization of pyridine. Mortimer and Laidler[48] report a value of
-5.70 ± 0.30 Kcal/mole for the same reaction at μ = 0.1. Krumholz[49,50]
determined the heat of neutralization of bipyridine at μ = .33 by varying
the temperature of the pKa determinations. Measuring this value at eight
different temperatures between 15° and 50°, he obtained a ΔH of -3.5 ± 0.5
Kcal/mole. Baxendale and George[102] obtained a ΔH of -2.0. These values
of heats of neutralization agree well with the present determinations.

For a closer look at the stability constants it is instructive to
examine the ratios of the successive formation constants for the bipy-
ridine. The stepwise-constants tend to decrease as complex-ion formation
proceeds. From statistical considerations, this is expected since the
number of sites on the central metal ion for ligand attachment becomes
progressively less. Also since relatively small waters of hydration are
being replaced with more bulky organic ligands, steric factors operate
to decrease the tendency for subsequent ligand addition. For many of
the systems studied heretofore, the values of log $k_n/k_{(n+1)}$ have been
positive and nearly equal.

Below are calculated the ratios of the first two sets of stability
constants for bipyridine complexes.

	$\dfrac{\log k_1}{\log k_2}$	$\dfrac{\log k_2}{\log k_3}$
Mn(II)	1.07	1.02
Ni(II)	1.07	1.24
Cu(II)	1.21	—
Zn(II)	1.07	1.07

The ratios of five out of the seven tested are clearly constant as would

be expected from the discussion above. However it is instructive to ex-

amine log k_1/log k_2 for Cu(II) and log k_2/log k_3 for Ni(II). In the for-

mer case, the high ratio indicates that the second stability constant

for Cu(II) is much lower than the other three metals would predict. This

is also evident from the more gradual slope of the formation curve. It

indicates that the second mole of bipyridine goes on with considerably

more difficulty than the first. Such a result is not surprising when

one remembers that the Jahn-Teller effect for Cu(II) complexes often is

the overiding factor influencing stability. This causes the Cu(II) ion

to depend on the tetragonality of the ligand field for its stability,

and makes it very sensitive to the rigid geometrical requirements of bi-

pyridine.

The Ni(II) ion appears to have an unusually low k_3 with bipyridine.

This again indicates a change in geometry in going from the four-coordi-

nate to the six-coordinate species.

Similar trends can be shown from a treatment of Irvings data.[43]

	$\dfrac{\log k_1}{\log k_2}$	$\dfrac{\log k_2}{\log k_3}$
Mn(II)	1.31	1.82
Ni(II)	1.03	1.13
Cu(II)	1.48	1.89
Zn(II)	1.16	1.22

Ignoring the high values for Mn(II) where the data are subject to some

variation, the Cu(II) complexes stand out with high ratios of successive

constants.

Table V presents the thermodynamic data for bipyridine in terms of ΔF, ΔH, and ΔS. The individual complexes are designated by subscripts 1 through 3.

It is evident that the ΔS_1 terms are approximately constant for all of the metals. However ΔS_2 for Cu(II) is out of line. This is similar to the effect noted above regarding the ratio of log k_1/k_2. In the ΔS_3 column, Ni(II) appears out of line. Mn(II) and Zn(II) maintain a very close relationship throughout chelation. This is in agreement with the concept of entropy changes being non-selective in such a process. There is an evident trend to lower values of ΔS at higher values of μ. Ignoring the two negative values, an average ΔS for each step can be calculated and appears to decrease progressively.

$$\Delta \bar{S}_1 = 4.2 \text{ eu}$$

$$\Delta \bar{S}_2 = 2.8 \text{ eu}$$

$$\Delta \bar{S}_3 = 2.0 \text{ eu}$$

An estimate of the errors associated with the experimental measurement of ΔFi and ΔH is included in Table V. As common practice dictates, extra figures of little significance have been carried in reporting the data to minimize rounding-off errors in the discussion which follows.

Thermodynamic data for pyridine complexes is reported in Table VI. The variation in free energies and enthalpies across the transition metal series is less than with the bipyridine complexes. The entropies of com-

TABLE V

Thermodynamic Data for Bipyridine Complexes

in Kcal/Mole

	$-\Delta F_1$	$-\Delta F_2$	$-\Delta F_3$	$-\Delta H$ per step
Mn(II)	5.53	5.16	4.95	4.30
Ni(II)	9.27	8.81	7.09	8.07
Cu(II)	9.47	7.83	--	8.33
Zn(II)	6.67	6.25	5.82	5.27

	ΔS_1 eu	ΔS_2 eu	ΔS_3 eu
Mn(II)	4.1	2.9	2.2
Ni(II)	4.0	2.5	-3.3
Cu(II)	3.8	-1.7	--
Zn(II)	4.7	3.3	1.8

where

$$\Delta F_i \;=\; -RT \ln k_i \;=\; -1.364 \log k_i$$

$$\Delta S_i \;=\; \frac{\Delta H_i - \Delta F_i}{T}$$

All determinations at 25°C in 1M $NaClO_4$ medium.

Estimated Errors:

$$\Delta F_i \;\pm\; 2\%$$

$$\Delta H \;\pm\; 5\%$$

$$\Delta S_i \;\pm\; 6\%$$

TABLE VI

Thermodynamic Data for Pyridine Complexes

in Kcal/Mole

	$-\Delta F_1$	$-\Delta F_2$	$-\Delta F_3$	$-\Delta F_4$	$-\Delta H$ per step
Mn(II)	2.54	2.17	1.22	.82	2.39
Ni(II)	2.90	2.26	1.53	.89	2.65
Cu(II)	3.35	2.66	1.73	1.15	2.95
Zn(II)	2.84	2.31	1.40	.87	2.58

	ΔS_1 eu	ΔS_2 eu	ΔS_3 eu	ΔS_4 eu
Mn(II)	.5	-1.5	-3.9	-5.3
Ni(II)	.8	-1.3	-3.8	-5.9
Cu(II)	1.3	-1.0	-4.1	-6.0
Zn(II)	.9	-.9	-4.0	-5.7

where

$$\Delta F_i = -1.364 \log k_i$$

$$\Delta S_i = \frac{\Delta H_i - \Delta F_i}{T}$$

All determinations at 25°C in 1M NaClO$_4$ medium.

Estimated Errors:

$$\Delta F_i \pm 3\%$$

$$\Delta H \pm 2\%$$

$$\Delta S_i \pm 4\%$$

plexation are more negative. This indicates that the pyridine complex

is more ordered with respect to the hydrated metal ion than is the bi-

pyridine complex. Due to the higher pH necessary for forming pyridine

complexes the precision of the measured stability constants with pyridine

is slightly less than with bipyridine. However higher concentrations of

pyridine may be used in calorimetry experiments. This gives more pre-

cision to ΔH than the corresponding bipyridine complexes.

Figure 12 shows a comparison between log k_1 for bipyridine and ethyl-

enediamine as well as for pyridine and ammonia. An examination of the

base strengths of the two sets of ligands reveals that the primary ali-

phatic amines are the stronger bases by a factor of 10^5.

	pKa
bipyridine	4.33
ethylenediamine	7.49, 10.17
pyridine	5.15
ammonia	9.3

Despite this vast difference in base strength, the magnitude of the sta-

bility constants is of the same order for Mn(II), Ni(II), and Zn(II).

There does appear to be a marked difference in the Cu(II) stabilities.

