A STUDY OF 3,3'3''-PHOSPHINIDYENETRIPROPIONIC ACID AS AN ACID AND A CHELATING AGENT

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A STUDY OF 3,3'3''-PHOSPHINIDYENETRIPRO-

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AND A CHELATING AGENT

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PREFACE

Although many organic chelating agents are known and stability constants are tabulated for their complexes with a wide variety of metal ions, very few chelating ligands are known in which phosphorus is the actual doner. This paper treats the synthesis of such a ligand and a study of some of the properties of the ligand including chelate formation with transition metal ions.

Indebtedness is acknowledged to Dr. Neil Purdie without whose help this study could not have been completed. Dr. Purdie offered valuable guidance in preparation of the experimental procedures as well as the mathematical treatment of the data. Also of special help were Dr. K. D. Berlin, whose aid in the preparation of the compound and the NMR studies was very valuable, and Dr. O. C. Dermer without whose aid there would have been no time to complete this report. I also wish to thank Dr. T. E. Moore and Dr. J. P. Devlin for their aid and assistance as well as the many other students and instructors of the Chemistry Department whose aid was very valuable in the preparation of this report.

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CHAPTER I

INTRODUCTION

The Problem

The problems considered in this paper are three in number: First the preparation of an organophosphorus chelating agent 3,3',3"-phosphinidyenetripropionic acid; second a study of the acid itself to determine the thermodynamic values of the ionization constants by use of the Davies (1) extension of the Debye-Huckel limiting law; and, third, a study of the chelates formed with this ligand and several transition metal ions.

The Theory of Chelate Formation

Organic chelates and complexes in general have been known and studied for some time. In 1891 Werner (2) published his proposed coordination theory to explain the phenomenon of apparently stable, saturated molecules combining to give "molecular complexes." In brief, Werner stated that certain atoms or ions can have a secondary valence and can combine with a certain maximum number of other atoms, molecules, or radicals. Depending on the central atom, this number is usually four or six with the latter being most common. This number is called the coordination number of the atom or ion. The groups that attach themselves to the central atom or ion are called ligands and have in common the ability to donate a pair of electrons to an electron acceptor. The ligands are arranged in a definite position around the central ion and make up the "first coordination sphere." There may be other layers of solvent and ligand molecules around the first sphere, but these other layers are held very weakly in comparison to the ligands in the first coordination sphere and are very rapidly exchanging with other solvent molecules and ligands in the environment. Water molecules themselves are weak ligands, and in aqueous solution the metal ion is surrounded by water ligands. According to Werner, coordinate bonds are formed by donation of a pair of electrons to the central ion by the ligand. Therefore one way to look at complex formation is to view it as the "neutralization" of a Lewis acid with a Lewis base. This explanation associates the stability of the complexes with the base strength of the ligand; and this is borne out for the most part, although a number of other factors are also involved.

In more recent years several theories have been proposed to more fully explain complex formation. These include the valence-bond approach of Pauling and Slater, the crystal field theory of Bethe and van Vleck, and the molecular orbital with ligand field theory. These are discussed in almost any book on general inorganic chemistry.

Chelates are a special type of complex in which there are two or more possible electron donating sites on one ligand which attach to the same central ion. Werner was the first to report a chelate as such. In 1901 he described potassium dichloro-acetylacetono platinate (II). Since chelates form a ring by the ligand attaching at two points on the central ion, steric factors become very important. For saturated rings the most stable chelates are formed when the rings are five membered and the next most stable when the rings are six membered. Four and seven membered rings are rare. Chelates have several important properties, including an increased stability over simple complexing agents. This can be explained qualitatively by noting that if one end of the chelate ring is exchanged with the surrounding media, the second end keeps the exchanged end in the vicinity of the central ion thus assuring a rapid reformation of the ring. Ligands such as NTA and EDTA form several rings and greatly enhance the stability of the complex formed. It is hoped that the 3,3',3"-phosphinidyenetripropionic acid, hereafter referred to as PTP, will form six membered rings and will form three rings with each central ion while occupying four coordination sites. The proposed structure of these chelates is given in figure 1.

For several years after Werner's work, the emphasis in the study of chelates and coordination compounds in general was in the discovery of new ligands and in the description of structures of complexes. Industrial use of chelating agents also began to be important as a spur to the development of these agents. Between 1935 and 1958 the production of EDTA, ethylenediaminetetraacetic acid, grew from nothing to over ten million pounds per year (3). Because of their ability to "remove" metal ions from reactions and their ability to form soluble complexes with metal ions, chelating agents have found such diverse uses as stabilization of ascorbic acid, which is sensitive to oxidation by Cu (II), to removing the heavy-metal based sprays which have been used as insecticides and fungicides from fruits and softening water. Chemists themselves found chelating agents very helpful, especially in analytical chemistry. The use of EDTA in determining metal ion concentration is very common today.

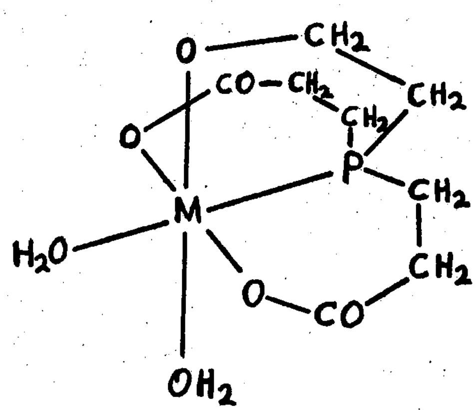

Figure 1. The Structure of PTP Complexes

The next great change in complex chemistry began with Bjerrum's (4) publication in 1941 of a study of the stability constants for the formation of metal ammines in aqueous solutions. Bjerrum viewed the formation of a complex in solution as the step-wise addition of ligands to the metal. Consider X steps in the formation of a complex where X is both the coordination number of the metal ion and the maximum number of ligands. We may now write X equations as follows:

$$M + A \rightleftharpoons MA; \quad k_1 = \frac{[MA]}{[M][A]}$$

$$MA + A \rightleftharpoons MA_2; \quad k_2 = \frac{[MA_2]}{[MA][A]}$$

$$MA_2 + A \rightleftharpoons MA_3 \quad k_3 = \frac{[MA_3]}{[MA_2][A]}$$

$$\vdots \qquad\qquad \vdots$$

$$MA_{x-1} + A \rightleftharpoons MA_x \quad k_x = \frac{[MA_x]}{[MA_{x-1}][A]}$$

k_1, k_2, ... k_x are the step-wise stability or formation constants which are related to the overall formation constant by

$$k_1 k_2 k_3 \cdot \cdot \cdot k = K \quad \frac{[MA]}{[M][A]}$$

In this description several simplifications are made. For example, the fact that water molecules are being replaced by ligands is ignored, and the charges neglected. In addition, the "constants" described above are conditional constants. They are constant only under prescribed conditions of constant ionic strength. For a more general comparison of stabilities to be made, thermodynamic constants are more useful. To find the thermodynamic constants, concentrations must be changed to activities, which is possible if the activity coefficients of the various ions present are known, since the activity of an ion equals the concentration of that ion times f_m where f_m is the activity coefficient for ions of charge m. At fairly low ionic strengths it is possible to calculate these from the Davies equation,

$$-\log f_i = Z_i^2 \times 0.509\left(\frac{\sqrt{u}}{1+\sqrt{u}} - 0.3u\right) .$$

Here Z_i is the charge of the ion and u is the ionic strength. The ionic strength is given by the expression:

$$u = \tfrac{1}{2} \sum Z_i X_i$$

where X_i is the concentration of all ionized species present. From these expressions, the thermodynamic formation constants can be calculated if the ionic strength is known. The thermodynamic formation constant is given by

$$K_f = \frac{[MA^{(m-y)+}]}{[M^{m+}]\,[A^{y-}]} \times \frac{f_{(m-y)}}{f_m\, f_y} .$$

Another way to calculate the thermodynamic stability constants is to measure the conditional constants at several values of ionic strength and extrapolate to zero ionic strength. The calculation of stability constants for complex formations can be very involved because of the complexity of the equilibrium system. However, the formation of chelates may simplify these calculations since a single ligand may occupy several of the possible sites around the central ion. Some ligands, including EDTA and NTA, are able to occupy a sufficient number of sites so that a 1 to 1 complex only is formed and k_1 becomes K_t. PTP should also be of this type if it can form three rings.

To experimentally evaluate the several formation constants, various methods are available. The choice of method depends upon which experimental variables can be measured. To find the concentration of free uncomplexed metal ion, it may be possible to use an electrode sensitive reversibly to the metal ion concentration and to do a potentiometric titration much in the same manner as one does a pH titration. Two other possible ways of finding the metal ion concentration are polarography and cation exchange on an ion-exchange resin. To find the concentration of the metal complex one can often use spectrophotometric methods. This method is applicable only where there is a color change associated with the complex formation. The most common experimental method and the one used in this report enables one to find the concentration of the free ligand by pH titration. If the ligand is a weak base, the concentrations of acid species may be determined by pH measurements if the ionization constants for the conjugate base are known. This method will be treated in greater detail in a following chapter, as it is the method used in this paper.

