

ON THE KINETICS AND CHEMISTRY OF
SOME REACTIONS OF PHOSPHONITRILIC DERIVATIVES

by

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B.Sc(Hons.), University of British Columbia, 1967

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

Chemistry

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

October, 1970

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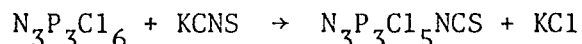
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ABSTRACT

The kinetic parameters in acetonitrile of the nucleophilic substitution reaction:



have been determined. The Arrhenius activation energy is 15.5 ± 5 Kcal mole⁻¹ and the common logarithm of the pre-exponential factor is 10.2 ± 3 . The reaction is first order in each reagent and is probably bimolecular. Comparison with similar reactions indicates a lone pair electron donation from the nitrogen to the phosphorus atoms of the ring.

The compound, $\text{N}_4\text{P}_4(\text{NMe}_2)_8\text{HCuCl}_3$ was prepared by the reaction of tetrameric phosphonitrilic dimethylamide with copper (II) chloride in butanone. The infra-red spectrum indicates that the copper atom is bound to one ring nitrogen atom, and the proton to the opposite nitrogen atom. The ring is found to be too small to allow chelation of the copper atom.

The salt, $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{CuCl}^+\text{CuCl}_2^-$ was prepared by the dehydrohalogenation of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{HClCu}_2\text{Cl}_3$. The hydrochloride was prepared by the reaction of hexameric phosphonitrilic dimethylamide (H.P.D.) with copper (II) chloride in the reducing solvent butanone. The salt was also produced by the reaction of H.P.D. with an equimolar mixture of copper (I) chloride and copper (II) chloride in acetonitrile.

Chemical and magnetic studies on the salt showed it to have one copper (II) atom per molecule. The x-ray crystal structure showed the copper (II) atom to be in a distorted square pyramidal environment, bonded

to four ring nitrogen and one chlorine atom.

The salt contains the first known example of the CuCl_2^- anion. This is linear with a Cu-Cl bond length of 2.11Å. The anion is also one of the few examples of a finite species containing a two co-ordinate copper (I) atom.

The infra-red spectrum of the salt was very similar to that of the parent H.P.D. The main difference was in the frequencies of the stretching modes of the phosphorus nitrogen ring bonds; which is consistent with copper chelation.

Conductiometric and analytical studies showed that the salt does not retain the form $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{CuCl}^+\text{CuCl}_2^-$ in acetonitrile solution; the limiting molecular conductance $377 \pm 10 \text{ Ohms}^{-1}$ being too large to be consistent with a 1:1 electrolyte.

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ACKNOWLEDGEMENT

I wish to record my gratitude to
Professor N.L. Paddock under whose guidance and
instruction I completed this work.

CHAPTER ONE

GENERAL INTRODUCTION

Phosponitric derivatives contain the formally unsaturated repeating unit $\text{--}\overset{\text{||}}{\text{N}}=\text{P}(\text{X}_2)\text{--}$ for which several types of chemical reactions are possible. Among these are nucleophilic substitution of the ligands (X) which has been extensively studied, mainly from a preparative point of view. Addition reactions either to the double bond or of a donor-acceptor type have also been studied, but not so extensively.

Since nitrogen is more electronegative than phosphorus, binding electrons tend to accumulate near it. This causes the phosphorus and nitrogen atoms to be respectively electrophilic and nucleophilic.

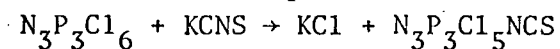
Of the various types of reactions at the phosphorus and nitrogen centres which could occur, two are studied in this thesis:

- (1) acceptor properties typified by nucleophilic substitution at phosphorus by the thiocyanate anion,
- (2) and donor properties, through the chelation of copper (II) by nitrogen.

Little information exists about the kinetics of nucleophilic substitution at phosphorus in phosponitriles. This may, in part, be due to the difficulty of studying reaction rates with a molecule having many

potential attack sites. Therefore, it was felt that a kinetic study would be worthwhile, because it would give some information in a field where few facts are known. Also, it might throw some further light on the nature of the π -bonding systems in phosphonitrilic compounds.

For this work the initial reaction of potassium thiocyanate with trimeric phosphonitrilic chloride was studied.



The reaction was found to be bimolecular and its rate constant and activation energy were determined.

The study of the preparation of transition metal complexes of phosphonitriles is also a field in which very little information is available. Metal halides have been made to react with phosphonitriles, but the resulting complexes have, at most, one ring nitrogen bonded to the metal.

In this work, two copper complexes have been prepared;

$\text{N}_4\text{P}_4(\text{NMe}_2)_8\text{HCuCl}_3$, and $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu(II)ClCu(I)Cl}_2$. The former probably has a structure similar to $\text{N}_4\text{P}_4(\text{Me})_8\text{HCuCl}_3$ with one nitrogen bound to a proton and one bound to the CuCl_3^- group. Determination of the crystal structure of the complex of the hexameric dimethylamide showed it to contain a unique porphyrin-like framework in which copper (II) is co-ordinated to four endocyclic nitrogen atoms in the same molecule with the phosphonitrile acting as a macrocyclic ligand. The detailed geometry shows evidence of competitive donor-acceptor interactions which are compatible with π -electron theory.

CHAPTER TWO

KINETIC STUDIES OF NUCLEOPHILIC SUBSTITUTION IN PHOSPHONITRILES

Phosphonitrilic halides undergo many nucleophilic substitution reactions. Their reactions with primary and secondary amines, alcohols, phenols, halide ions, and the thiocyanate ion have all been reported. These reactions are among the most important and interesting in phosphonitrilic chemistry, and it is therefore surprising that there exists almost no quantitative information concerning their kinetics. Since the rates of substitution reactions would be expected, as a first approximation, to depend on π -electron density at the phosphorus atom, an increase in kinetic information should therefore lead to a greater understanding of the π -molecular orbitals. Some quantitative work has already been done⁽¹⁻⁶⁾, and the results are summarized in Table I. However the mass of kinetic information is qualitative, dealing mainly with the types of observed orientation patterns.

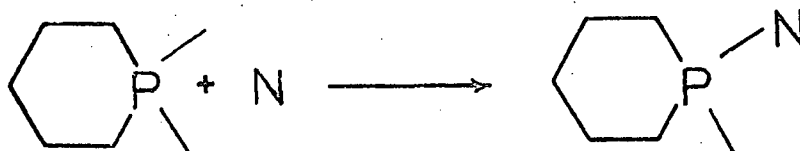
The object of this work has been to obtain quantitative kinetic data on nucleophilic substitution in trimeric phosphonitrilic chloride. The reaction studied was that producing the mono-substituted derivative. It should be noticed that phosphonitrilic halides offer many different reaction sites to substitution and therefore, for any reaction there exist several steps.