This is due either to a specific Cu(II)-primary amine interaction which

enhances the stability with respect to the rest of the transition metal

series, or to serious hydrolysis problems involving Cu(II) in the basic

pH area in which complexation occurs. The difference between log k_1

values for the monodentate ligands is approximately 1.5; for the biden-
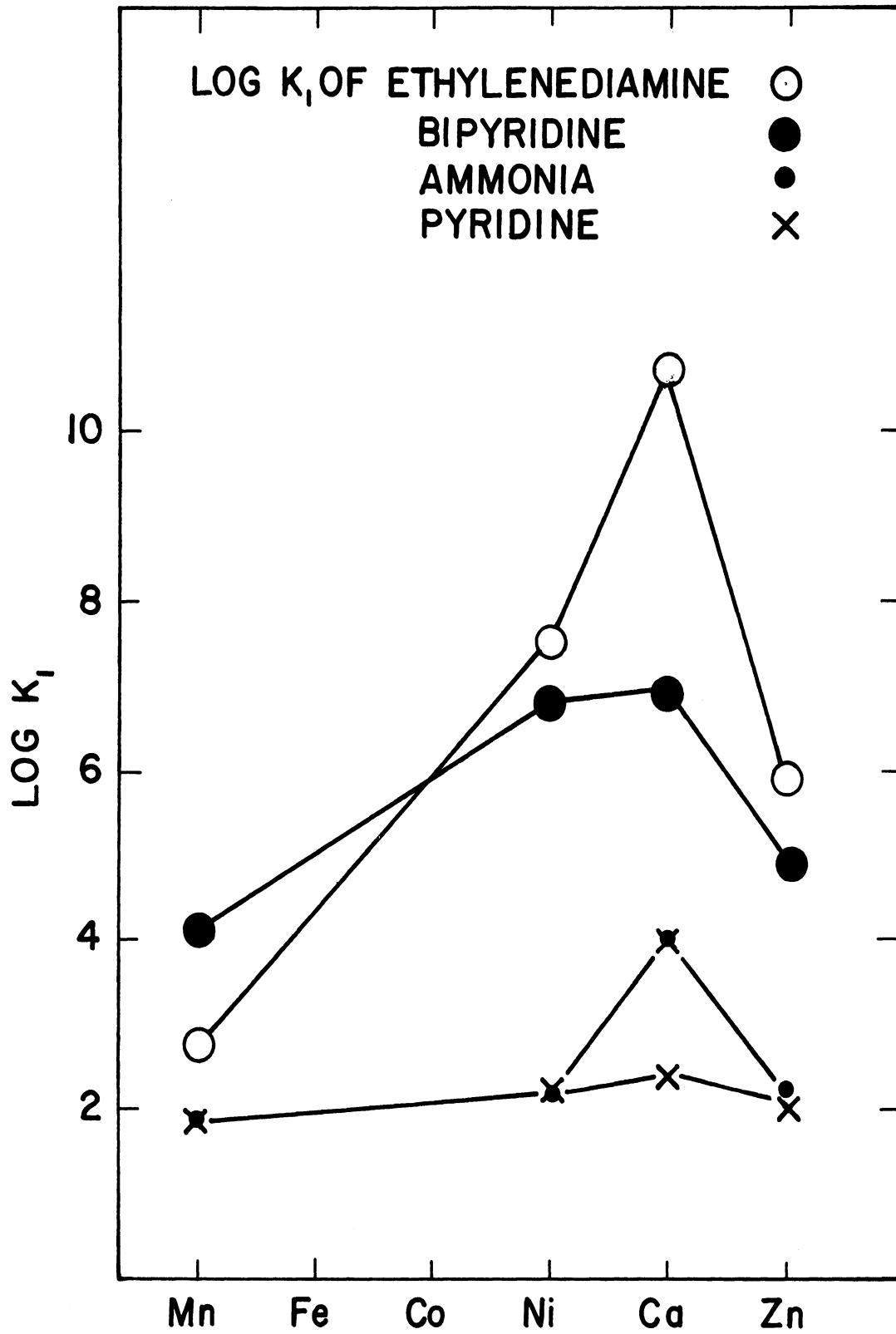
Fig. 12. Log k_1 for bipyridine, ethylene-diamine, pyridine, and ammonia.

tate ligands 3.8. Since Cu(II) bipyridine may be depressed because of steric factors, the latter interval is about twice that of the pyridine-ammonia difference as expected.

An examination of the literature for successive enthalpies leads to the following table reproduced from ref. 35, page 35.

TABLE VII

Step-Wise Enthalpies at 25°C in Kcal/mole

	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5	ΔH_6	Reference
Ni-NH$_3$	-4.0	-4.0	-4.0	-4.0	-4.3	-4.3	(76)
Ni-en	-9.01	-9.18	-9.71				(58)
Ni-tn	-7.8	-7.2	-6.2				(58)
Cu-NH$_3$	-5.6	-5.5	-5.6	-5.3	-5.1		(76)
Cu-en	-13.0	-12.4					(58)
Cd-NH$_3$	-3.5	-3.5	-3.5	-3.5	-3.5	-3.4	(77)
Cd-en	-7	-6.3	-6.4				(3)

It is not possible to detect a trend from this set of data. One can only state that the successive enthalpies appear to be constant. This is not too surprising when one considers that the addition of a ligand to a completely hydrated metal must be very similar to the addition of a ligand to a partially complexed species. The charge of the ion has not changed so the main contributing effect (which is constant) will be the difference between the heat of vaporization of the ligand and of the displaced water. Using very precise calorimetry one could

expect to detect a difference as complexation increased. This could show

up especially with Cu(II)-bipyridine.

Figure 13 gives a plot of ΔH for pyridine and bipyridine as a func-

tion of atomic number. Taking a base-line as the line drawn between

Mn(II) and Zn(II), one can calculate the crystal field stabilization

energy (CFSE) for the complexes. Mn(II) and Zn(II) have half-filled d-

electron shells respectively so they cannot be stabilized by a crystal

field. However they do indicate the trend in covalent and electrostatic

contributions to the enthalpies. Cu(II) and Ni(II) bipyridine show a

CFSE of 3.28 and 3.20 Kcal/mole respectively. Note that this is for a

single complex; thus, the tris-bipyridine complex of Ni(II) would show

a CFSE of 3 x 3.2 or 9.6 Kcal/mole. It is instructive to compare this

with the CFSE obtained by spectroscopy.[78] Considering Ni(II) to have ap-

proximately cubic symmetry, the five 3-d orbitals are split into two

groups under the application of a crystal field, the lower T_{2g} level

which is three-fold degenerate and the upper E_g level which is two-fold

degenerate. The energy difference $(E_1 - E_2)$ between the levels can be

observed in absorption spectra. The stabilization of this state is given

by

$$E_{(oct)} = (.4n_{T_{2g}} - .6n_{E_g})(E_1 - E_2)$$

where n refers to the number of electrons in each of the two levels.

For the d^8 case, one has 6 electrons in the T_{2g} state and 2 in the E_g

state. This gives a value of stabilization energy:

$$E_{(oct)} = (2.4 - 1.2)(E_1 - E_2) = 1.2 \, \Delta E$$

The value of the first absorption band gives a measure of ΔE. For $Ni(H_2O)_6^{+2}$ this is 8500 cm^{-1}, for $Ni(bipy)_3^{+2}$, one finds 12,200 cm^{-1}. The difference of 3700 cm^{-1} multiplied by 1.2 and converted to Kcal/mole is 10.6. Thus we have the following stabilization bipyridine complex with respect to water:

$$Ni(6H_2O)^{+2} + 3Bipy \rightleftharpoons Ni(Bipy)_3^{+2} + 6H_2O$$
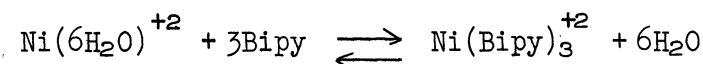
ΔH (Kcal/Mole)

9.6 by calorimetry

10.6 by spectra

The agreement is very good considering the assumption of cubic symmetry and the experimental variations of both determinations.

The chelate effect can be shown for the following reactions:

$$\text{I} \quad M(py)_2 + bipy \rightleftharpoons Mbipy + 2 \, py$$

$$\text{II} \quad M(py)_4 + 2 \, bipy \rightleftharpoons M(bipy)_2 + 4 \, py$$
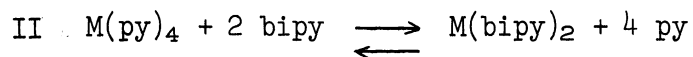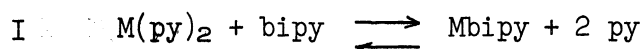
Table VIII presents values of ΔF, ΔH, and ΔS for each of these reactions.

The chelate effect is most noticeable with Ni(II) and Cu(II) due to the contribution of a large enthalpy term. The consistency of the entropy portion of the chelate effect is remarkable if one excludes Cu(II). With this ion the low entropy change of the bis-chelate is closely related to the low values of entropies observed earlier with Cu(II) bipyridine com-

TABLE VIII

The Chelate Effect

I $M(py)_2 + bipy \rightleftharpoons M\ bipy + 2\ py$

II $M(py)_4 + 2\ bipy \rightleftharpoons M(bipy)_2 + 4\ py$
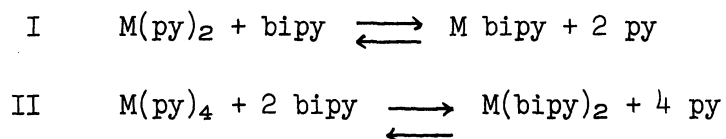
	ΔF_I Kcal/Mole	δ	ΔF_{II} Kcal/Mole
Mn(II)	-.82	-3.12	-3.94
Ni(II)	-4.11	-6.39	-10.50
Cu(II)	-3.46	-4.95	-8.41
Zn(II)	-1.52	-3.98	-5.50

	ΔH_I Kcal/Mole	δ	ΔH_{II} Kcal/Mole
Mn(II)	+.48	+.48	+0.96
Ni(II)	-2.77	-2.77	-5.54
Cu(II)	-2.43	-2.43	-4.86
Zn(II)	-0.11	-0.11	-0.22

	ΔS_I eu	δ	ΔS_{II} eu
Mn(II)	+5.1	12.1	17.2
Ni(II)	+4.5	12.1	16.6
Cu(II)	+3.4	8.5	11.9
Zn(II)	+4.7	13.0	17.7

where

δ refers to the difference between reaction II and

reaction I for each thermodynamic property.

plexes. The chelate effect in both Mn(II) and Zn(II) is made up solely of an entropy effect. Those metal ions having unfilled d shells and therefore capable of crystal-field stabilization show a significant enthalpy effect.