The Reasons for the Study of PTP

The study of PTP should be of interest for several reasons. Phosphorus chemistry has become much more important in recent years, especially in the preparation of novel organophosphorus compounds. Previously the main source of interest has been in its profound ability to form a stable bond with carbon. It is hoped that this study will help shed some light on organophosphorus compounds as ligands.

There are many reports in the literature on ligands with oxygen and nitrogen as donors, and a growing interest in sulfur is evident (5). So far phosphorus has had very little attention. The original suggestion for this study is due to Chatt, who has recently reported some exciting new complexes with the coinage metals in which phosphorus participates.

Phosphorus should behave very much like nitrogen as it has two electrons to donate, and its electronegativity is comparable to nitrogen, N = 3.0 and P = 2.1 (6). On the other hand, significant differences are to be expected since phosphorus has d orbitals available for π-d back bonding from the metal. From the standpoint of molecular orbital theory, this should greatly increase the effectiveness of phosphorus as a ligand. The effect of the back bonding of the phosphorus is somewhat offset by the fact that phosphorus is a larger atom than nitrogen and is therefore less basic in reactions.

Types of Experiments

The types of experiments carried out in preparation for this report include infared spectrographic studies and nuclear magnetic resonance studies which help to confirm the structure of the prepared compound. Also mass spectrographic studies and cryogenic freezing point determinations aided in the evaluation of the molecular weight of the prepared compound. Potentiometric titrations aided in the determination of the molecular weight as well as establishing both ionization constants of the acids and formation constants of the chelates.

CHAPTER II

EXPERIMENTAL AND THEORETICAL TREATMENT

Preparation and Identification

For the preparation of PTP, a sample of 3,3',3"-phosphinidyenetripropionitrile was obtained from the American Cyanamid Company. Simple acid hydrolysis converts this compound to the desired product.

$$\begin{array}{l} CH_2CH_2CN \\ | \\ P-CH_2CH_2CN \\ | \\ CH_2CH_2CN \end{array} + 6\,H_2O + 3\,HCl \rightleftharpoons$$

$$\begin{array}{l} CH_2CH_2COOH \\ | \\ P-CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{array} + 3\,NH_4Cl$$

In a typical preparation 1.0 grams of the nitrile were placed in 20ml. of 37% hydrochloric acid and heated for one hour at 55 to 65° C. Forty milliliters of water were then added and the mixture heated for six hours under reflux. The sample was reduced in volume over the steam bath until three fractions of crystals had been collected, the first two by filtration and the last by total evaporation over the steam bath. The first two fractions were dissolved in water and fractioned again into two new fractions. The first fractions in each case were pure enough to take a melting point. In one case this yielded 0.1374gms. of product that melted at 171.5 to 174 C. The yield was only 19% from these two fractions but was improved by further crystallization. Repeated fractional crystallization was necessary because the product is soluble only in very polar solvents such as dimethylsulfoxide (30% by weight), dimethylformamid (20% by weight) and water, as is the other principal product in the reaction, ammonium chloride.

To identify the product, an infrared spectrum was taken and is shown in figure 2. This indicates that the product is indeed a carboxylic acid but is not conclusive with respect to possible oxidation of the phosphorus to $P \rightarrow O$. Elemental analysis for phosphorus, carbon, and hydrogen provided the figures phosphorus 10.75%, carbon 37.91% and hydrogen 5.70%. This is not compatible with $P(CH_2CH_2COOH)_3$ but is compatible with the hydrochloride $HP(CH_2CH_2COOH)_3^+$ Cl^- of molecular weight 286.5. A mass spectrogram was taken of the material but unfortunately it was not possible to get the exact molecular weight, although the estimated result was 185amu. ±5amu as shown in figure 3. From freezing point depression experiments with methanol as solvent the molecular weight was calculated to be 134amu, but in this medium the hydrochloride would be ionized which would suggest a molecular weight of 268amu.

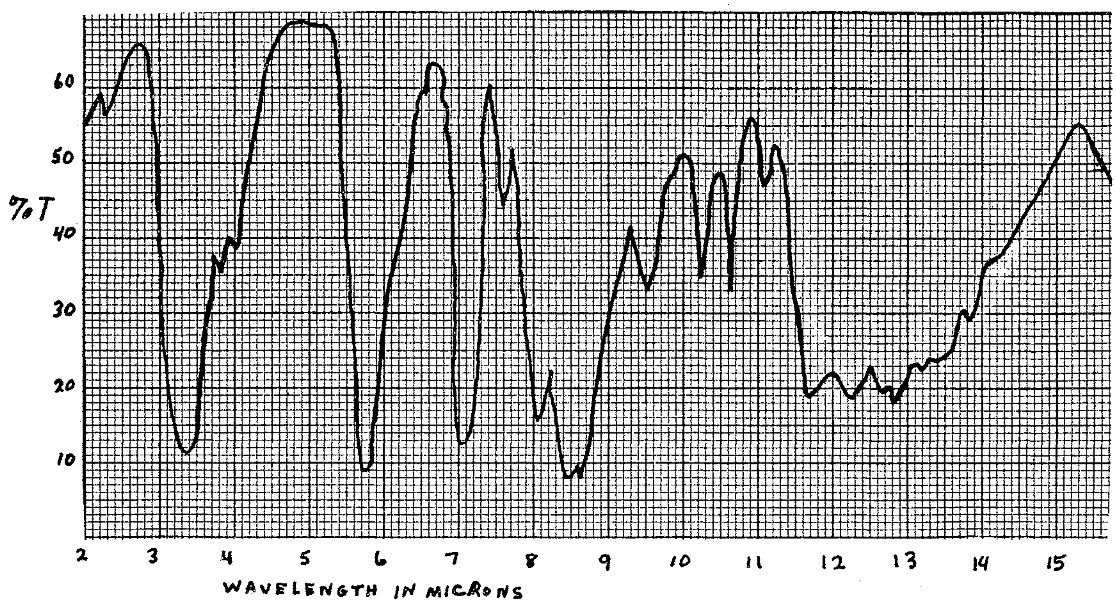

Figure 2. Infrared Spectrum of PTP Hydrochloride

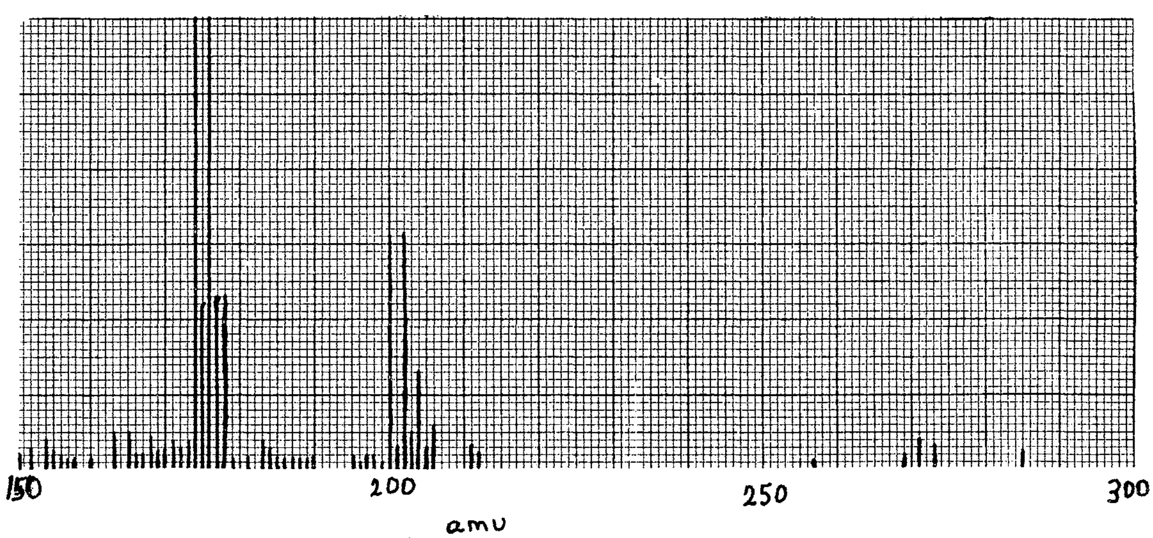

Figure 3. Mass Spectrogram of PTP Hydrochloride

Since the compound is a weak acid incomplete dissociation is perhaps responsible for the low molecular weight. The only real conclusion that could be drawn from this determination was that the product was not the simple acid PTP. Titration with base gave two end points, the second of which corresponded to four equivalents of base. The molecular weight was calculated to be 284amu. The graph of the titration is shown in figure 4.