Attention was concentrated on the first step, because alternative paths are open to the second substituent. Because of the

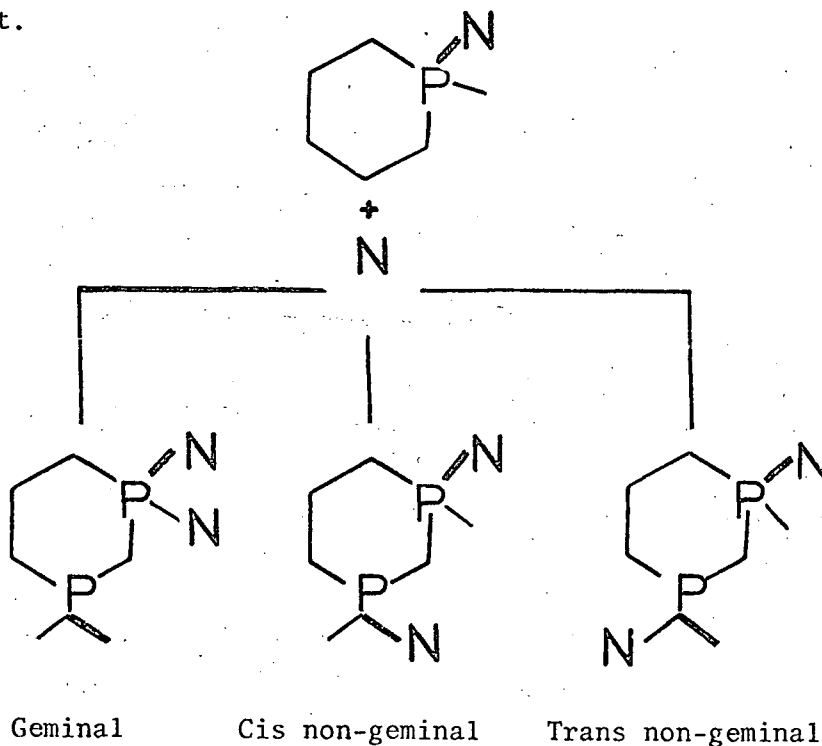
Table I Kinetic Parameters of Substitution Reactions of Phosphonitriles

Compound	Reagent	Solvent	Temp.	Parameters		Ref.
				$E_a \cdot (\text{Kcal/mole})^{-1}$	$\log_{10} A$	
$(\text{NPCl}_2)_3$	Cl^-	Acetonitrile	0-35°C	18.3	12.1	(3)
$(\text{NPCl}_2)_4$	"	"	"	16.3	12.0	"
$(\text{NPCl}_2)_5$	"	"	"	17.0	11.9	"
$(\text{NPCl}_2)_6$	"	"	"	16.3	11.2	"
$(\text{NPCl}_2)_3$	Aniline	Ethanol-Benzene	34.5°C	$k_2 = 148 \times 10^{-3} \text{ mole}^{-1} \text{ sec}^{-1}$		(1)
"	Ethanol	"	"	$k_2 = 0.01 \times 10^{-3} \text{ mole}^{-1} \text{ sec}^{-1}$		"
"	Piperidine	Toluene	0°C	$k_2 = 2.2 \times 10^{-3} \text{ mole}^{-1} \text{ sec}^{-1}$		(2)

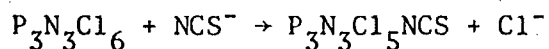
equivalence of the chlorine atoms in the parent phosphonitrile, the first step can only go to form one derivative.



However, the mono-substituted derivative has three non-equivalent sites for nucleophilic attack which cannot be discriminated in a single experiment.



The reaction used was the nucleophilic displacement of a chlorine atom on phosphorus by a thiocyanate ion.



The thiocyanate ion was chosen because it reacts more rapidly than many other nucleophiles. Also, while the mono-substituted derivative has not

been isolated, the reaction does go to produce the completely substituted $\text{N}_3\text{P}_3(\text{NCS})_6$ which has been prepared and characterized⁽⁸⁾. Preliminary experiments showed that the reaction proceeds at a suitable rate. Also, there is a possible interest in the thiocyanate group because it has a π -system which could interact with that of the ring and modify the rate of reaction. Finally, a convenient method of following the reaction is possible because of the conductivity of the thiocyanate ion.

Materials:

Trimeric phosphonitrilic chloride was purified by recrystallization from benzene followed by sublimation and recrystallization to a constant melting point. (113.5°C, literature 112.8⁽⁹⁾ and 114°C⁽¹⁰⁾). The reagent was examined by infra-red and mass spectrometry and found to contain no tetrameric chloride. Before the reactions, the trimeric phosphonitrilic chloride was dried in vacuo for three hours at 50°C.

Reagent grade potassium thiocyanate was purified by repeated recrystallization from 95% ethanol and then dried in vacuo at 100°C⁽¹¹⁾.

Potassium chloride was dried by repeated washings with reagent grade acetone and stored at 150°C.

Reagent grade acetonitrile was dried over calcium oxide by heating it under reflux for several hours. This was followed by distillation under nitrogen on to phosphoric anhydride. After two distillations over the acid anhydride, the acetonitrile was transferred to a dry-box. It was found important to exclude oxygen from the solutions as well as moisture. At this stage, it was checked for dryness by electroconductivity measurement on a Wayne Kerr Universal Bridge

B221A. If the specific conductance was above the arbitrarily set limit of $1.9 \times 10^{-6} \text{ Ohm}^{-1}$ (literature specific conductance 10^{-8} Ohm^{-1} ⁽¹²⁾), it was redistilled.

Due to the warnings of Audrieth⁽⁷⁾ about the instability of the isothiocyanate derivatives, all the purified materials and dried apparatus were handled in the dry box.

Preparation:

The preparation of the reaction solutions was done by clean dry pipettes in the dry box. A quantity of reagent was placed in a weighing bottle which was then removed from the box and weighed. This was returned to the box and a suitable quantity of the reagent was added to a conical flask. Both the flask and bottle were weighed, and the flask was returned to the dry box. Acetonitrile was added and the flask was removed and weighed again. The concentration was then calculated in units of moles per gram of solution.

This procedure was used because the pipettes did not deliver reproducible volumes. Also, it was more accurate to use weight measurements which do not vary with temperature. The results were changed later into moles per litre using the densities of solvent and solute.

Apparatus:

Two constant temperature baths were used during the experiment. The one for 25°C varied no more than $\pm 0.01\text{C}^\circ$, and the other by $\pm 0.02\text{C}^\circ$.

An electroconductivity cell was constructed of the type shown in Figure 1. Because the electrodes were held in place only by their connecting wires, utmost caution had to be exercised so as not to alter the cell constant.

The cell was calibrated with potassium thiocyanate at 25°C. First the background conductance due to potassium chloride and acetonitrile was measured. Next, an amount of thiocyanate solution with a known concentration was added to the tared cell with a syringe, (a pipette gave non-reproducible results). The total conductance was measured and the background conductance was subtracted from it. The cell was then weighed and the concentration was calculated.

The plot of thiocyanate concentration against thiocyanate conductance gave a curve upon which three excellent straight lines could be fitted:

$$C = \frac{k - 0.428}{0.5307} \quad \text{for } k = 1.8 - 6.4 \quad (2-1)$$

$$C = \frac{k - 1.3563}{0.4497} \quad \text{for } k = 6.4 - 10.8 \quad (2-2)$$

$$C = \frac{k - 2.974}{0.3733} \quad \text{for } k = 10.8 - 14.5 \quad (2-3)$$

C = concentration KCNS $\times 10^6 \cdot \text{g} \cdot \text{mole}^{-1}$

k = conductance $\times 10^3 \cdot \text{Ohms}$

No significance is attached to these lines other than that they made the calculation of the concentration of thiocyanate easier and more accurate.