A comparison of the chelate stabilization observed with ethylene-diamine and ammonia is in order. Table IX presents a comparison of this data as well as the EDTA and iminodiacetate data of Scwarzenbach.[2]

TABLE IX

Free Energies of Chelation in Various Systems

ΔF_1 in Kcal/Mole

	bipy-py	en-NH$_3$	EDTA-iminodiacetate
Ni(II)	-4.1	-3.7	-7.2
Cu(II)	-3.5	-4.3	-3.2
Zn(II)	-1.5	-1.6	-5.2

$$\text{I} \quad MA_2 + B \; \underset{\longleftarrow}{\longrightarrow} \; MB + 2A$$
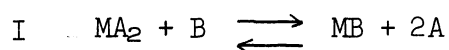
where B represents a chelating ligand which is approximately the dimer
        of A

It is seen that chelate stabilization of ethylenediamine and ammonia is quite similar to the bipyridine-pyridine system. However the positions of Cu(II) and Ni(II) are reversed in the two series. EDTA shows even more instability with Cu(II) than bipyridine.

At this point it is appropriate to attempt to break-down the "chelate" effect further. Following Gurney's theoretical work[79] Adamson recalculated

much of the early "chelate effect" data.[5] Gurney demonstrated that both

ΔF and ΔS should be written as the sum of what he calls the "unitary"

part and the "cratic" part.

$$\Delta F = \Delta F_{(unitary)} + \Delta F_{(cratic)}$$

$$\Delta S = \Delta S_{(unitary)} + \Delta S_{(cratic)}$$

In this he demonstrates that one can distinguish between the change due

to a change in the number of particles during a reaction and the change

due to the individual particle characteristics. That is, for any reac-

tion of the type

$$A + B \rightleftharpoons C$$
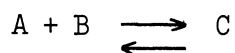
the "cratic" ΔF and ΔS will be the same. However, the "unitary" effect

will depend on the individual A, B and C entities. The correction can

be made most simply (though approximately) by putting ΔF and ΔS on a mole

fraction concentration basis. At 25°C in water this is done by:

$$\Delta F' = \Delta F_{(unitary)} = \Delta F - \Delta n \, RT \, \ln 55.5$$

$$\Delta S' = \Delta S_{(unitary)} = \Delta S + \Delta n \, RT \, \ln 55.5$$

Here, Δn is the change in number of particles going from left to right

across the reaction e.g., $\Delta n = -1$ for the reaction given above. It is

easily demonstrable that the release or tie up of a solvent molecule does

not contribute to the cratic term and that ΔH is always unitary.

Adamson in his work, almost implied that the "chelate stabilization" disappeared when the correction was applied. This is far from the case. The correction only allows us to attempt a more fundamental analysis of the effect in terms of the particular metal-ligand system at hand.

Table X shows the unitary chelate effect for two steps of chelate formation. The elimination of the cratic term gives negative entropy terms for reaction I.

$$\text{I} \qquad \text{Mpy}_2 + \text{bipy} \rightleftharpoons \text{Mbipy} + 2 \text{ py}$$
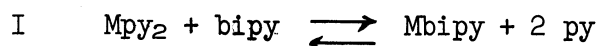
This is to be expected since considerably more ordering is necessary to form a chelate ring than the corresponding bis-coordination complex. The appearance of positive free energies for Mn(II) and Zn(II) complexes indicates the chelated form is no longer the more stable. However the specific stabilization due to the enthalpy term remains to give a net stabilization to Cu(II) and Ni(II). $\Delta S'_{II}$ for the Cu(II) chelation clearly shows the increased ordering necessary to add a second mole of bipyridine.

It is worthwhile to speculate somewhat further on the entropy relationship in the organic bases involved.

If we write the reaction

$$\text{B} + \text{H}^+ \rightleftharpoons \text{BH}^+$$
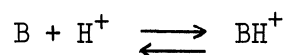
then for pyridine, bypyridine and the closely related 1, 10-phenanthroline the thermodynamic values are given in Table XI.

TABLE X

Unitary Chelate Effect

$$\Delta F_i' = \Delta F_i - 2.36 \, \Delta n$$

$$\Delta S_i' = \Delta S_i + 7.92 \, \Delta n$$

where

$$\Delta n = -1 \quad \text{for} \quad i = I$$

$$\Delta n = -2 \quad \text{for} \quad i = II$$

	$\Delta F_I'$ Kcal/Mole	δ	$\Delta F_{II}'$ Kcal/Mole
Mn(II)	+1.54	-.76	+.78
Ni(II)	-1.75	-4.03	-5.78
Cu(II)	-1.10	-2.59	-3.69
Zn(II)	+0.84	-1.62	-0.78

	$\Delta H_I'$ Kcal/Mole	δ	$\Delta H_{II}'$ Kcal/Mole
Mn(II)	+0.48	+0.48	+0.96
Ni(II)	-2.77	-2.77	-5.54
Cu(II)	-2.43	-2.43	-4.86
Zn(II)	-0.11	-0.11	-0.11

	$\Delta S_I'$ eu	δ	$\Delta S_{II}'$ eu
Mn(II)	-2.8	+4.2	+1.4
Ni(II)	-3.4	+4.2	+0.8
Cu(II)	-4.5	+0.5	-3.9
Zn(II)	-3.2	+5.1	+1.9

where

$$\delta = \text{column II} - \text{column I}$$

TABLE XI

Thermodynamics of Protonation of Ligands

Base	ΔF (Kcal/mole)	ΔH (Kcal/mole)	ΔS (eu)
Pyridine	-5.91	-2.93	+10.0
2,2'- bipyridine	-7.02	-5.04	+6.6
1,10-Phenanthroline	-6.77	-7.82	-3.5

On comparing pyridine with bipyridine we see that protonation is less exothermic with bipyridine and the entropy change is more positive. One can account for the enthalpy difference by the energy needed to rotate the bipyridine from the unprotonated trans form to the protonated cis form. Other possibilities are a difference in the bonding of the proton to the base or differences in the hydration-dehydration steps of the process.

It is interesting to examine the entropy of protonation of bipyridine and 1,10-phenanthroline in the context of this last idea. We may write the protonation reactions for the two bases as follows.

A. $phen \cdot (H_2O)_x + H^+(H_2O)_n \rightleftharpoons H^+phen (H_2O)_m + (x + n - m) H_2O$

B. $bipy \cdot (H_2O)_y + H^+(H_2O)_n \rightleftharpoons H^+bipy (H_2O)_\ell + (y + n - \ell) H_2O$
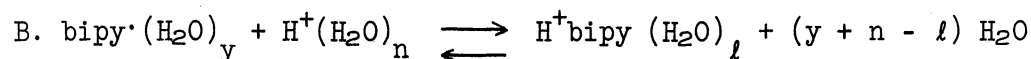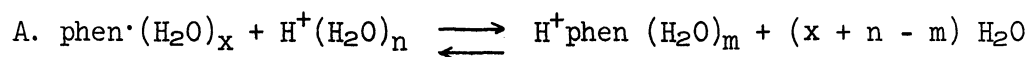
If we ignore the differences between the normal standard state and our 1 molar $NaClO_4$ medium we may write

$$\Delta S_A = \bar{S}^\circ_{HP} + (x + n - m)\, \bar{S}^\circ_{H_2O} - \bar{S}^\circ_P - \bar{S}^\circ_{H^+}\ ,$$

and

$$\Delta S_B = \bar{S}^\circ_{HB} + (y + n - \ell)\, \bar{S}^\circ_{H_2O} - \bar{S}^\circ_B - \bar{S}^\circ_{H^+}\ ;$$

where

$\bar{S}^\circ_{HP}$ = partial molal entropy of protonated base,

$\bar{S}^\circ_P$ = partial molal entropy of base,

$\bar{S}^\circ_{H_2O}$ = partial molal entropy of water,

and so forth.