A study of the proton magnetic resonance spectrum of the compound was made using a Varian A-60 spectrometer. It was extremely difficult to find a suitable solvent for this compound since the solution had to be from 30 to 40% by weight because of the high molecular weight of the compound. Only very polar solvents solvate this compound to any extent because of its ionic character. A 30% solution in water gave a very poor spectrum because of the high viscosity of the solution. A very broad water peak interfered with the analysis of the spectrum. Deuterium oxide was also tried as solvent and a pair of close quartets could be observed and identified as due to the methylene protons. The acidic protons were essentially absent because of exchange with deuterium. The acidic protons, however, were visible in a 30% solution in dimethylsulfoxide. A composite of the two spectra taken versus an external tetramethylsilane reference is given in figure 5. Exact integration of these spectra was not practical so no definite conclusion could be drawn as to the number of protons,

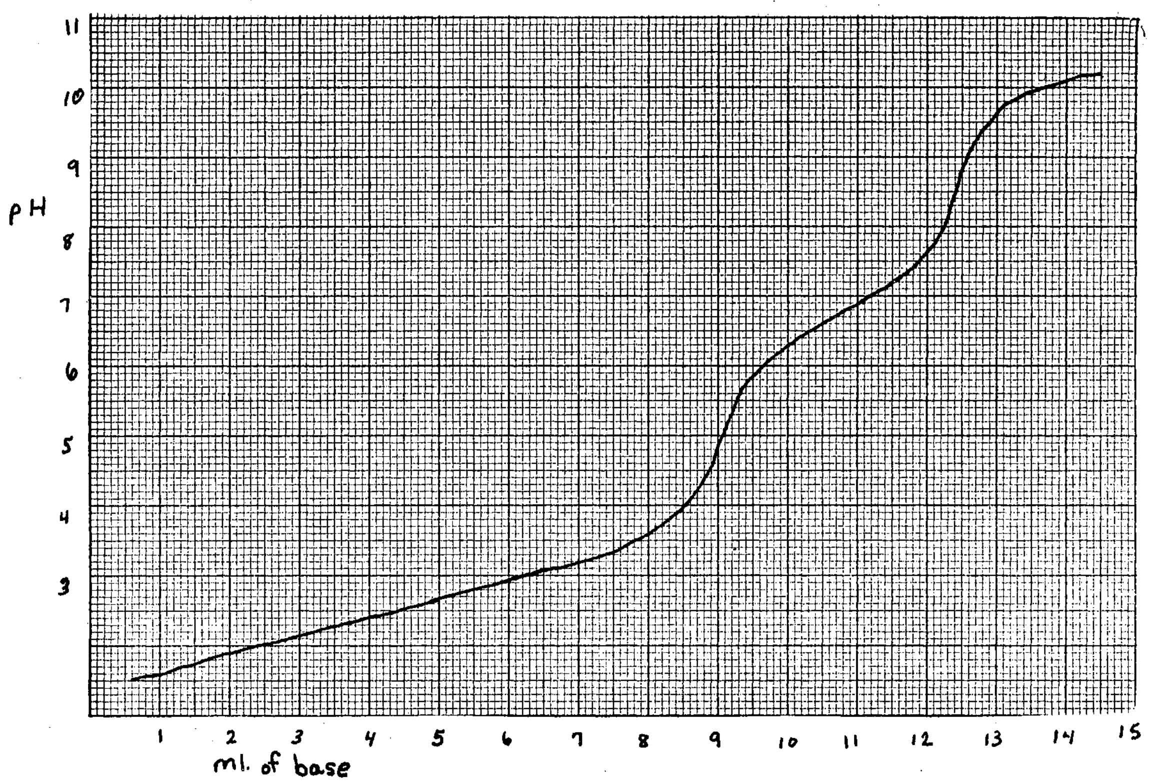

Figure 4. Titration of PTP Hydrochloride ($6,80 \times 10^{-3}$M) With 0.1106 M Base

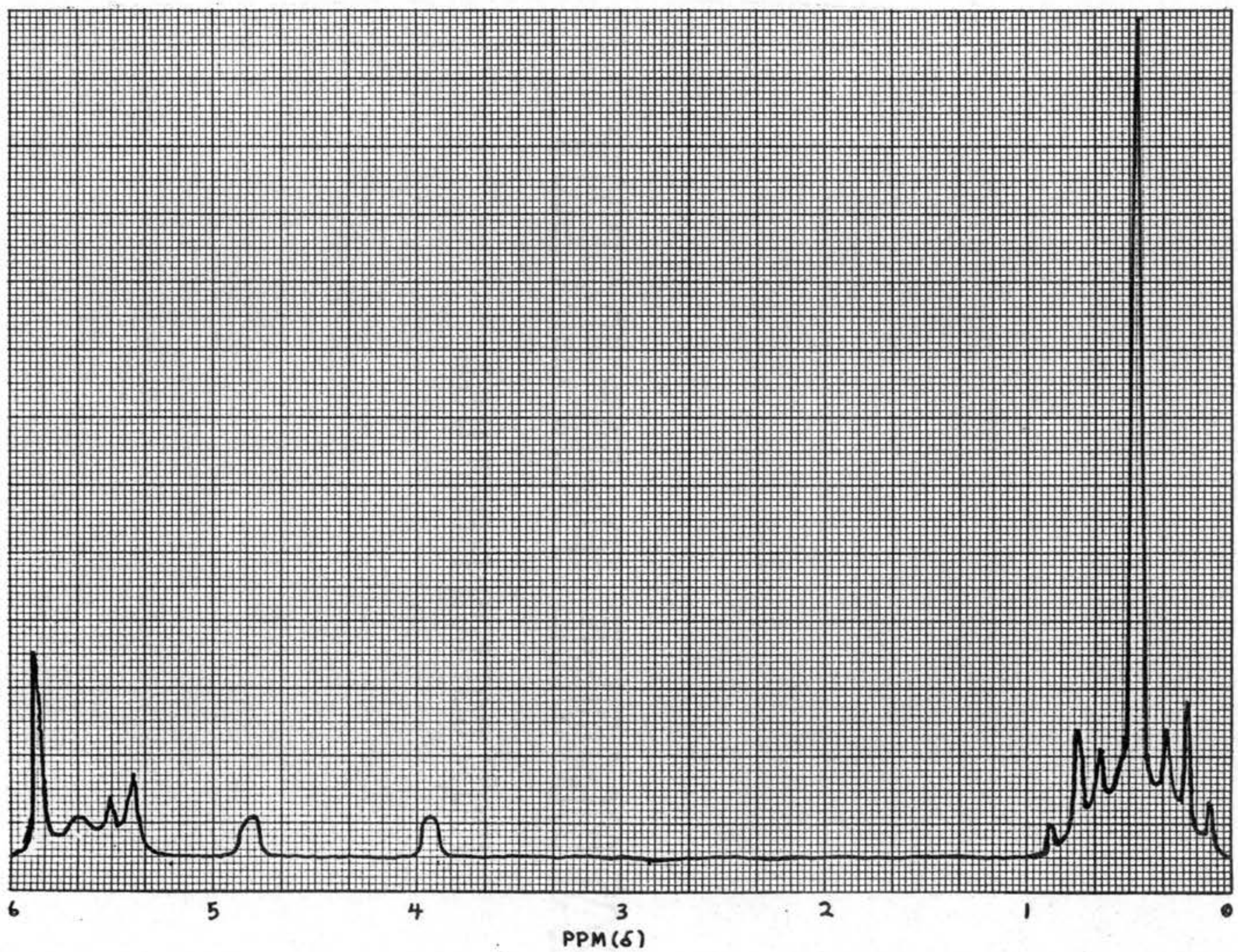

Figure 5. Composite PMR Spectrum of PTP Hydrochloride Versus a DMSO Standard

but there was general agreement with the results expected for the desired compound.

These several determinations, together with a sodium fusion test which indicated the presence of chloride, combined to identify the compound as PTP hydrochloride.

When the compound had been identified as the hydrochloride of PTP further search of the literature showed that it had been prepared by Rauhut (7). He prepared the PTP hydrochloride by base hydrolysis of the 3,3',3"-phosphinidyenetripropionitrile and reported a melting point of 175-177° C which agreed with the present result. Further search of the literature gave no evidence of use of this compound as a chelating agent.

Chemical Properties of PTP

Both PTP and the parent nitrile are unusual phosphorus compounds in their resistance to oxidation. Phosphorus differs from nitrogen in that it has vacant d orbitals and therefore, unlike nitrogen, it is not limited to three covalent bonds and one ionic or coordinate bond. In its compounds phosphorus will form five or six bonds by appropriate hybridization of its valence orbitals viz, sp^3d, and sp^3d^2 respectively. Because of this ability, most phosphines are easily air oxidized (8). Apparently this is one of the major reasons why phosphines have not been extensively studied in complex formation. On the other hand, comprehensive studies have been made of $P \rightarrow O$

containing ligands where the actual donor atom is oxygen. In the case of PTP the resistance to oxidation is probably a result of steric factors. The parent nitrile is also unusually resistant to oxidation but the corresponding 3,3'-phosphinidienedipropionitrile is readily oxidized in open air (7). This is good evidence that the functional groups themselves apparently have little to do with the resistance to oxidation. It should also be noted that triphenylphosphine, a very sterically hindered molecule, is also resistant to oxidation. The fact that in the hydrochloride the phosphorus, if protonated, will certainly stabilize the molecule to oxidation because of both the added steric blockage and the fact that the lone pair of phosphorus electrons are no longer available.