The background conductance was small and never exceeded 1% of the lowest measured conductance. It was none the less, not quite steady

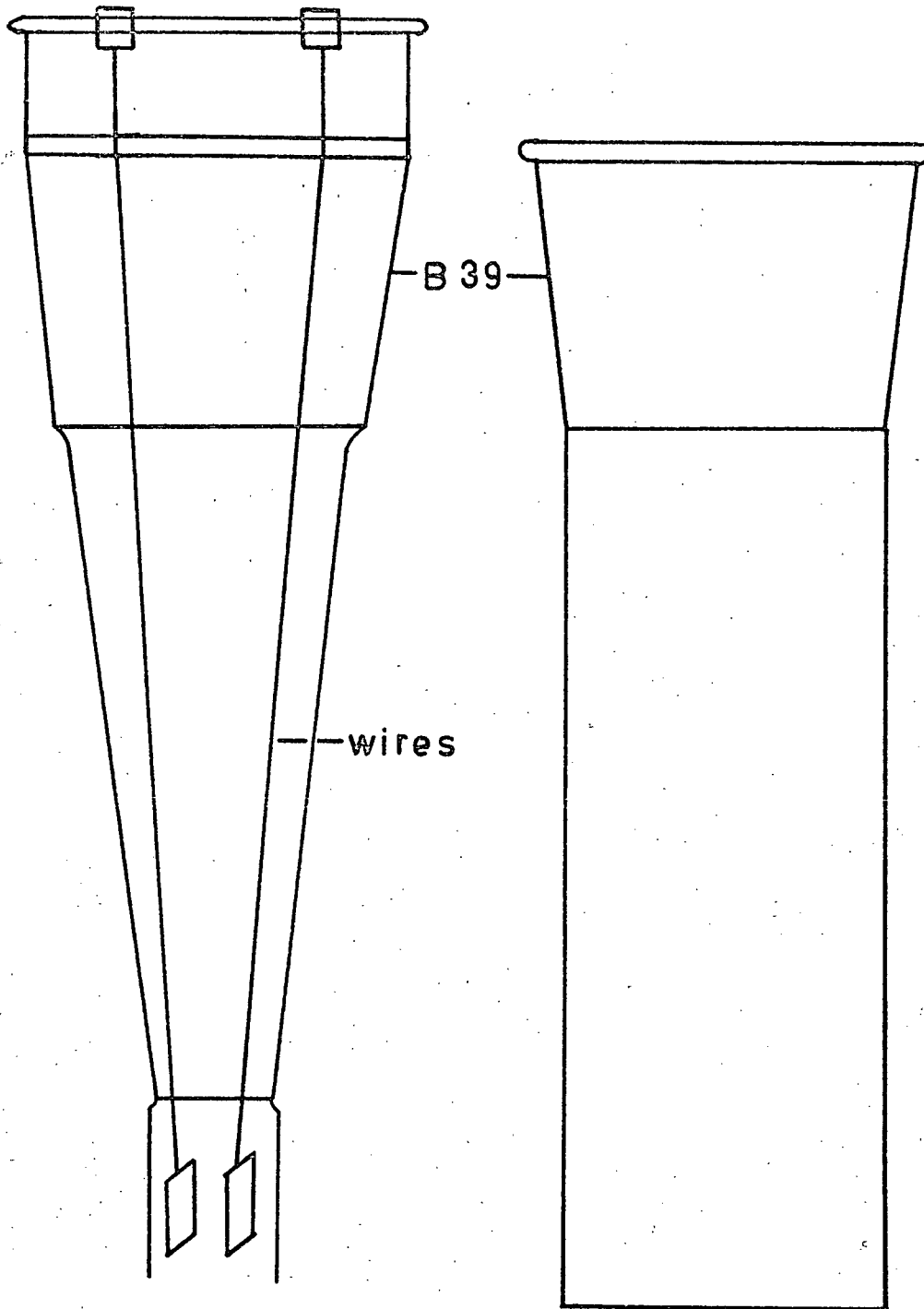


Figure 1. Conductivity Cell

and a correction for it was always applied.

Procedure:

The different kinetic runs were carried out using the same chemical procedures. For all of them this meant making reagent solutions with known concentrations, equilibrating these solutions, mixing them, and then following the decrease in thiocyanate concentration as a function of time.

The reactant solutions were prepared in the dry-box. A few ml. of one stock solution were added to the cell which was then weighed. A 50 ml. flask was treated in the same way, using the other solution. The flask was then replaced in the dry-box and pure acetonitrile was added.

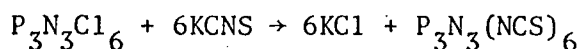
All reactions were carried out with 30 ml. of solution, and the final concentrations were varied by varying the amount of stock solutions. Once the cell had been filled, it could not be put back into the dry-box because it could not be sealed well enough.

The two reactant solutions were then equilibrated in the constant temperature bath, (usually 30 minutes). The flask was then removed from the bath and its contents poured into the cell. At this point, the clock and conductivity runs were started. In all cases the reaction was followed until 20% of the thiocyanate had been used. Once the reaction was finished, the full cell was weighed. This gave the amount of both reaction solutions present, and from this the concentrations could be calculated.

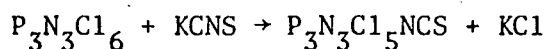
When the two solutions were mixed, there was an unavoidable increase in the temperature of one of the solutions which was caused by removing the solution from the bath by hand in order to pour the solution. This caused the illusion of a sharp decrease in thiocyanate ion concentration. That this was an illusion was illustrated by taking the conductance of an equilibrated KCNS solution then pouring the solution into an equilibrated flask. After this had equilibrated, it was poured back into the cell and conductance was measured as a function of time (Figure 2). A downward curve leveling off at the original value within one or two minutes, showed that what appeared to be a decrease in concentration was in fact a temperature effect. Because many of the experiments have concentration readings within one minute of addition, this curve is superimposed on their concentration graphs.

Kinetics:

The reaction:



has been reported by R.J.A. Otto and L.F. Audrieth⁽⁷⁾. It has been assumed for the present work that the reaction takes place by a series of individual and separate substitution steps, therefore, the first reaction will be:



If this reaction is first order in each reagent, then:

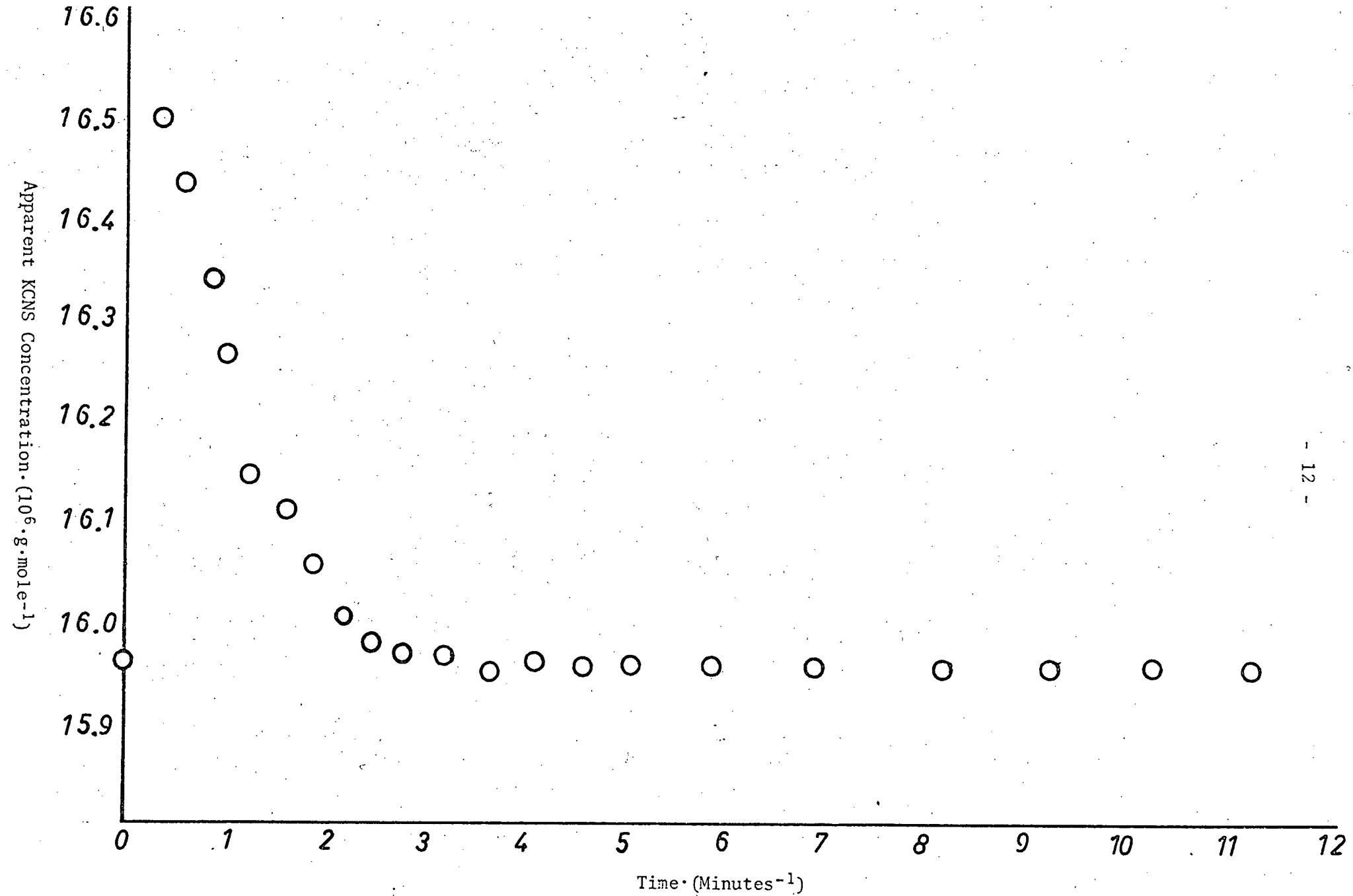


Figure 2. Graph of the Temporary Thermal Effect at 8.8°C

$$\frac{-d[\text{KCNS}]}{dt} = k[\text{KCNS}][\text{P}_3\text{N}_3\text{Cl}_6] \quad (2-4)$$

The initial rate, $[\frac{-d[\text{KCNS}]}{dt}]_i$, will then be directly proportional to the product of the initial concentrations of the two reactants, $[\text{P}_3\text{N}_3\text{Cl}_6]_i$ and $[\text{KCNS}]_i$.

$$[\frac{-d[\text{KCNS}]}{dt}]_i = k[\text{P}_3\text{N}_3\text{Cl}_6]_i [\text{KCNS}]_i \quad (2-5)$$

(The subscript 'i' will be omitted from all future equations.)

If the reaction is of the second order, then a plot of $\frac{-d[\text{KCNS}]}{dt}[\text{KCNS}]^{-1}$ against $[\text{P}_3\text{N}_3\text{Cl}_6]$ with $[\text{KCNS}]$ constant will be linear. This will also be true for a plot of $\frac{-d[\text{KCNS}]}{dt}[\text{P}_3\text{N}_3\text{Cl}_6]^{-1}$ against $[\text{KCNS}]$ when $[\text{P}_3\text{N}_3\text{Cl}_6]$ is constant. This results in two equations which must be satisfied for a reaction of second order.

$$\frac{-d[\text{KCNS}]}{dt}[\text{KCNS}]^{-1} = k[\text{P}_3\text{N}_3\text{Cl}_6] \quad (2-6)$$

$$\frac{-d[\text{KCNS}]}{dt}[\text{P}_3\text{N}_3\text{Cl}_6]^{-1} = k[\text{KCNS}] \quad (2-7)$$

Therefore, equations (2-6) and (2-7) will produce two coincidental straight lines with slope k originating at the origin.

The reaction rate $\frac{-d[\text{KCNS}]}{dt}$ can be determined from a plot of $[\text{KCNS}]$ against time. This plot should result in a good approximation of a straight line at small time.

The initial concentrations of both reagents can be calculated knowing the quantities of reagents used in their preparation. Once k has been determined for several temperatures, then the Arrhenius