Now, since the solution properties of the protonated bases are quite

similar we can make the assumption that

$$\bar{S}^\circ_{HP} = \bar{S}^\circ_{HB}\ ,$$

and

$$m = \ell\quad .$$

then

$$\Delta S_B - \Delta S_A = (\bar{S}^\circ_B - \bar{S}^\circ_P) + (y - x)\, \bar{S}^\circ_{H_2O}$$

where

(y - x) = difference in hydration between bipyridine and phenan-
throline.

Since

$$\Delta S_B - \Delta S_A = 13.5\ \text{eu}\quad \text{(experimental)}$$

$$\bar{S}^\circ_{H_2O} = 16.7\ \text{eu}$$

$$\bar{S}^\circ_B - \bar{S}^\circ_P = 13.5 - (y - x)\, 16.7$$

If we assume

$$(y - x) =$$

then

$$\bar{S}_B^\circ - \bar{S}_P^\circ = -3.2 \quad eu$$

This can be attributed to the rotational freedom of bipyridine and compares well with the ΔS_{ROT} of biphenyl which is -2.8 eu. The assumption that (y-x) = 1 could be further rationalized by pointing to the known monohydrate of 1,10-phenanthroline and attributing one water to each N-group of the normally trans bipyridine. This is proof of nothing but demonstrates that the entropies observed are of the right size.

The discussion of the entropy changes on the coordination of pyridine and bipyridine is much more difficult. The following can all make contributions.

1. The difference in entropy between the hydrated metal ion and the metal ion surrounded by organic base;

2. loss (or gain) in configurational entropy of the ligand;

3. release (or attachment) of water molecules;

4. statistical effect depending on number of sites available for ligand attachment.

Although many correlations depending on one or more of the above contributions have been attempted, few have done more than rearrange the obvious. To give an example of the problems consider the entropy of the reaction

$$Ni^{+2} + bipy \rightleftharpoons Ni^{+2}(bipy), \quad \Delta S \approx 4.2 \ eu$$
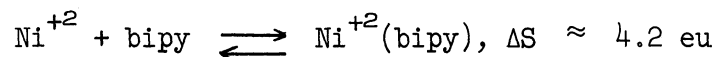
If we correct this by Gurney's rules we obtain

$$\Delta S_{(unitary)} = 12.1 \text{ eu}$$

Now

$$\Delta S = \bar{S}^\circ_{NiB} - \bar{S}^\circ_{Ni} - \bar{S}^\circ_{B}$$

and since

$$\bar{S}^\circ_{Ni} = -23 \text{ eu} \qquad (ref. 99)$$

and

$$\bar{S}^\circ_{bipy} = 52 \text{ eu} \qquad (ref. 100)$$

$$\Delta S = 12.1 = \bar{S}^\circ_{NiB} + 23 - 52$$

or

$$\bar{S}^\circ_{NiB} = {}^+41.1 \text{ eu}$$

This means that the partial molal entropy of the Ni^{+2} has gone from -23 eu to $+41$ eu upon the addition of a single uncharged chelate molecule! Now, Cobble[100] suggests that this is not a very useful number and that we should write the reaction

$$Ni(H_2O)_6^{+2} + bipy\,(H_2O)_x \rightleftharpoons Ni(H_2O)_y bipy^{+2} + (6 + x - y)\,H_2O$$
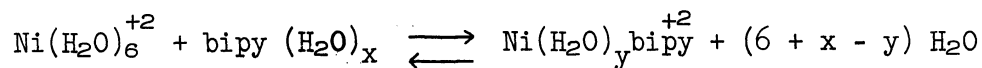
and write

$$\Delta S = \bar{S}'_{NiB} + (6 + x - y)\bar{S}^\circ_{H_2O} - \bar{S}^\circ_{Ni} - \bar{S}^\circ_{B} \quad,$$

therefore,

$$\bar{S}'_{NiB} = \bar{S}^\circ_{NiB} - (6 + x - y)S^\circ_{H_2O} \quad.$$

If we assume

$$x = 2 \qquad \text{(see previous section)}$$

$$y = 4 \qquad \text{(1 bipy replaces 2 } H_2O)$$

$$\bar{S}'_{NiB} = 41.1 - (6 + 2 - 4)\ 16.7$$

$$= 25.7 \text{ eu}$$

This at least looks more reasonable. Even more problems plague us if we attempt to do a more elegant gas phase treatment for we are left with a variety of hydration entropy terms that can only be guessed at.

One further approach to an analysis of the entropies of coordination of the monodentate ligand pyridine can be made. Following Benson[101] and Leussing[47] we can correct for the symmetry number of the complex. In effect this is a correction that depends on the number of sites available for coordination at any step of the complexation process.

The following table illustrates the process using the average ΔS_i's for pyridine complexation.

	exp't.	corrected (N=4)	corrected (N=6)
ΔS_1	+0.9	-1.8	-2.5
ΔS_2	-1.2	-2.0	-3.0
ΔS_3	-3.9	-3.1	-4.5
ΔS_4	-5.7	-3.0	-5.1

The correction smooths out the monatonic trend seen in the experimental

data. The correction for maximum coordination of 4 seems to provide a better fit than $N = 6$ but the difference is not a conclusive one. It is much more difficult to apply this type of correction to a bidentate ligand yet an approximate calculation shows that this approach could yield another rationalization of ΔS_2 for Cu-(bipyridine) and (S_3 for Ni-bipyridine.

At the present state of knowledge it is not fruitful to attempt a further analysis of the enthalpy data. Such analyses are too dependent on assumed hydration enthalpies that are often larger than the enthalpy of coordination being explained.

VI. SUMMARY

Free energies and enthalpies were determined for the coordination

of Mn(II) Ni(II), Cu(II) and Zn(II) with pyridine and 2,2'-bipyridine.

ΔF was determined by pH titrations of the metal ion solution with the

ligands at 25°C. The Bjerrum technique was used and the ionic strength

was held constant with a 1 molar $NaClO_4$ medium to avoid activity correc-

tions. An adiabatic calorimeter was built for the ΔH determinations.

By means of a buret device enthalpic titrations could be made which were

analogous to those of the ΔF work. In addition, electron spin resonance

spectra were obtained for the Mn(II) complexes in aqueous solution.

The sequential decrease in ΔF during complex formation is an entropy

effect since ΔH remains constant. For both bipyridine and pyridine the

order of stabilities is Mn < Ni < Cu > Zn. However Cu(II) is much less

stable than in the ethylenediamine case. It is possible to calculate a

thermodynamic crystal field stabilization energy for $Ni(bipy)_3^{++}$ which a-

grees very well with the spectral value. Another very good point of

agreement arises from the electron spin resonance results with $Mn(bipy)_3^{++}$.

These lead to information on the species present in aqueous solution

which is confirmed by alternate analyses.

The chelate stabilization can be observed by comparing ΔF, ΔH and

ΔS for bipyridine and pyridine complexes. This stabilization is small

for Mn(II) and Zn(II) but large for Ni(II) and Cu(II). It appears to

result primarily from an entropy effect for Mn(II) and Zn(II). However

Cu(II) and Ni(II) are stabilized additionally by an enthalpy effect.

The breakdown of the results into unitary and cratic segments does not

change the conclusions. It does illustrate, however, that a non-discrimi-

natory entropy effect is largely responsible for the chelate stabiliza-

tion of transition metal ions having no possibility of crystal field

effects. For ions with unfilled d levels, crystal field stabilization,

and hence a unique chelate effect is observable.

APPENDIX A

CALCULATION OF STABILITY CONSTANTS FROM GLASS ELECTRODE DATA

Since the bulk of precise measurements of stability constants on complexes involving transition metal ions and nitrogen ligands have been done by glass electrode potentiometry it is fitting to discuss the calculations of stability constants from the raw pH data. As Sillen[57] points out, not only do calculations consume the bulk of the experimenter's time, but they are very much the determining factor in the sort of equilibrium information one is able to obtain from a titration.

For the case of a titration of the metal and acid solution by a monobasic ligand, the instantaneous total concentrations of metal ion C_M, hydrogen ion C_H, and ligand C_B, are known. In addition the free hydrogen ion concentration $[H^+]$ can be measured by the pH meter. To obtain a rough idea of the extent of complexation and a measure of the stability constants of the species produced it is instructive to plot a formation curve where $\bar{n}_m$, the average number of ligands per metal ion, is a function of the negative log of the free ligand concentration, pB. Since the actual measurement is made on the hydrogen ion, the equilibrium constant of the proton with the ligand must be determined. This is given by a titration involving only ligand and acid.

$$HB^+ \underset{\longleftarrow}{\overset{k_a}{\longrightarrow}} H^+ + B$$

77
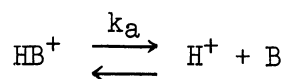
$$pk_a = pH + \log \frac{BH^+}{B} = pH + \log \frac{C_H-[H^+]}{C_B-C_H+[H^+]}$$

In all of the equilibria to be discussed in this section, the reactants are at approximately millimolar concentration in the presence of approximately 1 M neutral salt. Hence the activities of the reacting species remain rather constant in direct proportion to their concentrations.