Determination of Ionization Constants

Since the potential ligand would be the acid with all its protons ionized, the fact that the material was PTP hydrochloride instead of PTP presumably would not cause any difficulties in chelate formation.

From the graph of the titration of the acid alone, figure 4, it is apparent that three protons are very similar with respect to dissociation. From the very symmetrical nature of the molecule it seemed likely that these were the protons from the carboxylic acids the fourth proton being associated with the phosphorus. This is analogous to Zwitter ion formation of the amino acids. Some of the reasons for the similarity in the ionization constants for the carboxylic acid functions include the fact that the central phosphorus has a localized positive charge which assists in the first ionization as this is a separation of a positive proton from a volume whose total charge is zero. The next proton comes off an essentially uncharged species so this is the simple separation of a positive and negative charge. The third proton essentially has to overcome the effect of two negative charges instead of three.

An argument presented by Schwarzenbach (9) for the dissociation of NTA proposes that for this amino acid the protons migrate from the carboxylic acids to the central nitrogen in rotation prior to ionization. This seems to be a false argument since the proton would be transferred to a more stable position when it moves from the carboxylate to the nitrogen and it seems very unlikely that the dissociation from nitrogen would be more acidic than the next carboxylic acid even though the nitrogen would then have a positive charge. Other triprotic amino acids ionize from the nitrogen only after the acid functions have lost all their protons (10). The phosphorus should be an even stronger acid than nitrogen but it is apparently still less acidic than the carboxylic acids.

All pH titrations were done using a Beckman Research pH meter, model 1019, with a cell with liquid junction.

Ag | AgCl, 1N HCl | glass | solution under study | saturated calomel

Nitrogen was bubbled through the solution for at least fifteen minutes or until the pH had stabilized before all titrations and continued during the titration. The temperature was kept at $25^{\circ} \pm 0.1^{\circ}$ C by a constant temperature bath. In the case of the acid titrations and the acid with zinc ion titrations the pH meter was standardized using Beckman standard buffer solutions at pH 4.01 and 6.86 respectively. In the case of the acid with copper ion titrations, cell E. M. F.'s were read and converted to pH readings by means of the following relationship.

$$(E_1 - E_2) = k(pH_2 - pH_1)$$

k is a constant equal to 2.303RT/F which was evaluated by measuring the cell EMF when the solutions under study were the same standard buffer solutions. Both of these methods have the advantage of cancelling out the asymmetry potential and liquid junction potentials in the range of the experiment provided that these are changing linearly.

Analysis of the data was difficult because the first three ionizations overlap to produce a single buffer region. A graphical treatment for two overlapping ionizations has been reported for succinic acid by Speakman (11). However, to evaluate the first three ionization constants unambiguously, it was necessary to derive an equation for the three constants in terms of the analytical acid and base concentrations and hydrogen ion activity. The equation (see below) is cubic in hydrogen ion concentration and a graphical solution was not feasible.

In the equations for total acid

$$a = [H_4A^+] + [H_3A] + [H_2A^-] + [HA^=] \qquad 1$$

and for electroneutrality

$$b + [H^+] [OH^-] + [H_4A^+] = [H_2A^-] + 2[HA^=] + a \qquad 2$$

where b is the analytical base concentration, all acid species can be written in terms of $[H_4A^+]$ using the expressions for the stepwise dissociation constants.

$$K_1 = \frac{h[H_3A]}{[H_4A^+]f_1} \; ; \qquad [H_3A] = \frac{K_1[H_4A^+]f_1}{h} \qquad 3$$

$$K_2 = \frac{h[H_2A^-]f_1}{[H_3A]} \; ; \qquad [H_2A^-] = \frac{K_1K_2[H_4A^+]}{h^2} \qquad 4$$

$$K = \frac{h[HA^=]f_2}{[H_2A^-]f_1} \; ; \qquad [HA^=] = \frac{K_1K_2K_3[H_4A^+]f_1}{h^3 \quad f_2} \qquad 5$$

where f_i is the activity coefficient of the ion of charge $|i|$ and h is the hydrogen ion activity. Note: In this region both $[A^{\equiv}]$ and $[OH^-]$ are considered negligible.

Substituting from equations 3, 4 and 5 into equations 1 and 2 gives

$$[H_4A^+] = \frac{(b+h-oh-a)}{\left(-1+\frac{K_1K_2}{h^2}+\frac{2K_1K_2K_3f_1}{h^3f_2}\right)} = \frac{(b+h-oh-a)}{\left(\frac{-h^3f_2+hf_2K_1K_2+2K_1K_2K_3f_1}{h^3f_2}\right)}$$

$$a = \left(\frac{h^3f_2+K_1h^2f_1f_2+K_1K_2hf_2+K_1K_2K_3f_1}{h^3f_2}\right)[H_4A^+]$$

$$a = \left(\frac{h^3f_2+K_1h^2f_1f_2+K_1K_2hf_2+K_1K_2K_3f_1}{h^3f_2}\right)\left(\frac{(b+h-OH-a)(H^3f_2)}{-h^3f_2+hf_2K_1K_2+2K_1K_2K_3f_1}\right).$$

$$-ah^3f_2 + ahf_2K_1K_2 + 2aK_1K_2K_3f_1 = (b+h-oh-a)h^3f_2 + (b+h-oh-a)K_1h^2f_1f_2 + (b+h-oh-a)K_1K_2hf_2 + (b+h-oh-a)K_1K_2K_3f_1$$

$$(b+h-oh)h^3f_2 = K_1(-b-h+oh+a)h^2f_1f_2 + K_1K_2(2a-b-h+oh)hf_2 + K_1K_2K_3(3a-b-h+oh)f_1$$

$$\frac{(b+h-oh)h^3f_2}{(3a-b-h+oh)f_1} = \frac{K_1(a-b-h+oh)h^2f_2}{(3a-b-h+oh)} + \frac{K_1K_2(2a-b-h+oh)hf_2}{(3a-b-h+oh)\quad f_1} + K_1K_2K_3$$

Let $L = b+h-oh$

$M = a-b+oh$

$N = 2a-b-h+oh$

$p = 3a-b-h+oh$

$$\frac{Lh^3f_2}{pf_1} = \frac{K_1Mh^2f_2}{p} + \frac{K_1K_2Nhf_2}{pf_1} + K_1K_2K_3 \qquad 6$$

Thus equation 6 is the final solution and is cubic in h.

Activity coefficients f_i are evaluated using the Davies equation

$$-\log f_i = Z_i^2(0.509)\left(\frac{\sqrt{u}}{1+\sqrt{u}} - 0.3u\right) \qquad 7$$

and the ionic strength u is given by

$$u = b + h + [H_4A^+] + [HA^=] \qquad 8$$

Constant f_i values and ionization constants were obtained by successively recycling around equations 6, 7, and 8.

Analysis required the simultaneous solution of three equations of type 6 for three points selected at random from the first buffer region. To relieve the burden of this calculation, the following computer program was written:

```
   READ(5,100)ACID,HYDROX
 1 READ(5,100)VOLAA,PHA,VOLBA
   READ(5,100)VOLAB,PHB,VOLBB
   READ(5,100)VOLAC,PHC,VOLBC
   VOLTA=VOLBA+VOLAA
   TBA=VOLBA*HYDROX/VOLTA
   HA=EXP(-2.302585*PHA)
   TAA=VOLAA*ACID/VOLTA
   UA=TBA+HA
   VOLTB=VOLBB+VOLAB
   TBB=VOLBB*HYDROX/VOLTB
   HB=EXP(-2.302585*PHB)
   TAB=VOLAB*ACID/VOLTB
   UB=TBB+HB
   VOLTC=VOLBC+VOLAC
   TBC=VOLBC*HYDROX/VOLTC
   HC=EXP(-2.302585*PHC)
   TAC=VOLAC*ACID/VOLTC
   UC=TBC+HC
   DO 4 I=1,5
   SA=0.509*((UA**0.5/(1.0+UA**0.5))-0.3*UA)
   FIA=EXP(SA*(-2.302585))
```

```
F2A=EXP(4.0*SA*(-2.302585))
XA=((TBA+HA)*HA**3.0*F2A)/((3.0*TAA-TBA-HA)*FIA)
YA=((TAA-TBA-HA)*HA**2.0*F2A)/(3.0*TAA-TBA-HA)
ZA=((2.0*TAA-TBA-HA)*HA*F2A)/((3.0*TAA-TBA-HA)*F1A)
SB=0.509*((UB**0.5/(1.0+UB**0.5))-0.3*UB)
F1B=EXP(SB*(-2.302585))
F2B=EXP(4.0*SB*(-2.302585))
XB=((TBB+HB)*HB**3.0*F2B)/((3.0*TAB-TBB-HB)*F1B)
YB=((TAB-TBB-HB)*HB**2.0*F2B)/(3.0*TAB-TBB-HB)
ZB=((2.0*TAB-TBB-HB)*HB*F2B)/((3.0*TAB-TBB-HB)*F1B)
SC=0.509*((UC**0.5/(1.0+UC**0.5))-0.3*UC)
FIC=EXP(SC*(-2.302585))
F2C=EXP(4.0*SC*(-2.302585))
XC=((TBC+HC)*HC**3.0*F2C)/((3.0*TAC-TBC-HC)*F1C
YC=((TAC-TBC-HC)*HC**2.0*F2C)/(3.0*TAC-TBC-HC)
ZC=((2.0*TAC-TBC-HC)*HC*F2C)/((3.0*TAC-TBC-HC)*F1C)
XD=XA-XC
YD=YA-YC
ZD=ZA-ZC
XF=XB-XC
YE=YB-YC
ZE=ZB-ZC
XF=XD/ZD
YF=YD/ZD
XG=XE/ZE
YG=YE/ZE
XH=XG-XF
```

```
      YH=YG-YF
      CK1=XH/YH
      CK2=(XF/CK1)-YF
      CK3=(XA/(CK1*CK2))-(YA/CK2)-ZA
      DENA=(HA**3.0+(HA**2.0)*CK1+HA*CK1*CK2+CK1*CK2*CK3)
      H4A=(HA**3.0)*TAA/DENA*F1A
      H1A=(CK1*CK2*CK3)*TAA/DENA*F2A
      DENB=(HB**3.0+(HB**2.0)*CK1+HB*CK1*CK2+CK1*CK2*CK3)
      H4B=(HB**3.0)*TAB/DENB*F1B
      H1B=(CK1*CK2*CK3)*TAB/DENB*F2B
      DENC=(HC**3.0+(HC**2.0)*CK1+HC*CK1*Ck2+CK1*CK2*CK3)
      H4C=(HC**3.0)*TAC/DENC*F1C
      H1C=(CK1*CK2*CK3)*TAC/DENC*F2C
      UNEWA=TBA+HA+H4A+H1A
      UA=UNEWA
      UNEWB-(TBB+HB+H4B+H1B)
      UB=UNEWB
      UNEWC=TBC+HC+H4C+H1C
      UC=UNEWC
      WRITE(6,100)SA
      WRITE(6,100)VOLBA
      WRITE(6,100)VOLBA,VOLBB,VOLBC
      WRITE(6,100)CK1,CK2,CK3
    4 CONTINUE
      GOTO1
  100 FORMAT (4E15.7)
    8 STOP
```