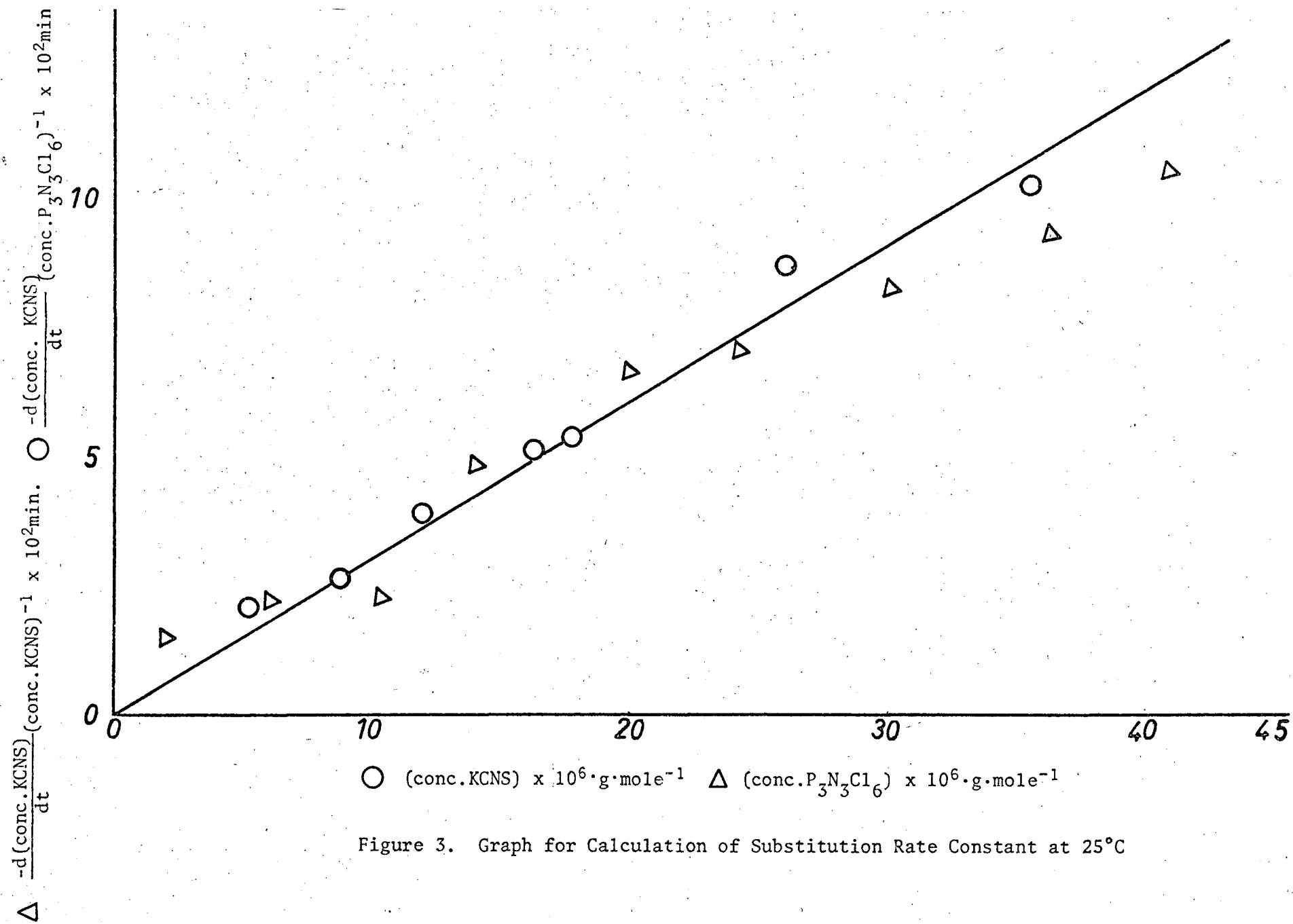


Figure 3. Graph for Calculation of Substitution Rate Constant at 25°C

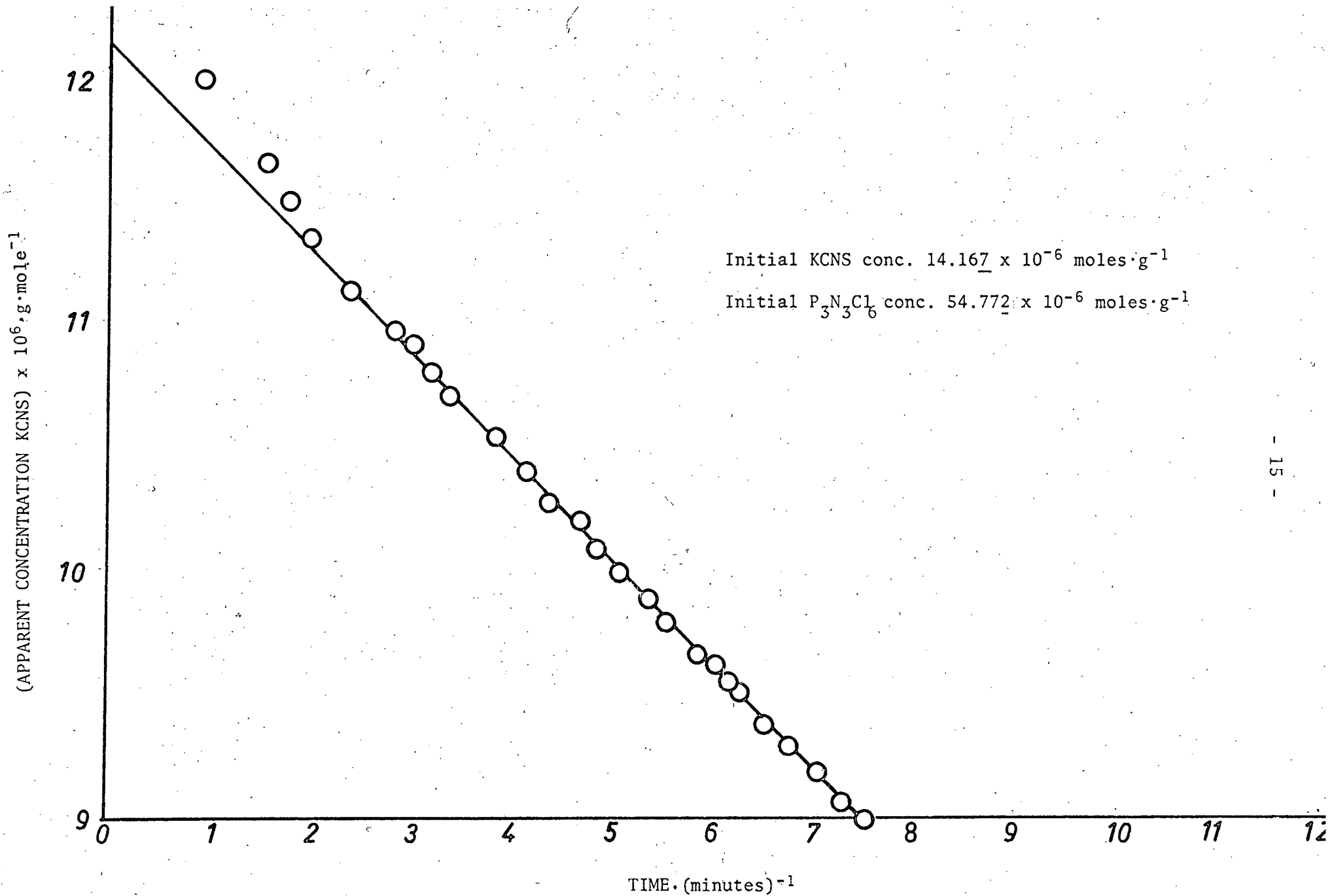


Figure 4. Plot of isothiocyanate substitution reaction at 8.8°C.

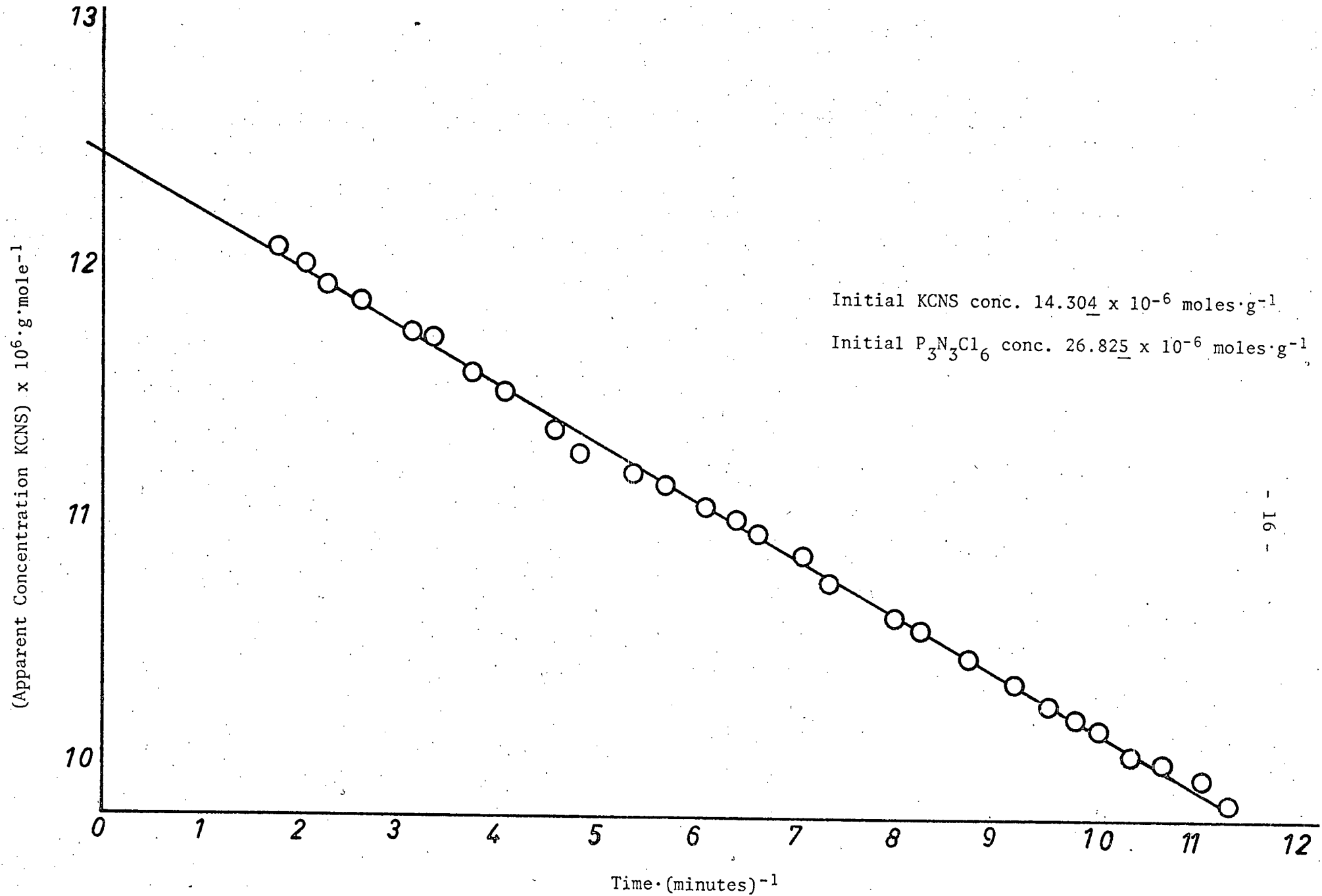


Figure 5. Plot of isothiocyanate substitution reaction at 8.8°C

(Apparent Concentration KCNS) $\times 10^5 \cdot \text{g} \cdot \text{mole}^{-1}$

Initial KCNS conc. $14.358 \times 10^{-6} \text{ moles} \cdot \text{g}^{-1}$

Initial $\text{P}_3\text{N}_3\text{Cl}_6$ conc. $40.299 \times 10^{-6} \text{ moles} \cdot \text{g}^{-1}$