On the introduction of a metal ion, one can calculate the value for $\bar{n}_m$ at each point of the titration curve as:

$$\bar{n}_m = \frac{C_B-[B]-[BH^+]}{C_M} = \frac{C_B-(C_H-[H^+])(1+\frac{k_a}{[H^+]})}{C_M}$$

where

C_B, C_M, C_H represent the total concentration of ligand, metal ion, and proton

$[H^+]$ represents the hydrogen ion concentration as determined by the pH meter

k_a represents the acid dissociation constant for the protonated ligand as determined above.

The remaining quantity pB can be found as the negative log of the free ligand concentration

$$[B] = \frac{k_a (C_H-[H^+])}{[H^+]}$$

The case of the dibasic ligand demands that two acid constants be calculated.

$$BH_2^{++} \xrightleftharpoons{k_{a1}} BH^+ + H^+$$

$$BH^+ \xrightleftharpoons{k_{a2}} B + H^+$$
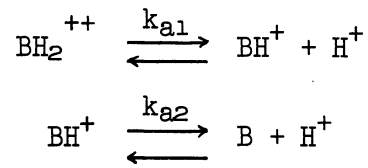
If the two constants are sufficiently separated (differing by two log units) they may be determined by defining $\bar{n}_B$ as the average number of hydrogen ions per each amine molecule.

$$\bar{n}_B = \frac{C_H}{C_B}$$

At half-integer values of $\bar{n}_B$, i.e. at 0.5 and 1.5, pk_1 and pk_2 are equal to the respective pH values at these points. On substitution of the acid constants into the expressions for $\bar{n}_m$ and pB, one obtains: (see Spike, ref. 3)

$$\bar{n}_m = \frac{\dfrac{[B]_o V_B}{V_o} - \left\{ \dfrac{k_{a1}k_{a2}+k_{a2}[H^+]+[H^+]^2}{k_{a2}[H^+]+2[H^+]^2} \right\}[H^+]_o}{[M]_o}$$

and

$$[B] = \frac{k_{a1}k_{a2}[H^+]_o \dfrac{V_o}{V}}{[H^+]k_{a2}+2[H\ ]^2}$$

where

$[B]_o$ = concentration of ligand titrated in moles/liter

$k_{a1}k_{a2}$ = acid constants of dibasic ligand

$[M]_o$ = initial concentration of metal ion in moles/liter

$[H^+]_o$ = initial concentration of protons in moles/liter

V_o = initial volume of solution in ml

V_B = volume of titrant in ml

For a titration of the protonated ligand and metal ion with a base such

as NaOH, one can calculate the acid dissociation constants as

$$pK_a = pH + \log \frac{[BH^+]}{[B]} = pH + \log \frac{C_B - [Na^+]}{[Na^+]}$$

where
where $[Na^+]$ represents the concentration of sodium ion in moles per liter.

For the dibasic ligand we can define $\bar{n}_B$ as the average number of

protons produced by the BH_2^{++} ion

$$\bar{n}_B = \frac{[BH^+] + 2[B]}{[B]} = \frac{[Na^+] + [H^+] - [OH^-]}{C_B} = \frac{k_{a1}[H] + 2 K_a}{K_a + k_{a1}[H^+] + [H^+]^2}$$

where $K_a = k_{a1}k_{a2}$ the product of the successive dissociation constants.

at $\bar{n}_B = 1$, $pH = 1/2\ pK_a$. Substituting in the above equation will give

k_1.

Gustafson and Martell[42] have outlined the methods of calculating

stability constants from NaOH titrations.

Let

$$k_{MB} = \frac{C_B - X[B]}{X[B]^2}$$

where

$$X = \frac{[H^+]^2}{k_{a1}} + \frac{[H^+]}{k_{a2}} + 1$$

for dibasic ligands, and

$$X = \frac{[H^+]}{k_{a1}} + 1$$

for monobasic ligands.

and

$$[B] = \frac{(2-a)C_B - [H^+] + [OH^-]}{\dfrac{2[H^+]^2}{K_a} + \dfrac{[H^+]}{k_{a2}}}$$

where

a = ratio of KOH to ligand.

For bipyridine, since the chelate is already formed in solutions of copper and nickel further calculations are necessary.

$$K_{MB} = \frac{Y}{K_{MB_2}[B] (C_M - a \, C_B) - [H^+] + [OH^-] + [B] + Y}$$

where

$$Y = \frac{K_{MB_2}[B] (C_B - [B] \, X)}{2 \, K_{MB_2}[B] + 1}$$

From two sets of experimental data, KMA and KMA$_2$ may be calculated.

In the case of a protonated monobasic ligand in such a NaOH titration:

$$[BH^+] = C_B - [Na^+] - [H^+] \quad ,$$

$$\log (B) = pH - pK_a + \log BH^+ \quad ,$$

and

$$\bar{n}_m = \frac{C_B - ([B] + [BH])}{C_M} \quad .$$

1. CALCULATIONS SPECIFIC TO THIS RESEARCH

The ligand was used as titrant against an acidified solution. A reading on the pH meter fine scale was taken initially, E_0. Also known were the concentration of the acid, C_H^o, concentration of the ligand C_B^o, volume of the acid V_0, and a series of emf readings Ei corresponding to the addition of successive volumes of ligand V_B. First the change in apparent pH was calculated (ΔpH_{app}).

$$\Delta pH_{app} = pHi - pH_0 = \frac{\frac{(E_i - E_0) \cdot 200}{2.3026 \; RT}}{F} = .0033812 \; (E_i - E_0)$$

at 25°C.

The apparent ΔpH value is then converted to the concentration pH by means of a calibration curve for the pH meter. This calibration had been obtained under identical operating conditions but was found to vary slightly from week to week. A knowledge of pH in terms of concentration permits the hydrogen ion concentration to be used to calculate a stoichiometric acid dissociation constant.

$$pK_a = pH + \log \frac{[BH^+]}{[B]} = pH + \log \frac{C_H - [H^+]}{C_B - C_H + [H^+]}$$

where

$$C_H = \frac{C_H^o \cdot V_0}{V_0 + V_B}$$

and

$$C_B = \frac{C_B^o \cdot V_B}{V_0 + V_B}$$

A computer program was designed to calculate these terms for each point of the titration curve.

The calculation of formation constants demanded the computation of $\bar{n}_m = f(pB)$, the typical formation curve. For this purpose a concentration of metal ion, C_M^o, was introduced and the above titration repeated. Then

$$[B] = \frac{K_a \; (C_H - [H^+])}{[H^+]}$$

where

$$\bar{n}_m = \frac{C_B - (C_H - [H^+])\left(1 + \frac{K_a}{[H^+]}\right)}{C_M} \quad ,$$

where

$$C_M = \frac{C_M^\circ \cdot V_o}{V_o + V_B} \quad ,$$

and all other terms are defined above.

The formation curve then consists of a plot of $\bar{n}_m$ versus pB, the negative log of [B]. Approximate values of log k_i values can be read off this curve at $\bar{n}_m = 0.5, 1.5, 2.5, 3.5 \ldots$respectively. However these constants are only approximate and must be improved.

The most simple method for obtaining better constants was used by Bjerrum.[1] In the case of a symmetrical formation curve and average constant can be found at $\bar{n}_m = N/2$ where N is the maximum number of ligands which will coordinate with the metal ion.

$$\text{average constant } k = \frac{1}{[B]_{n = \frac{N}{2}}}$$

The slope at this point $= \Delta = -.4343 \dfrac{d\bar{n}_m}{dpB}$

For the case $N = 2$

$$x = \frac{1 - \Delta}{\Delta} \qquad \qquad \begin{cases} k_1 = 2xk \\ \\ k_2 = k/2x \end{cases}$$

where x is defined as the spreading factor which represents the devia- tion of the ratio of successive formation constants from the statistical

case shown below.