The average values from fifty-one independent selections were used as the best values for ionization constants. These values were, $K_1 = 1.31 \times 10^{-3}$, $K_2 = 1.51 \times 10^{-4}$, and $K_3 = 2.07 \times 10^{-5}$.

To find K_4, more normal procedures could be used. Since it was different from K_3 by a factor of approximately one thousand, the ionization could be treated as the ionization of a monoprotic acid.

$$HA^{=} \rightleftharpoons H^{+} + A^{\equiv} \qquad 9$$

Therefore we may write

$$pK_4 = pH - \log \frac{[A^{\equiv}]}{[HA^{=}]} - \log \frac{f_3}{f_2}$$

$$pK_4 = pH - \log \frac{[A^{\equiv}]}{[HA^{=}]} - \log f_3 + \log f_2$$

$$pK_4 = pH - \log \frac{[A^{\equiv}]}{[HA^{=}]} + 9(.509)\left(\frac{\sqrt{u}}{1+\sqrt{u}} - 0.3u\right) - (.509)4\left(\frac{\sqrt{u}}{1+\sqrt{u}} - 0.3u\right)$$

$$pK_4 = pH - \log \frac{[A^{\equiv}]}{[HA^{=}]} + 2.545\left(\frac{\sqrt{u}}{1+\sqrt{u}} - 0.3u\right)$$

$$a = [HA^{=}] + [A^{\equiv}] \; ; \quad [A^{\equiv}] = a - [HA^{=}]$$

$$b + h = 2[HA^{=}] + 3[A^{\equiv}] + 9$$

$$b + h = 3a - [HA^{=}] + a \; ; \; [HA^{=}] = 4a - b - h$$

$$[A^{\equiv}] = a - 4a + b + h \; ; \; [A^{\equiv}] = b + h - 3a$$

$$pK_4 = pH - \log \frac{b + h - 3a}{4a - b - h} + 2.545\left(\frac{\sqrt{u}}{1+\sqrt{u}} - 0.3u\right) \qquad 10$$

This derivation removes the need to cycle the activity coefficients. The ionic strength expression is derived as follows:

$$u = \frac{1}{2}(b+h+4[HA^{=}]+9[A^{\Xi}]+a)$$

$$u = \frac{1}{2}(b+h+16a-4b-4h+9b+9h-27a+a)$$

$$u = \frac{1}{2}(6b+6h-10a)$$

$$u = (3b+3h-5a) \qquad 11$$

The following table of values was obtained from a treatment with the expressions derived above:

TABLE I

VALUES OF pK_4

ml. base	pH	ux10^2	pK_4
25.0	7.677	3.909	8.408
25.2	7.731	3.962	8.412
26.0	7.224	4.168	8.415
27.0	8.149	4.421	8.420
28.0	8.408	4.667	8.434
29.0	8.749	4.906	8.440
29.4	8.928	5.000	8.412
		ave. =	8.421

The value of K_4 was taken to be 3.79×10^{-9}.

Treatment of Complex Formation Constants

Metal complex formation with PTP was examined by titrating PTP with sodium hydroxide solution after the addition of varying amounts of copper (II) perchlorate and zinc (II) perchlorate and analyzing the data in the new buffer regions. Neither the sodium ions nor the perchlorate ions should enter into complex formation to any appreciable extent. Copper (II) was chosen as a first example because from the Irving-Williams order it forms the most stable complexes with most ligands and zinc (II) because of its possible different coordination. Several other metal ions would have been studied except for lack of time.

From Bjerrum's treatment of complex formation we see that if a single complex is formed the following equilibrium is set up:

$$[M^{2+}] + [A^{3-}] \rightleftharpoons [MA^{-}] \qquad 12$$

This affects the pH by lowering the concentration of $[A^{\equiv}]$, which causes the acid to ionize and hence decrease the pH.

PTP might be expected to form a single complex if it behaves like the amino acids to which it is related. NTA and nitrilotripropionic acid both form only a single complex over a wide range of pH and ligand concentration (3).

Titrations were run using Cu (II) and Zn (II) in the ratios to ligand of one to two, one to one, and two to one. The results of these titrations are shown in figures 6, 7, 8, 9, 10, and 11. The depression of the pH definitely showed complex formation and the regularity of the curves indicated that a one to one complex was being formed.

The reasons for varying the ratio of metal to ligand are two fold. First, as a check on the accuracy of the titrations and second, to determine if two complexes of the types MA^{-} and MA_2^{4-}, MA^{-} and MHA were being formed. The formation of MA_2^{4-} or MHA would be almost eliminated in the

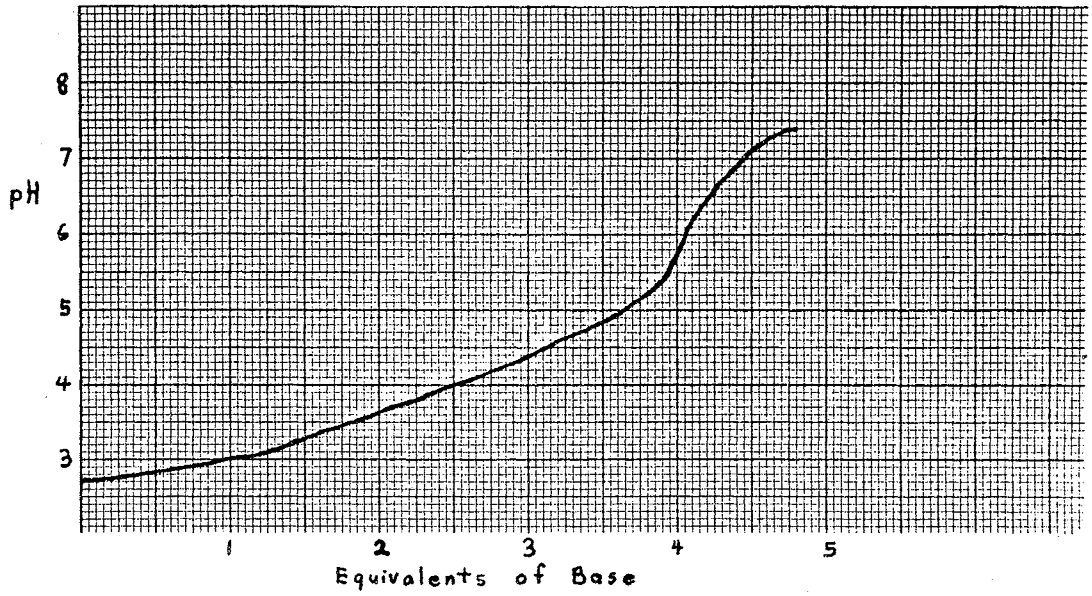

Figure 6. Titration With Cu^{2+} in a One to Two Ratio With PTP Hydrochloride Using $7.866x10^{-3}$M NaOH