12

11

10

0 1 2 3 4 5 6 7 8 9 10 11 12

Time $\cdot (\text{minutes})^{-1}$

Figure 6. Plot of isothiocyanate substitution reaction at 8.8°C

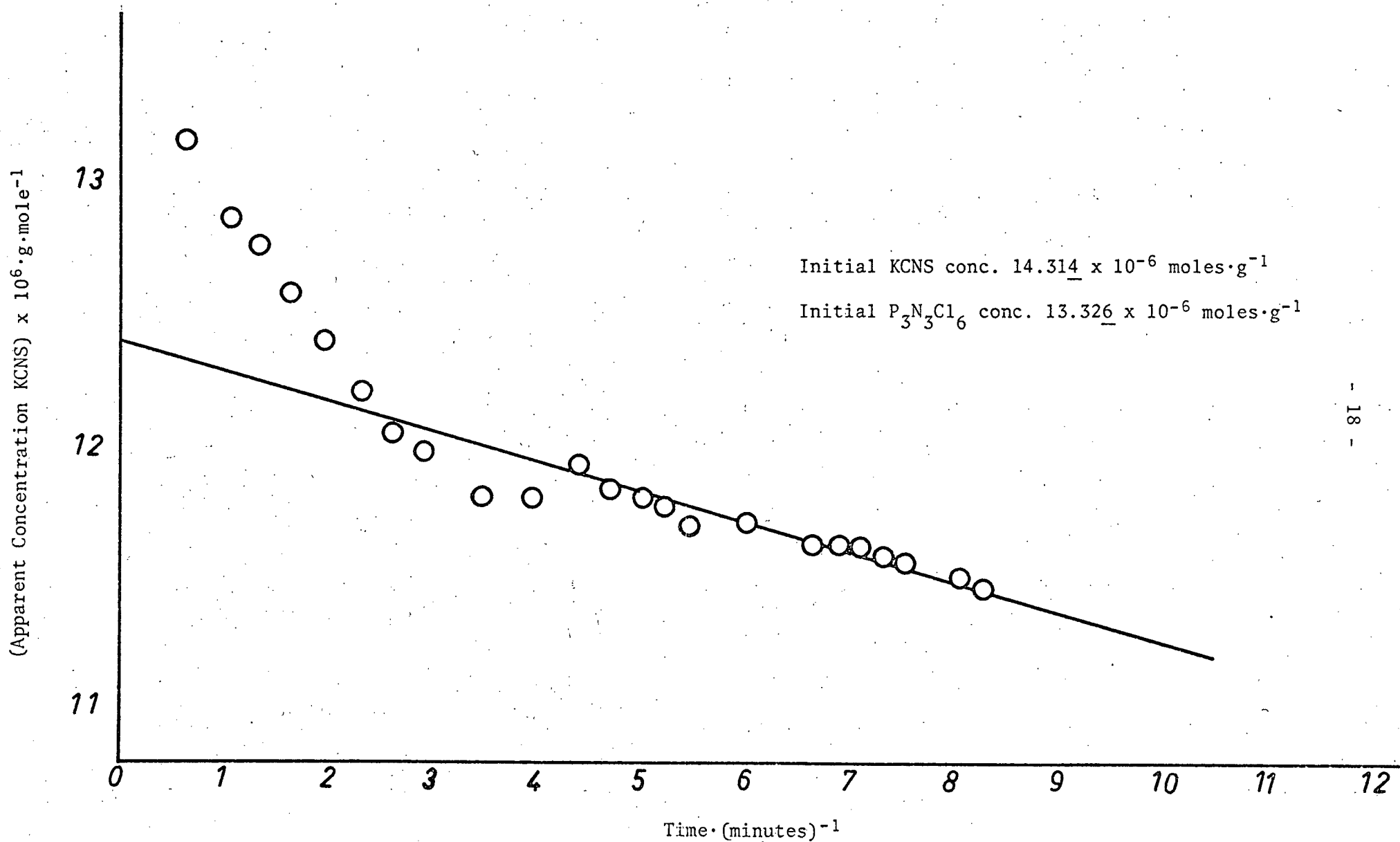


Figure 7. Plot of isothiocyanate substitution reaction at 8.8°C

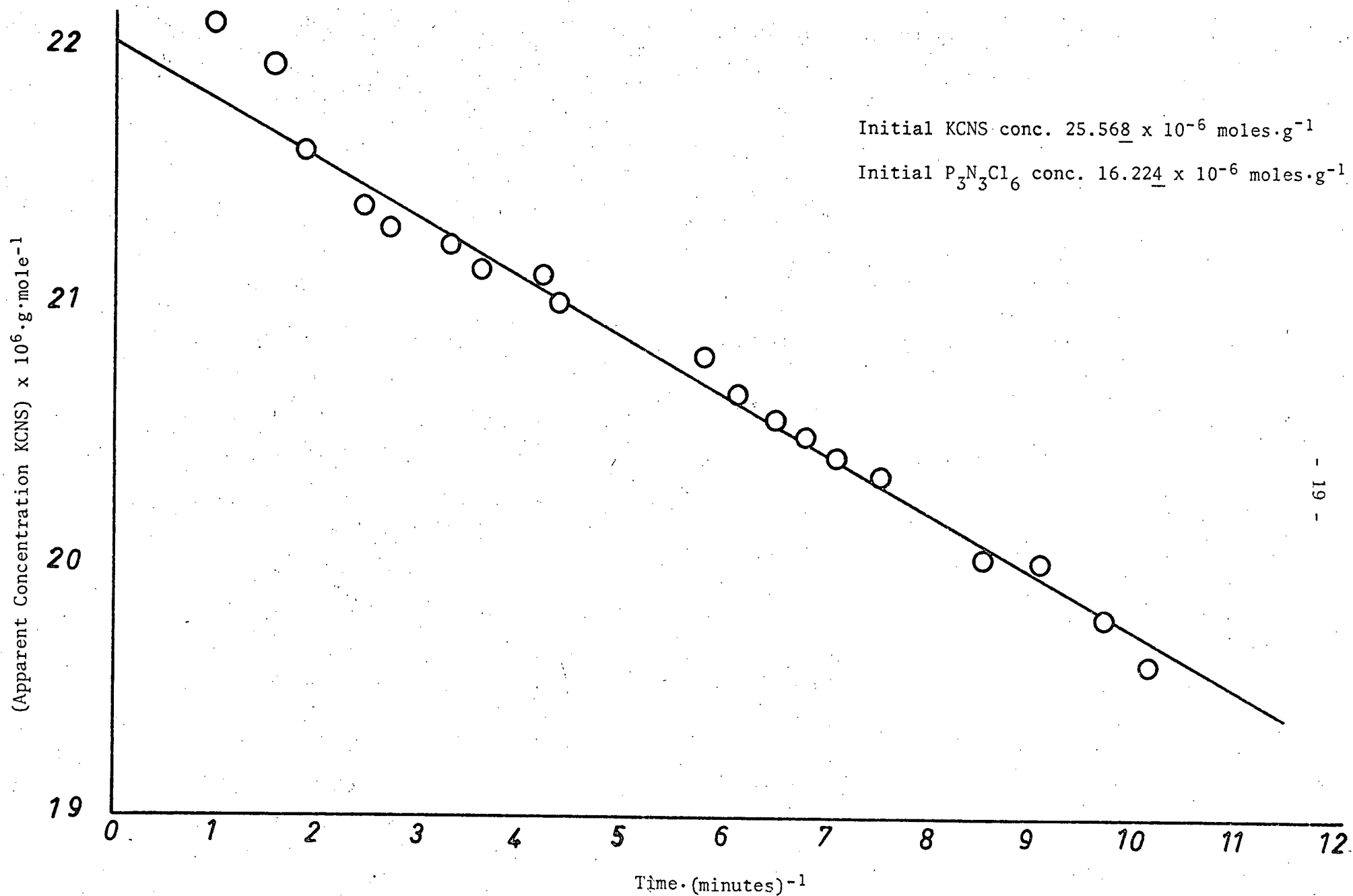


Figure 8. Plot of isothiocyanate substitution reaction at 8.8°C