For $N = 3$

$$x = \frac{9-4\Delta}{12\Delta-3}$$

$$\begin{cases} k_1 = 3x^2 k \\ k_2 = k \\ k_3 = \frac{k}{3x^2} \end{cases}$$

In general

$$k_n = \frac{N-n+1}{n} \cdot k \cdot x^{N+1-2n}$$

where

$$\frac{k_n}{k_{n+1}} = \frac{(n+1)(N-n+1)}{n(N-n)} x^2$$

This is good for constants which are very close together, i.e., $x \simeq 1$

$$\Delta = \frac{\sum\limits_{1}^{N} n(n-\frac{N}{2}) \binom{N}{n} x^{n(N-n)}}{1 + \sum\limits_{1}^{N} \binom{N}{n} x^{n(N-n)}}$$

This has solutions only for $N = 2$ or 3

For k_6

$$\log k_n = pB_{\bar{n}=3} + \log (\frac{7-n}{n} x^{7-2n})$$

For k_4

$$\log k_n = pB_{n=2} + \log (\frac{5-n}{n} x^{5-2n})$$

The problem here of course is to calculate a meaningful value of x.

Bjerrum presents curves of $\log x$ versus Δ for various values of N.

Rosotti[95] presents a review of graphical methods for obtaining equilibrium constants. In particular for ($\bar{n}$, [B]) data

$$\frac{\bar{n}}{(1-\bar{n})[B]} = \beta_1 + \beta_2 \frac{(2-\bar{n})}{(1-\bar{n})} [B] + \sum_{n=3}^{n=N} \frac{n-\bar{n}}{1-\bar{n}} \beta_n [B]^{n-1}$$

where

$$\beta_n = \frac{[MB_n]}{[M][B]^n}$$

A plot of $\dfrac{n}{(1-\bar{n})[B]}$ against $\dfrac{(2-n)[B]}{(1-\bar{n})}$ tends to be a straight line of intercept β_1 and slope β_2 as [B] $\longrightarrow$ 0. For any constant β_t where

(0 < t < N)

$$\sum_{n=0}^{n=t-1} \left(\frac{\bar{n}-n}{t-\bar{n}}\right) \beta_n [B]^{n-t} = \beta_t + \sum_{n=t+1}^{n=N} \left(\frac{n-\bar{n}}{t-\bar{n}}\right) \beta_n [B]^{n-t}$$

If values of $\beta_1 \ldots \beta_{t-1}$ are known a plot of the left term against $\dfrac{(t-1-\bar{n})[L]}{(t-\bar{n})}$ gives β_t as intercept and an approximate value of β_{t+1} as limiting slope as [B] $\longrightarrow$ 0. Other methods of Fronaeus[96] and Olerup are described which demand graphical integration in the first case and extrapolation from a curve in the second case.

Scatchard[52] has defined a function

$$Q = \frac{\bar{n}}{(N-\bar{n})[B]}$$

which has limiting values of β_1/N and $\dfrac{nB_N}{\beta_{(N-1)}}$ as [B] approaches 0 or ∞

respectively. Also approximate values of the ratios of β_2/β_1 and $\dfrac{\beta_{(N-1)}}{\beta_{(N-2)}}$ may be obtained from the limit of $d\ln Q/d\bar{n}$ as $\bar{n} \longrightarrow 0$ and N.

Sullivan has reviewed the methods of calculating stability constants[97] and along with Rydberg[98] has developed a computer program which calculates the constants from $\bar{n}_m$ and $[B]$ data. The program treats an expression

$$\sum_{n=0}^{N} (C_B - [B] - \bar{n}\, C_M)\, \beta_n\, [B]^n = 0$$

For a set of measured values of C_B, $[B]$, C_M, and the estimated standard deviations in the measurement of $[B]$, the program finds the set of β's which best satisfies the above expression in the least square sense. This program also gives the standard deviations in the β's, the sum of the weights used in fitting the curve, and the quantity $\bar{n}$.

APPENDIX B

POTENTIOMETRIC TITRATION DATA

Several determinations were made on each of the pK_a values as well
as the metal-ligand systems. Below is a typical titration for each sys-
tem. The following abbreviations are used, with all concentrations ex-
pressed in terms of molarity.

C_H^o = initial concentration of $HClO_4$

C_M^o = initial concentration of metal perchlorate

C_B = concentration of ligand as titrant

V_o = volume of solution in milliliters

V_B = volume of ligand added in milliliters

1. DETERMINATION OF pK_a FOR $[H \, bipy]^+$

C_H^o = 8.433×10^{-4} mol/liter

C_B = 2.121×10^{-3} mol/liter

V_o = 60.00 ml

pK_a = $pH + \log \dfrac{[BH^+]}{[B]}$

V_B	pH	pK_a
0	3.074	-
10	3.376	-
20	3.902	5.279
25	4.091	4.714
30	4.233	4.558

V_B	pH	pK_a
35	4.314	4.470
37	4.339	4.439
39	4.357	4.403
40	4.365	4.386
41	4.373	4.368
42	4.382	4.357
43	4.387	4.340
44	4.396	4.327
45	4.403	4.313
46	4.412	4.301
47	4.421	4.290
48	4.426	4.277
49	4.432	4.265
50	4.441	4.253

2. Cu(II) BIPYRIDINE

C_H^o = 9.638 x 10^{-4} moles/liter C_M^o = 4.700 x 10^{-5} moles/liter

C_B^o = 2.121 x 10^{-3} moles/liter V_o = 105.00 ml

V_B	pH	pB	$\bar{n}_m$
.20	3.018	6.80	0.01
.40	3.019	6.74	0.09
.60	3.020	6.69	0.16
.80	3.021	6.71	0.26

V_B	pH	pB	$\bar{n}_m$
1.00	3.022	6.75	0.35
1.20	3.022	6.78	0.44
1.40	3.024	6.64	0.50
1.60	3.025	6.60	0.57
1.80	3.026	6.62	0.66
2.00	3.026	6.65	0.76
2.50	3.029	6.57	0.95
3.00	3.034	6.24	1.03
3.50	3.037	6.14	1.17
4.00	3.042	5.96	1.22
4.50	3.048	5.82	1.25
5.00	3.053	5.73	1.32
5.50	3.059	5.65	1.37
6.00	3.065	5.57	1.39
6.50	3.070	5.50	1.43
7.00	3.076	5.45	1.47
7.50	3.082	5.40	1.51
8.00	3.089	5.35	1.51
8.50	3.095	5.30	1.51
9.00	3.101	5.25	1.52
9.50	3.107	5.22	1.55
10.00	3.114	5.18	1.56
11.00	3.127	5.11	1.60

V_B	pH	pB	$\bar{n}_m$
12.00	3.140	5.05	1.63
13.00	3.150	5.01	1.76
14.00	3.164	4.96	1.78

3. Ni(II) - BIPYRIDINE

C_H^o = 8.433 x 10^{-4} moles/liter $\qquad$ C_M^o = 2.072 x 10^{-4} moles/liter

C_B^o = 2.121 x 10^{-3} moles/liter $\qquad$ V_o = 30.00 ml

V_B	pH	pB	$\bar{n}_m$
1.00	3.089	7.40	.34
2.00	3.105	6.54	.66
3.00	3.118	6.60	1.00
4.00	3.132	6.40	1.33
5.00	3.145	6.41	1.67
6.00	3.157	6.40	2.01
7.00	3.176	5.93	2.28
8.00	3.205	5.50	2.45
9.00	3.258	5.10	2.42

4. Mn(II) - BIPYRIDINE

C_H^o = 1.659 x 10^{-4} moles/liter $\qquad$ C_M^o = 1.547 x 10^{-2} moles/liter

C_B^o = 2.121 x 10^{-3} moles/liter $\qquad$ V_o = 40.00 ml

V_B	pH	pB	$\bar{n}_m$
6.00	4.088	4.02	.62

V_B	pH	pB	$\bar{n}_m$
9.00	4.257	3.84	1.11
10.00	4.302	3.80	1.33
12.00	4.362	3.76	1.79
18.00	4.465	3.58	2.78
21.00	4.498	3.53	3.38
23.00	4.512	3.50	3.72
25.00	4.521	3.47	4.07
27.00	4.532	3.45	4.43
29.00	4.535	3.42	4.71
31.00	4.558	3.39	5.00
33.00	4.571	3.37	5.29
35.00	4.584	3.34	5.50
37.00	4.597	3.31	5.62
39.00	4.609	3.28	5.63
42.00	4.630	3.23	5.63
45.00	4.648	3.21	5.87
48.00	4.663	3.14	5.15
50.00	4.676	3.09	4.39

5. Zn(II) - BIPYRIDINE

$C_H^o = 3.373 \times 10^{-4}$ moles/liter $C_M^o = 1.833 \times 10^{-4}$ moles/liter