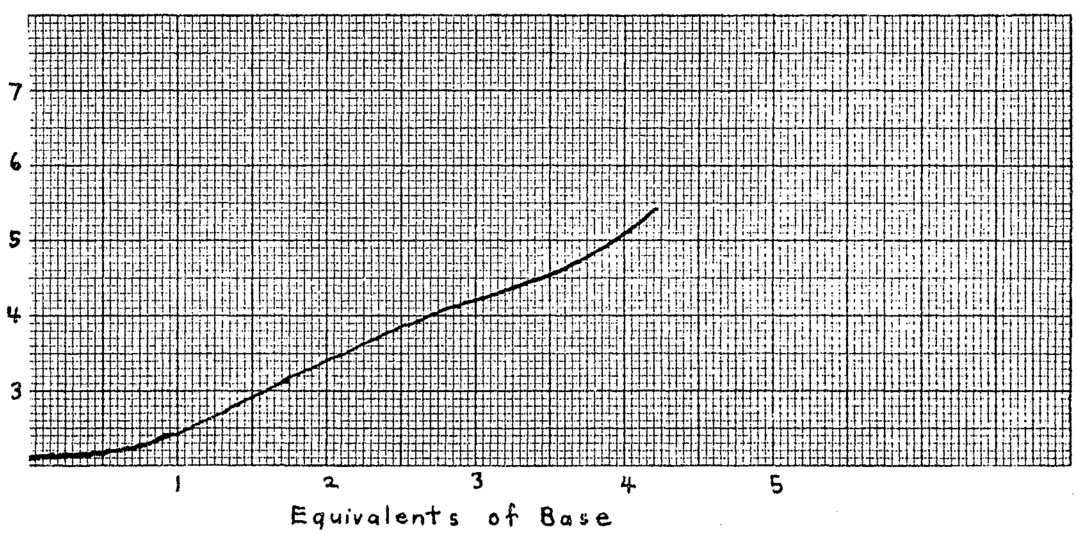

Figure 7. Titration With Cu^{2+} in a One to One Ratio With PTP Hydrochloride Using $7.866x10^{-3}$ NaOH

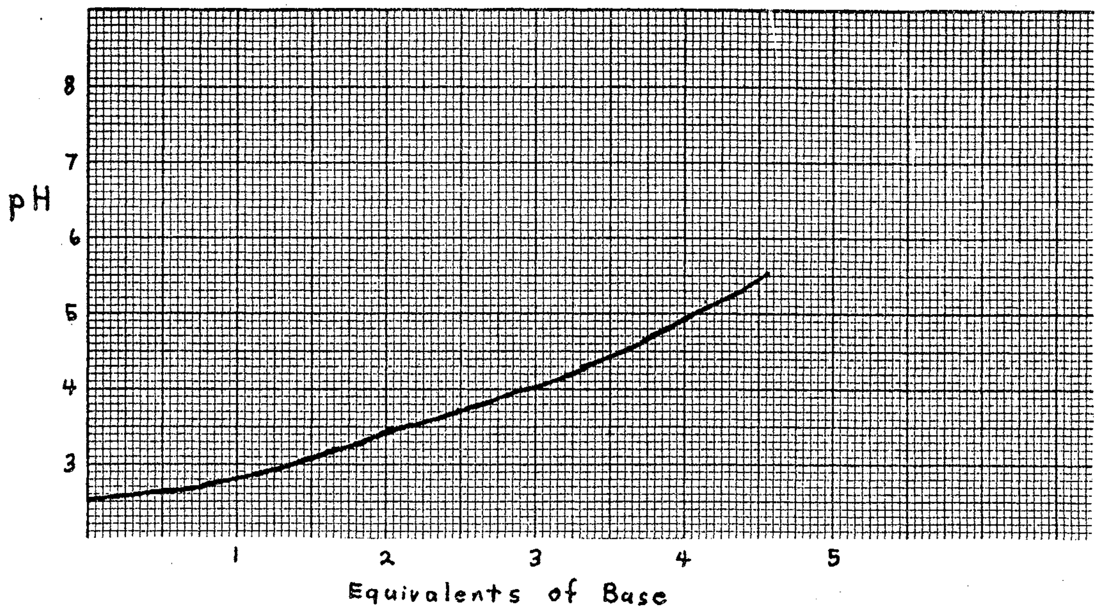

Figure 8. Titration With Cu^{2+} in a Two to One Ratio With PTP Hydrochloride Using 7.866×10^{-3} M NaOH

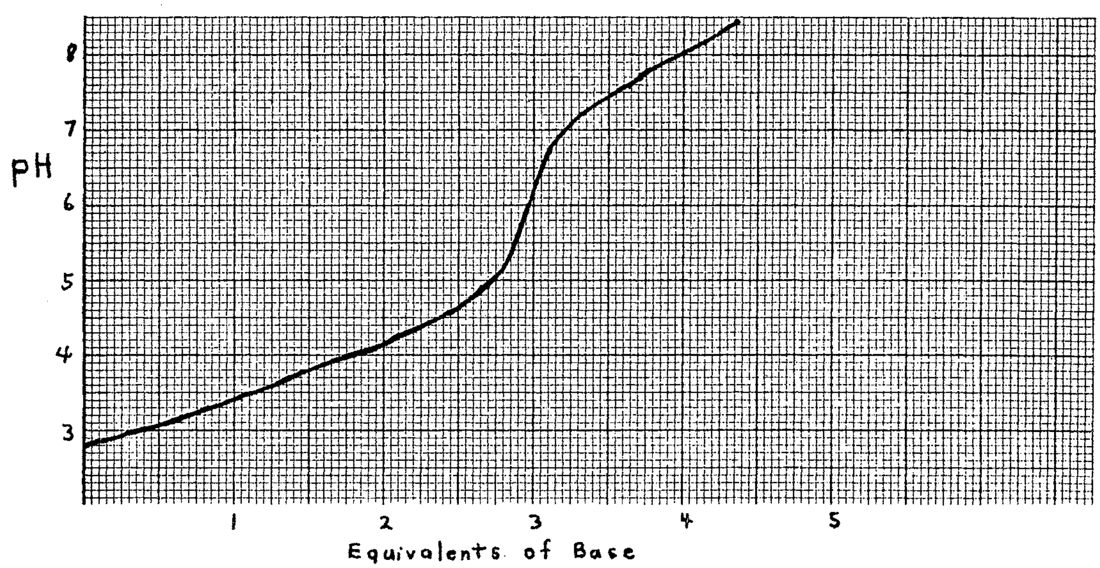

Figure 9. Titration With Zn^{2+} in a One to Two Ratio With 3.0415×10^{-3}M PTP Hydrochloride Using 7.866×10^{-2}M NaOH

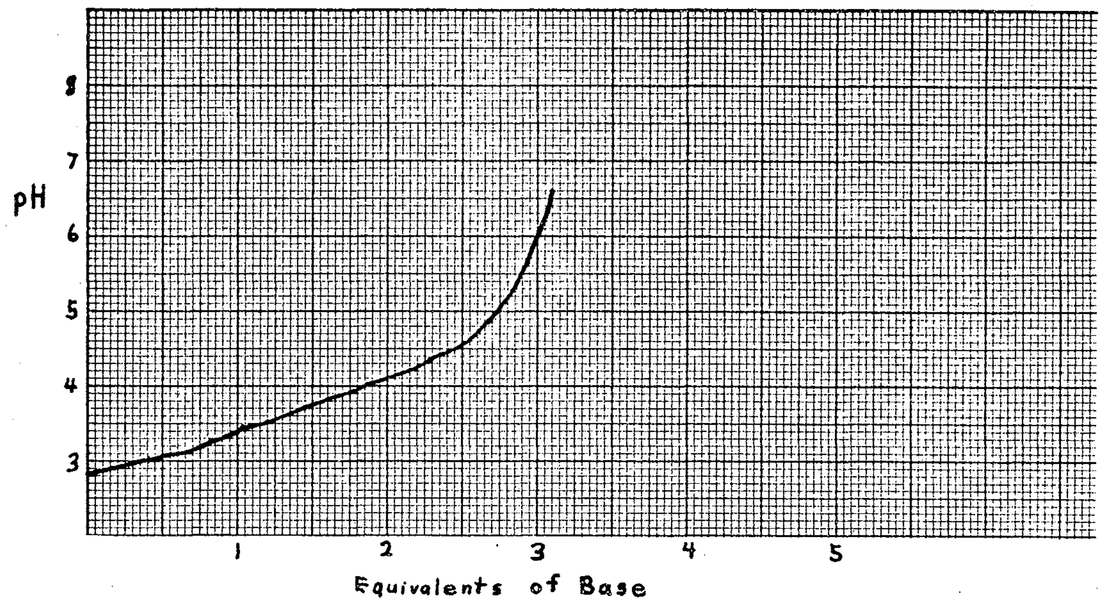

Figure 10. Titration With Zn^{2+} in a One to One Ratio With 3.0415×10^{-3}M PTP Hydrochloride Using 7.866×10^{-2}M NaOH