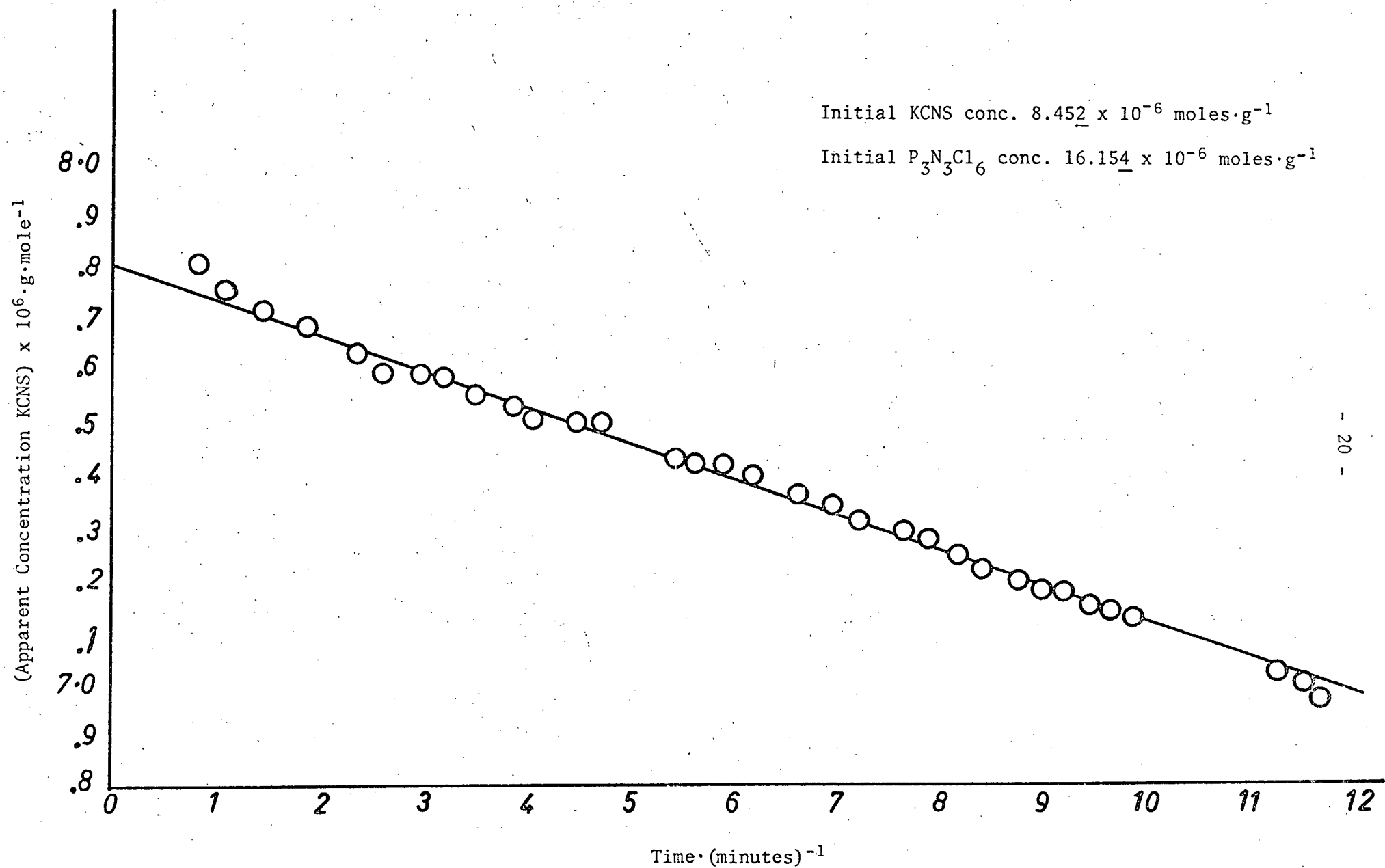


Figure 9. Plot of isothiocyanate substitution reaction at 8.8°C

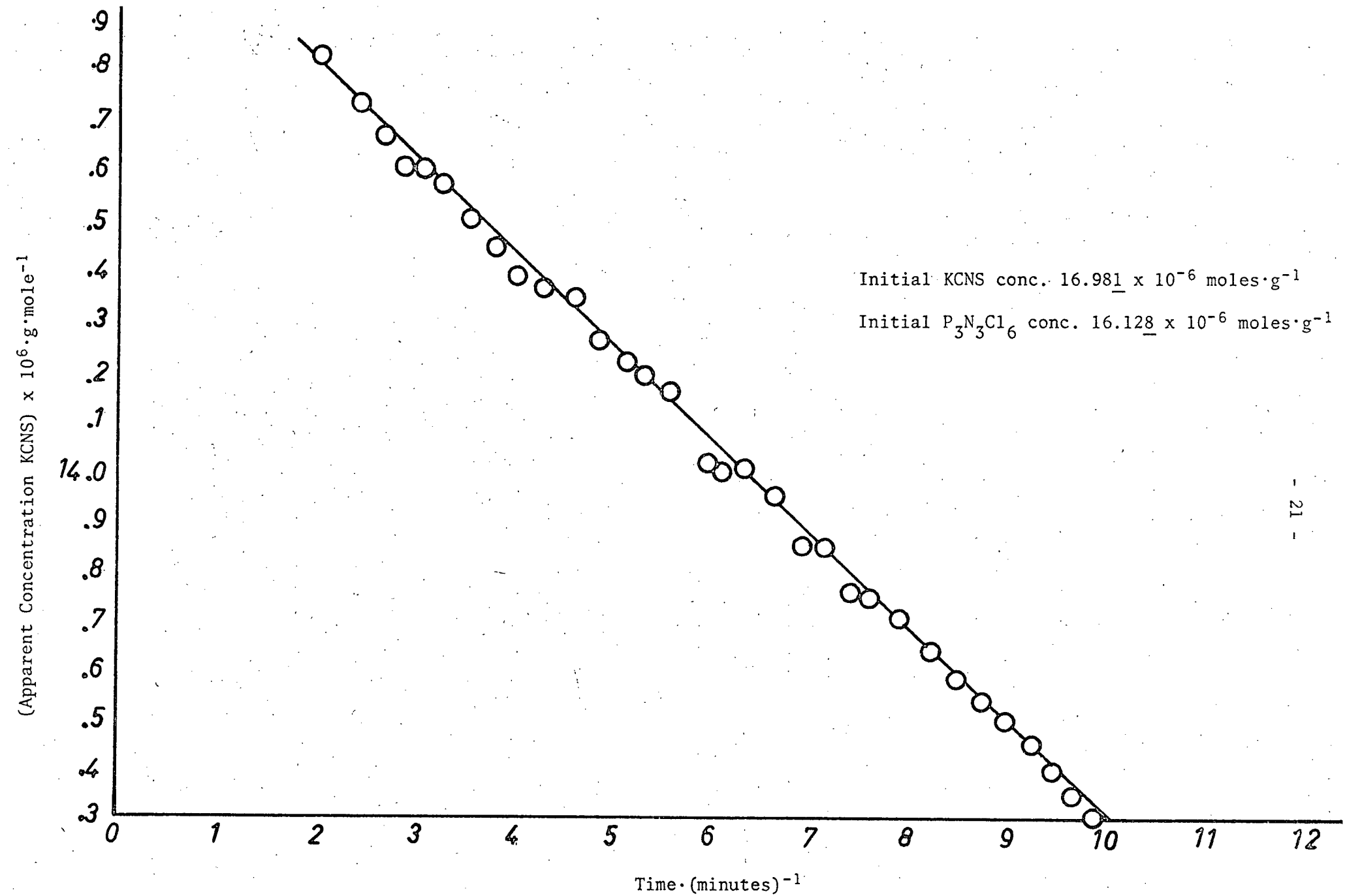


Figure 10. Plot of isothiocyanate substitution reaction at 8.8°C

(Apparent Concentration KCNS) $\times 10^6 \cdot \text{g} \cdot \text{mole}^{-1}$