$C_B^o = 2.121 \times 10^{-3}$ moles/liter $V_o = 60.00$ ml

V_B	pH	pB	$\bar{n}_m$
.99	3.493	5.83	.13
4.00	3.555	5.21	.52
7.01	3.626	4.91	.89
10.05	3.708	4.70	1.25
13.00	3.796	4.52	1.58
16.00	3.893	4.36	1.88
19.01	4.004	4.19	2.13
21.98	4.105	4.04	2.33
25.05	4.228	3.90	2.51
28.04	4.325	3.82	2.79
30.00	4.380	3.78	3.01
33.08	4.440	3.75	3.43
35.99	4.483	3.73	3.85
39.00	4.523	3.71	4.26
42.04	4.574	3.69	4.72
45.00	4.603	3.69	5.23
48.00	4.631	3.69	5.75
50.00	4.650	3.69	6.09

6. Pk_a of $[Py\ H]^+$

$C_H^o = 3.614 \times 10^{-3}$ moles/liter $V_o = 35.00$ ml

$C_B^o = 6.412 \times 10^{-2}$ moles/liter

V_B	pH	pK_a
1.70	3.317	9.654
1.92	3.904	8.506
2.01	4.135	7.324
2.13	4.320	6.673
2.23	4.409	6.350
2.34	4.470	6.088
2.43	4.512	5.926
2.63	4.580	5.648
2.72	4.604	5.548
2.80	4.628	5.478
3.00	4.676	5.311
3.20	4.716	5.175
3.41	4.756	5.060
3.73	4.814	4.919
4.02	4.873	4.828
4.50	4.953	4.699
5.00	5.038	4.605
5.50	5.116	4.531
6.00	5.209	4.492
6.50	5.293	4.460
7.50	5.549	4.517
8.50	5.829	4.632

7. Cu(II) - PYRIDINE

C_H^o = 3.614 x 10^{-3} moles/liter C_M^o = 7.050 x 10^{-4} moles/liter

C_B^o = 6.412 x 10^{-2} moles/liter V_O = 35.00 ml

V_B	pH	pB	$\bar{n}_m$
2.33	4.42	3.20	.04
2.41	4.45	3.17	.17
2.61	4.54	3.09	.46
2.80	4.58	3.05	.83
3.03	4.64	2.99	1.22
3.20	4.67	2.96	1.53
3.40	4.71	2.92	1.87
3.90	4.80	2.84	2.77
4.41	4.89	2.75	3.54
4.90	4.97	2.68	4.26
5.40	5.05	2.61	4.87
5.93	5.15	2.51	5.21
6.42	5.23	2.44	5.40
6.91	5.32	2.35	5.20

8. Ni(II) - PYRIDINE

C_H^o = 3.614 x 10^{-3} moles/liter C_M^o = 7.400 x 10^{-5} moles/liter

C_B^o = 6.412 x 10^{-2} moles/liter V_O = 35.00 ml

V_B	pH	pB	$\bar{n}_m$
2.42	4.51	3.11	.03
2.60	4.58	3.05	.30
2.80	4.64	2.99	.58
3.00	4.69	2.94	.90
4.00	4.89	2.75	2.37
5.00	5.06	2.59	3.52
6.00	5.24	2.42	3.92

9. Mn(II) - PYRIDINE

C_H° = 3.514 x 10^{-3} moles/liter C_M° = 6.697 x 10^{-4} moles/liter

C_B° = 6.412 x 10^{-2} moles/liter V_0 = 35.00 ml

V_B	pH	pB	$\bar{n}_m$
2.57	4.58	3.05	.25
2.77	4.64	2.99	.56
2.97	4.69	2.94	.89
3.47	4.80	2.84	1.74
3.97	4.91	2.73	2.42
4.47	5.01	2.64	3.00
4.97	5.09	2.56	3.52
5.97	5.30	2.36	3.30

10. Zn(II) - PYRIDINE

C_H^o = 3.614 x 10^{-3} moles/liter C_M^o = 6.697 x 10^{-4} moles/liter

C_B^o = 6.412 x 10^{-2} moles/liter V_o = 35.00 ml

V_B	pH	pB	$\bar{n}_m$
2.41	4.52	3.11	.01
2.60	4.58	3.05	.32
2.80	4.64	2.99	.64
3.00	4.70	2.93	.96
4.00	4.90	2.74	2.55
5.00	5.09	2.56	3.65
6.00	5.28	2.39	3.83

The stability constants reported are averages calculated using all of the titrations on a given system.

APPENDIX C

CALORIMETER DATA

The following data is presented for each system:

1. Initial quantity of $HClO_4$ in millimoles

2. Initial quantity of metal perchlorate in millimoles

3. Millimoles of ligand added as titrant

4. Quantity of heat produced in terms of calories

5. Calculation of the heat in terms of kcal/mole of titrant.

The pyridine heats of reaction were calculated by drawing titration curves (calories vs. ml. pyridine). In every case the acid concentration was held constant as was the total volume of solution.

For bipyridine, further information in the form of $\bar{n}_m$ is given, where $\bar{n}_m$ = average number of ligands per metal ion. These calculations may be made directly from the stoichiometric amounts of metal and ligand present.

1. PYRIDINE

System	m moles HClO$_4$	m moles M(ClO$_4$)$_2$	m moles ligand added	q cal.	kcal/mole py
Cu(II)-py	.316	.0247	.050	.37	7.4
			.056	.35	6.3
			.066	.42	6.4
			.063	.42	6.7
			.093	.27	2.9
Cu(II)-py	.316	.0247	.070	.45	6.4
			.061	.46	7.5
			.060	.39	6.5
			.119	.38	3.2
			.149	.12	.8
H-py	.316	0	.042	.19	4.6
			.056	.47	5.2
			.114	.56	4.9
			.055	.30	5.4
			.083	.22	2.7
Cu(II)-py	.316	.0740	.218	-	-
			.074	.49	6.6
			.063	.42	6.5
			.065	.17	2.6
			.072	.09	1.6

System	m moles HClO$_4$	m moles M(ClO$_4$)$_2$	m moles ligand added	q cal.	kcal/mole py
Zn(II)-py	.316	.0835	.065	.32	4.9
			.067	.25	3.7
			.065	.36	5.6
			.063	.33	5.2
			.062	.28	4.6
			.065	.09	1.4
			.069	.04	.6
Ni(II)-py	.316	.0778	.059	-	-
			.054	.36	6.9
			.067	.27	4.2
			.065	.29	4.4
			.066	.01	.2
Mn(II)-py	.316	.0703	.067	-	-
			.057	.38	6.8
			.063	.31	4.9
			.069	.33	4.9
			.067	.37	5.5
			.060	.02	.4

2. BIPYRIDINE

System	m moles $HClO_4$	m moles $M(ClO_4)_2$	m moles ligand added	q cal.	kcal/mole bipy
H-bipy	.1012	0	0.018	.064	3.6
			0.021	.047	2.2
			0.042	.067	1.4
			0.128	.086	6.7

Cu(II)-bipy   m moles $HClO_4$ = .1012

m moles $Cu(ClO_4)_2$ = .0247

C_B^o = 2.121 x 10^{-3} moles/liter

V_o = 141 ml

ml bipy	$\Delta \bar{n}_m$	q cal.	kcal/mole complex
5.02	.432	.132	12.3
4.94	.424	.117	11.1
4.98	.193	.069	14.4

Ni(II)-bipy   m moles $Ni(ClO_4)_2$ = .0518

C_B^o = 2.121 x 10^{-3} moles/liter

V_o = 125 ml

ml bipy	$\Delta \bar{n}_m$	q cal.	kcal/mole complex
5.26	.215	.387	34.9
4.85	.200	.136	13.1
4.82	.196	.238	23.6
4.85	.197	.150	14.6
6.17	.254	.156	11.9
4.21	.173	.127	14.1
4.93	.202	.267	27.3

Mn(II)-bipy   m moles $Mn(ClO_4)_2$ = .0235

C_B^o = 2.121 x 10^{-3} moles/liter

V_o = 125 ml

ml bipy	$\Delta \bar{n}_m$	q cal.	kcal/mole complex
7.94	.748	.049	2.9
4.86	.438	-.023	-1.3
5.01	.452	.098	9.2

Zn(II)-bipy   m moles $Zn(ClO_4)_2$ = .0279

C_B^o = 2.121 x 10^{-3}

V_o = 125 ml

ml bipy	$\Delta \bar{n}_m$	q cal.	kcal/mole complex
4.74	.361	.040	3.8
5.19	.395	.174	15.8
4.89	.373	.042	4.1
4.86	.370	.044	4.3
4.64	.353	.216	20.9

APPENDIX D

ELECTRON SPIN RESONANCE

Electron spin resonance (ESR) has been shown to be a very useful tool in the study of solutions of transition metal ions. This has been illustrated by the work of Sands[80] on vanadium solutions, Cohn and Townsend[81] with manganese, McGarvey[33] with copper and manganese, Kozyrev[82] with copper, recent work by Lutze and Bösnecher[83] on copper, and studies by Rivkind on Cu(II) agqeous solutions.[94] The extension of these measurements to the more involved compounds of biological interest has been studied by Beinert and Sands,[85] Vänngard and Mälmstrom,[32] Ingram[86] and many others. A sample of these applications is given by Blois.[84]

Reviews of the general theory and techniques of ESR are given by Wertz,[87] Ingram,[86] Feher,[88] and Townes and Schawlow.[89] Models for ESR in liquid solutions have been proposed by McConnell[90] and later by Rogers and Pake.[91] An application to transition metal ions is given by Griffiths.[92] Copper complexes have been studied using ESR by Feltham[93] in conjunction with spectral measurements.