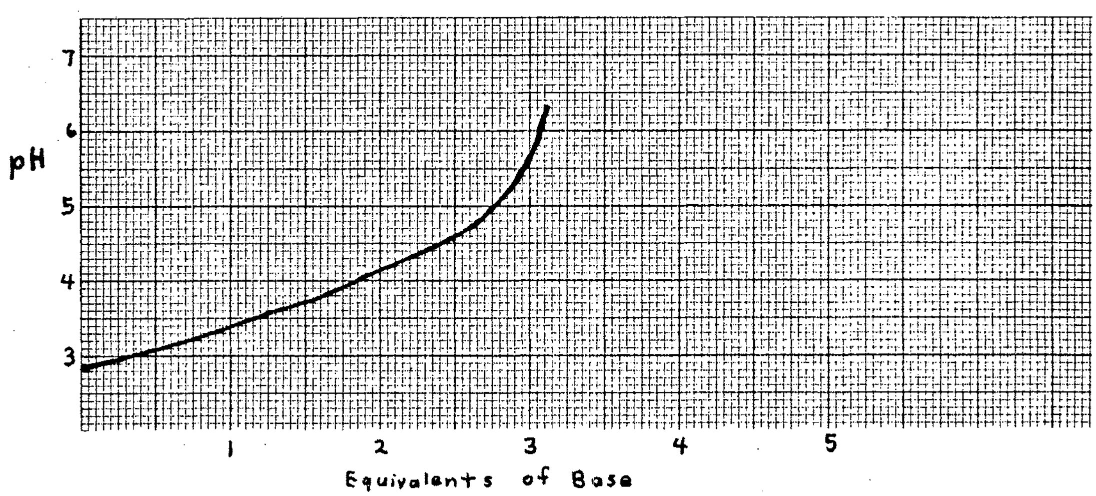

Figure 11. Titration With Zn^{2+} in a Two to One Ratio With 3.0415×10^{-3}M PTP Hydrochloride Using 7.866×10^{-2}M NaOH

case where the concentration of the metal ion was in excess over that of the ligand if the formation constants of the complexes varied by at least a factor of one hundred. One would expect the treatment of the case in which the metal ion was in excess to give a constant K_f but a varying K_f would be obtained for the case in which the ligand was in excess if two complexes are being formed.

The treatment for a single complex is fairly simple, as is shown in the following derivation: The concentrations of ionic species may be calculated from the equations for the thermodynamic dissociation constants for the acid

$$K_1 = \frac{h[H_3A]}{[H_4A^+]f_1} \qquad 3$$

$$K_2 = \frac{h[H_2A^-]f_1}{[H_3A]} \qquad 4$$

$$K_3 = \frac{h[HA^=]f_2}{[H_2A^-]f_1} \qquad 5$$

$$K_4 = \frac{h[A^{\equiv}]f_3}{[HA^=]f_2} \qquad 13$$

for total acid concentration

$$a = [H_4A^+] + [H_3A] + [H_2A^-] + [HA^=] + [A^{\equiv}] + [MA^-] \qquad 14$$

for total metal

$$m = [M^{2+}] + [MA^-] \qquad 15$$

and for electroneutrality

$$b + h + [H_4A^+] + 2[M^{2+}] = [H_2A^-] + 2[HA^=] + 3[A^{\equiv}] + [MA^-] + a + 2m \quad . \qquad 16$$

Solving equations 3, 4, 5, and 13 in terms of $[A^{\equiv}]$ gives

$$[HA^{=}] = \frac{h\ f_3 [A^{\equiv}]}{K_4 f_2}$$

$$[H_2A^-] = \frac{h\ f_2 [HA^{=}]}{K_2} = \frac{h^2 f_3 [A^{\equiv}]}{K_3 K_4\ f_1}$$

$$[H_3A] = \frac{h f_1 [H_2A^-]}{K_2} = \frac{h^3 f_3 [A^{\equiv}]}{K_2 K_3 K_4}$$

$$[H_4A^+] = \frac{h\ \ [H_3A]}{K_1\ \ f_1} = \frac{h^4\ f_3\ \ \ [A^{\equiv}]}{K_1 K_2 K_3 K_4\ f_1} \ .$$

Let

$$Q = \frac{h^4\ \ \ \ \ \ f_3}{K_1 K_2 K_3 K_4 f_1} \ , \quad [H_4A^+] = Q[A^{\equiv}]$$

$$R = \frac{h^3\ \ \ \ f_3}{K_2 K_3 K_4} \ , \quad [H_3A] = R[A^{\equiv}]$$

$$S = \frac{h^2\ f_3}{K_3 K_4 f_1} \ , \quad [H_2A^-] = S[A^{\equiv}]$$

$$T = \frac{h\ f_3}{K_4\ f_2} \ , \quad [HA^{=}] = T[A^{\equiv}]$$

$$a = (Q + R + S + T + 1)[A^{\equiv}] + [MA^-] \qquad 17$$

$$b + h + Q[A^{\equiv}] + 2[M^{2+}] = (S + 2T + 3)[A^{\equiv}] + [MA^-] + a + 2m$$

$$b + h + 2[M^{2+}] = (S + 2T - Q + 3)[A^{\equiv}] + [MA^-] + a + 2m \ . \qquad 18$$

Let $\quad \gamma = (Q + R + S + T + 1) \ .$

Then $\quad a = \gamma[A^{\equiv}] + [MA^-]; \ \ [MA^-] = a - \gamma[A^{\equiv}] \ . \qquad 19$

Substitute 19 into 18

$$b + h + 2[M^{2+}] = (S + 2T - Q + 3)[A^{\equiv}] + a - \gamma[A^{\equiv}] + a + 2m$$

$$b + h + 2[M^{2+}] = (T - 2Q - R + 2) + 2a + 2m \qquad 20$$

15 minus 19 is $\quad [M^{2+}] = m - a + \gamma[A^{\equiv}] \ .$

Substitute this in 20

$$b + h - 2a + 2\gamma[A^{=}] = (T - 2Q - R + T)[A^{=}] + 2a$$

$$b + h + (2Q + 2R + 2S + 2T + 2)[A^{=}] = (T - 2Q - R + 2)[A^{=}] + 4a$$

$$[A^{=}] = \frac{4a - b - h}{(4Q + 3R + 2S + T)} \quad . \qquad 21$$

$$[MA^{-}] = a - \gamma[A^{=}] \quad ; \quad [M^{2+}] = m - a + \gamma[A^{=}]$$

For the ionic strength we may write

$$U = b + h + (Q + Z + 3)[A^{=}] + 3[M^{2+}] \quad . \; 22$$

From the final expressions derived above the formation constant could be determined from each experimental pH value if an exact value for the ionic strength was known. The best way to find the ionic strength is to guess at a good value for the first ionic strength and then cycle as was done for the ionization constants.

The following computer program used the equations derived above and cycled for the ionic strength ten times. The ionic strength term became essentially constant after three cycles.

```
  READ(5,100)CK1,CK2,CK3,CK4
  READ(5,101)ACID,HYDROX,CMETAL
1 READ(5,100)VOLB,VOLM,VOLA,PH
  H=EXP(-2.302585*PH)
  VOLT=VOLB+VOLM+VOLA
  TA=VOLA*ACID/VOLT
  TM=VOLM*CMETAL/VOLT
  TB=VOLB*HYDROX/VOLT
  U=TB+H
```

```
      DO 4 I=1,10
      S=0.409*((U**9.5/(1.0+U**0.5))-0.3*U)
      WRITE(6,100)U,S,TB,H
      WRITE(6,100)TM,TA,VOLT,PH
      WRITE(6,100)VOLB,VOLM,VOLA,ACID
      WRITE(6,100)HYDROX,CMETAL
      WRITE(6,100)CK1,CK2,CK3,CK4
      F1=EXP(S*(-2.302585))
      F2=EXP(4.0*s*(-2.302585))
      F3=EXP(9.0*S)(-2.302585))
      WRITE(6,103)F1,F2,F3
      X=H**4.0*F3/(CK1*CK2*CK3*CK4*F1)
      Y=H**3.0*F3/(CK2*CK3*CK4)
      Z=H**2.0*F3/(CK3*CK4*F1)
      W=X+Y+Z+(H*F3/(CK4*F2))+1.0
      A=(4.0*TA-TB-H)/(4.0*X+3.0*Y=2.0*Z+(H*F3/(CK4*F2)))
      WA=W*A
      CMA=TA-W*A
      CM2=TM-TA+W*A
      WRITE(6,100)X,Y,Z,W
      WRITE(y,100)CMA,CM2,A,WA
      UNEW=TB+H+X*A+3.0*CM2+(H*F3*A/(CK4*F2))+3.0*A
      U=UNEW
    4 CONTINUE
      CKMA=CMA*F1/(CM2*F2*F3)
      WRITE(6,104)VOLB,CKMA
      GOTO1
```

```
100 FORMAT(4E15.7)
101 FORMAT(3E15.7)
103 FORMAT(1HO,5HF1 = ,E15.7,2X,5HF2 = ,E15.7,2X,5HF3 =
   ,E15.7)
104 FORMAT(1HO,7HVOLB = ,E15.7,2X,7HCKMA = ,E15.7)
  8 STOP
```

No constant nor near constant value for the formation constant was obtained for either zinc (II) or copper (II) under any conditions. This would indicate possibly that two complexes are being formed. Because of limited time for this study, this conclusion is not absolutely established. The original plan at this point called for careful re-evaluation of the experimental data followed by an attempt to obtain constant formation constants for the case in which there are two complexes formed.

For the first case in which there are two complexes the following complexes seem likely:

$$M^{2+} + A^{=} \rightleftharpoons MA^{-}$$

$$M^{2+} + HA \rightleftharpoons MHA$$

This situation is similar to one described by Scwarzenbach (13) for EDTA. The following is the derivation of formulas to treat this case: From the formation constants we obtain

$$K_{MA} = \frac{[MA^{-}]}{[M^{2+}][A^{=}]} \frac{f_1}{f_2 f_3}$$

$$K_{MHA} = \frac{[MHA]}{[M^{2+}][HA^{=}]\ 2f_2} \ ; \quad [MHA] = \frac{K_{MHA}\,[M^{2+}]\,h\,f_3}{K_4 \quad f_2}$$

From the ionization constants we obtain

$$K_1 = \frac{h[H_3A]}{[H_4A^+]f_1} \quad ; \quad [H_4A^+] = \frac{h^4 \quad f_3[A^{\equiv}]}{K_1K_2K_3K_4 f_1}$$

$$K_2 = \frac{h[H_2A^-]f_1}{[H_3A]} \quad ; \quad [H_3A] = \frac{h^3 \ f_3 \ [A^{\equiv}]}{K_2K_3K_4}$$

$$K_3 = \frac{h[HA^=]f_2}{[H_2A^-]f_1} \quad ; \quad [H_2A^-] = \frac{h^2[A^{\equiv}]f_3}{K_3K_4 f_1}$$

$$K_4 = \frac{h[A^{\equiv}]f_3}{[HA^=]f_2} \quad ; \quad [HA^=] = \frac{h[A^{\equiv}]f_3}{K_4 \quad f_2} \quad .$$

The analytical concentration of the acid is given by

$$a = [H_4A^+] + [H_3A] + [H_2A^-] + [HA^=] + [A^{\equiv}] + [MHA] + [MA^-].$$

From the electroneutrality principal we can write

$$b + h + [H_4A^+] + 2[M^{2+}] = [H_2A^-] + a + 2m + 2[HA^=] + 3[A^{\equiv}] + [MA^-] \; .$$

The total metal concentration is given by

$$m = [M^{2+}] + [MHA] + [MA^-] \qquad .$$

These equations may be rearranged as follows

$$a = \left(\frac{h^4 \quad f_3}{K_1K_2K_3K_4 f_1} + \frac{h^3 \quad f_3}{K_2K_3K_4} + \frac{h^2 \quad f_3}{K_3K_4 f_1} + \frac{h \ f_3}{K_4 f_2} + 1\right)[A^{\equiv}] +$$

$$[MHA] + [MA^-]$$

Let $$\gamma = \left(\frac{h^4 \quad f_3}{K_1K_2K_3K_4 f_1} + \frac{h^3 \ f_3}{K_2K_3K_4} + \frac{h^2 \quad f_3}{K_3K_4 f_1} + \frac{h \ f_3}{K_4 f_2} + 1\right)$$

$$a = \gamma [A^{\equiv}] + [MHA] + [MA^-]$$

$$[MHA] + [MA^-] = a - \gamma[A^{\equiv}]$$

$$[M^{2+}] = m - ([MHA] + [MA^-]) = m - a + \gamma[A^{\equiv}]$$

$$b + h + \frac{h^4 \qquad f_3[A^{\equiv}]}{K_1K_2K_3K_4\ f_1} + \quad 2[M^{2+}] = \frac{h^2\ f_2\ [A^{\equiv}]}{K_3\ K_4\ f_1} + a +$$

$$2m + 2\left(\frac{h\ [A^{\equiv}]\ f_3}{K_4 \quad f_2}\right) + 3[A^{\equiv}] + [MA^-] \ .$$

Let

$$W = \frac{h^4 \qquad f_3}{K_1K_2K_3K_4\ f_1} \ ,$$

$$X = \frac{h^3 \qquad f_3}{K_2K_3K_4} \ ,$$

$$Y = \frac{h^2 \quad f_3}{K_3\ K_4\ f_1} \ ,$$

$$Z = \frac{h\ \ f_3}{K_4\ f_2} \ .$$

Therefore

$$b + h + W[A^{\equiv}] + 2[M^{2+}] = Y[A^{\equiv}] + a + 2m + 2Z[A^{\equiv}] + 3[A^{\equiv}] + [MA^-]$$

$$b + h - 2a + 2\gamma[A^{\equiv}] + W[A^{\equiv}] = Y[A^{\equiv}] + a + 2Z[A^{\equiv}] + 3[A^{\equiv}] + [MA^-]$$

$$b + h - 3a - [MA^-] = (W + Y + 2Z - 2\gamma + 3)[A^{\equiv}]$$

$$[A^{\equiv}] = \frac{b + h - 3a - [MA^-]}{(W + Y + 2Z - 2\gamma + 3)}$$

$$K_{MA} = \frac{[MA^-] \qquad f_1}{[M^{2+}][A^{\equiv}]\ \ f_2f_3}$$

$$[MA^-] = \frac{K_{MA}\ [M^{2+}]\ [A^{\equiv}]\ f_2 f_3}{f_1}$$

$$[MA^-] = \frac{K_{MA}(m - a + \gamma[A^{\equiv}])[A^{\equiv}]\ \ f_2f_3}{f_1}$$

$$b + h - 3a = (W + Y + 2Z - 2\gamma + 3 + K_{MA} \cdot m\ f_1f_2 - K_{MA}\ a\ f_1f_2 +$$

$$K_{MA}\ \gamma[A^{\equiv}]\ f_1f_2)[A^{\equiv}]$$

$$0 = (3a - b - h) + (W + Y + 2Z - 2\gamma + 3 + K_{MA} \cdot m f_1 f_2 - K_{MA} f_1 f_2 [A^{=}] a$$

$$K_{MA} \gamma [A^{=}]^2 f_1 f_2 \quad .$$

Let $\alpha = (3a - b - h)$

$\beta = (W + Y + 2Z - 2\gamma + 3 + K_{MA} \cdot m f_1 f_2 - K_{MA}\, a f_1 f_2)$

$\delta = K_{MA} \gamma f_1 f_2$.

From these equations it is apparent that

$$[A^{=}] = \frac{-\beta \pm \sqrt{\beta^2 - 4\delta\alpha}}{2\delta}$$

The treatment of the two complexes system with the formulas derived above is somewhat difficult since both formation constants appear as unknowns in the equation. Although there are other ways to treat this problem the suggested approach is to make use of the aid of the computer and guess appropriate values for the first formation constant until a constant second formation constant is obtained.

If no success is met with this treatment, a treatment of a postulated MA_2^{4-} complex would then follow. The treatment of this species as a second complex is in every way similar to the treatment of the MHA complex.

CHAPTER III

SUMMARY AND CONCLUSIONS

The intent of this study was to accomplish three projects. The first of these was to prepare the organic chelating agent PTP and this requirement was satisfied by the production of PTP hydrochloride and the characterization of this compound by means of infrared spectroscopy, neuclear magnetic resonance spectroscopy, mass spectroscopy, elemental analysis, cryoscopic molecular weight determination, and potentiometric titration.

The second problem of this study was the determination of the ionization constants for the chelating agent. This was satisfied with statistical determinations of the four thermodynamic ionization constants. The constants determined were as follows: $K_1 = 1.31 \times 10^{-3}$, $K_2 = 1.51 \times 10^{-4}$, $K_3 = 2.07 \times 10^{-5}$, and $K_4 = 3.79 \times 10^{-9}$.

The third problem of this study was the determination of the formation constants of transition metal complexes of PTP. This problem is really not concluded. The results to date indicate that the postulated single complex system with copper (II) and zinc (II) is not formed. This is a somewhat negative result but it at least helps to make an elimination.

The possibilities for future study in this field are many and varied. The most obvious thing is a completion of the data on the complexes being studied. Other metal ions could then be studied including ones with a 3+ charge. These ions would be especially interesting because the formation of a 1 to 1 complex would result in a neutral species.

Another species of phosphine chelating agent that would be of special interest would be the phosphorous analogue of ethylenediaminetetrapropionic acid. This complexing agent would have six possible complexing sites. It would also be interesting to see if the resistance to oxidation would be one of the characteristics of this compound. This compound could probably be made from a reaction of 3,3'-phosphinidienedipropionitrile which is available with 1,2-dichloroethane and then hydrolyzing the results to the acid.

Other studies to be made on PTP include a NMR titration of the acid with and without metal ion addition. To carry out this study, appropriate mixtures of the tripotassium salt of the acid with metal ion addition or the salt of the acid alone are titrated to a variety of pH values with standard acid. The spectra of the methlyene protons are then observed. This technique has proved useful in determining the structures of EDTA at different pH values.

Another possible study to be made is a spectroscopic observation of the P-C bond as chelate formation takes place. This study would shed light on the structure of the chelate and provide some information about the strength of the metal-phosphorus coordinate bond.

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VITA

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