The experiment consists of placing paramagnetic ions of electronic spin S in a field H. This establishes 2S + 1 Zeeman levels corresponding to the allowed orientations of the magnetic moment in the field. Microwave radiation will cause transitions between adjacent levels. The basic resonance condition is

$$h\nu = g\beta H$$

where

h is the Planck's constant

ν is the microwave frequency

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β is the Bohr magneton

H is the strength of the magnetic field in gauss

g is the gyromagnetic ration having a value 2.0023 for the

    free electron.

In addition to these transitions, the electronic spin may interact with the nuclear spin I, producing $2I + 1$ hyperfine lines in the resonance spectrum. Such is the case with manganese where $I = 5/2$.

Experimentally a constant frequency of approximately 9100 megacycles was used. A Varian spectrometer and magnet power supply permitted the magnetic field to vary at a uniform rate through the resonance point. A crystal was tuned to the microwave frequency of resonance, and the derivative of the detected signal was recorded on a Varian recorder as a function of the magnetic field.

Due to the high dielectric loss of water at these microwave frequencies a very small sample was carefully centered in the electric field node. Amersil quartz tubing of 1 mm I.D. and 3 mm O.D. was used. This gave a sample approximately 0.1 cc in size.

Mn(II) exists in the hexaquo complex with cubic symmetry. The change in symmetry with complexation does not appear to shift the ground state, ^6S, to a state of lower multiplicity. This is evident from magnetic susceptibility measurements. Work by McGarvey[33] indicates that decreasing the symmetry causes the hyperfine resonance to disappear. With hexaquo manganese, the hyperfine line widths were 30-40 gauss. However, the broad resonance of the complex with pyridine was 610 gauss wide. Since the narrow signal essentially is superimposed upon a very broad base, it is merely necessary to measure the intensity of the narrow resonance to obtain a measure of the uncomplexed Mn(II) concentration. Most

simply, one can measure the heights of the derivative curve peaks to record this intensity. Since the hyperfine lines can be assumed to be Lorentzian, the derivative height x (derivative width)^2 would be proportional to the area of the integrated signal, and hence to the amount of uncomplexed manganese present.

To obtain quantitative information from ESR measurements, a series of solutions containing equal concentrations of manganese (approximately millimolar) were made up with varying concentrations of pyridine and bipyridine. To prevent the formation of an unknown number of hydroxy complexes at high pH values, the pH of the solutions was set at 4.94 by using a 0.1 molar acetate buffer. Samples of each solution were placed in quartz tubes of identical bore. The klystron power and the crystal were optimized with the Mn(II)-water solution in the cavity. Using a power of 7 d.b., adjusting the set screw at the cavity so that the crystal current measured 100 ua, using maximum 100 kc/sec modulation, and a fixed attenuation, each sample was run under the same conditions at room temperature. It was not necessary to retune the klystron between samples. The spectra were measured in arbitrary units of height. The sweep-rate was adjusted so that the resulting signal could give approximately 1% precision on a width measurement. To check the instrument, a series of $Mn(ClO_4)_2$ solutions over a ten-fold concentration range from 1×10^{-4} to 1×10^{-3} molar were measured. The sum of the heights of the six lines gave a strict linear plot against concentration. Data for the pyridine and bipyridine complexes is shown below. The total concentration of Mn(II) was 3.75×10^{-3} molar in all cases.
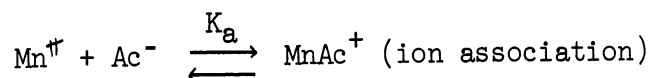
Sample	Signal Height	[Mn] moles/liter
1. $Mn(ClO_4)_2-H_2O$	404.5	.00375
2. (1) with buffer*	280.9	.00260
3. (2) with 4.19×10^{-3} pyridine**	260.1	.00241
4. (2) with 8.37×10^{-3} pyridine	256.4	.00238

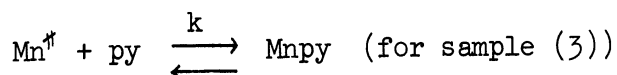*buffer solution of 0.1 molar acetic acid and 0.1 molar sodium acetate.

** $\dfrac{[B]}{[BH^+]} = \dfrac{k_a}{[H^+]} = .524;$ $[B] + [BH^+] = C_B;$ for first approximation,

solve for [B] using both equations. [B] represents bipyridine or

pyridine.

The equilibria involved are as follows:

$$Mn^{++} + Ac^- \underset{\longleftarrow}{\overset{K_a}{\longrightarrow}} MnAc^+ \text{ (ion association)}$$

$$K_a = \frac{[MnAc^+]}{[Mn^+][Ac^-]} = \frac{(.00375-.00260)}{(.00260)(.1)} = 4.43$$

$$Mn^{++} + py \underset{\longleftarrow}{\overset{k}{\longrightarrow}} Mnpy \text{ (for sample (3))}$$

$$k = \frac{[Mnpy^{++}]}{[Mn^{++}][py]} = \frac{(.00260-.00241)}{(.00241)(.00419-.00019)} = 19.7$$

A second determination (sample (4)) gave 11.7 for the constant. Since

these values seem rather small for pyridine, it is instructive to com-

pare the widths of the individual hyperfine lines. This gives (from low

field to high field) the following widths in arbitrary units for the re-

spective samples:

Line no.	(1)	(2)	(3)	(4)
1	14.5	15.6	16.8	16.6
2	13.6	15.1	15.3	14.9
3	12.5	14.3	14.5	14.3
4	12.5	13.7	13.5	14.5
5	12.5	14.3	14.3	14.0
6	13.0	14.5	14.6	15.4

This shows that the lines from the buffered solutions are wider than the hexaquo lines. Furthermore if one calculates the product height x (width)^2 from these data even lower complexity constants result.

A further series of runs were made as follows with the concentration of $Mn(ClO_4)_2 = 3.75 \times 10^{-3}$ molar in each case.

No.	Solvent	Signal Height	$[Mn^{++}]$ moles/liter
1	H_2O	419.3	.00375
2	H_2O + buffer	300.0	.00268
3	H_2O + buffer + .0418 molar py	236.0	.00211
4	H_2O + buffer + .0836 molar py	192.3	.00172
5	H_2O + buffer + .00124 bipy	183.4	.00164
6	H_2O + buffer + .00248 bipy	117.2	.00105
7	.583 molar pyridine	218.1	.00195
8	2.18×10^{-2} bipyridine	36.4	.000326
9	pure pyridine	36.9	.000330

From (2), $K_a = \dfrac{[MnAc^+]}{[Mn^{++}][Ac^-]} = 4.0$

From (3) and (4) $k_{py} = 6.5$ and 6.8 respectively

From (5) and (6) $k_{bipy} = 3.16 \times 10^3$ and 1.86×10^3 respectively

From (7) β_6 py = 23.3

From (8) β_3 bipy = 1.07×10^6

To estimate a value for $\bar{n}$ for the buffered solutions one may plot

$$\log \frac{[Mn(py)n]}{[Mn]} \quad \text{versus} \quad \log [py]$$

The slope should be $\bar{n}$. This was done for both pyridine and bipyridine. In each case the slope was unity within experimental error. The calculation of log β_6 for the pyridine complex is merely an estimate since the actual value of $\bar{n}$ is only estimated.

It is interesting to look at the tris bipyridine complex. The yellow solution gave a rather asymmetric spectra. Calculations of the overall complexity constant gave a value which is quite comparable to that obtained by Brandt[46] from spectrophotometry in the near ultraviolet. Brandt's log β_3 = 6.33; our value 6.03.

A quantitative appraisal of the chelate effect from the ESR data can be shown by comparing the log k values for bipyridine and pyridine respectively. The average values are 3.39 and 0.82, giving a chelate effect of 2.57 on subtraction.

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