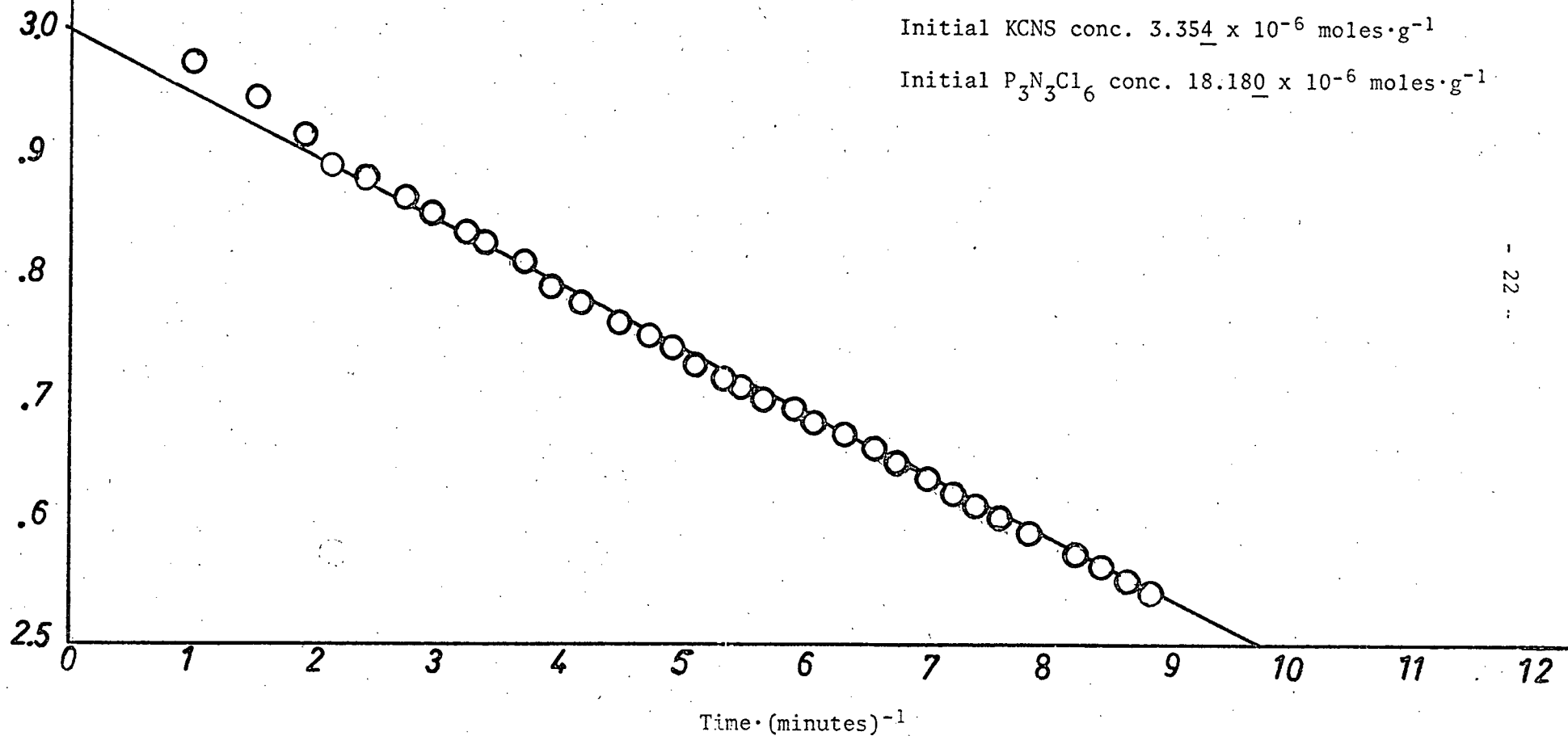


Figure 11. Plot of isothiocyanate substitution reaction at 8.8°C

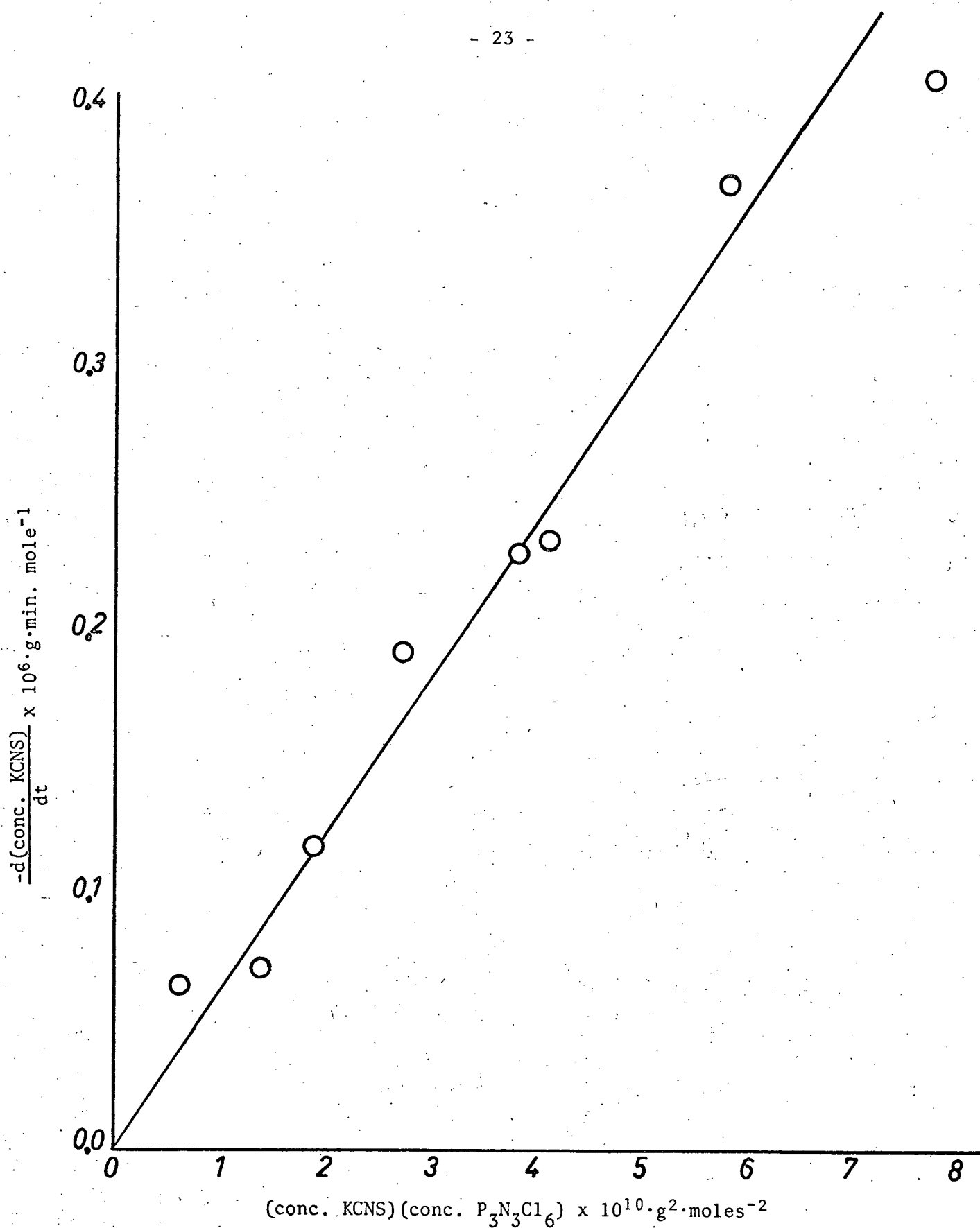


Figure 12. Graph for calculation of substitution rate constant at 8.8°C

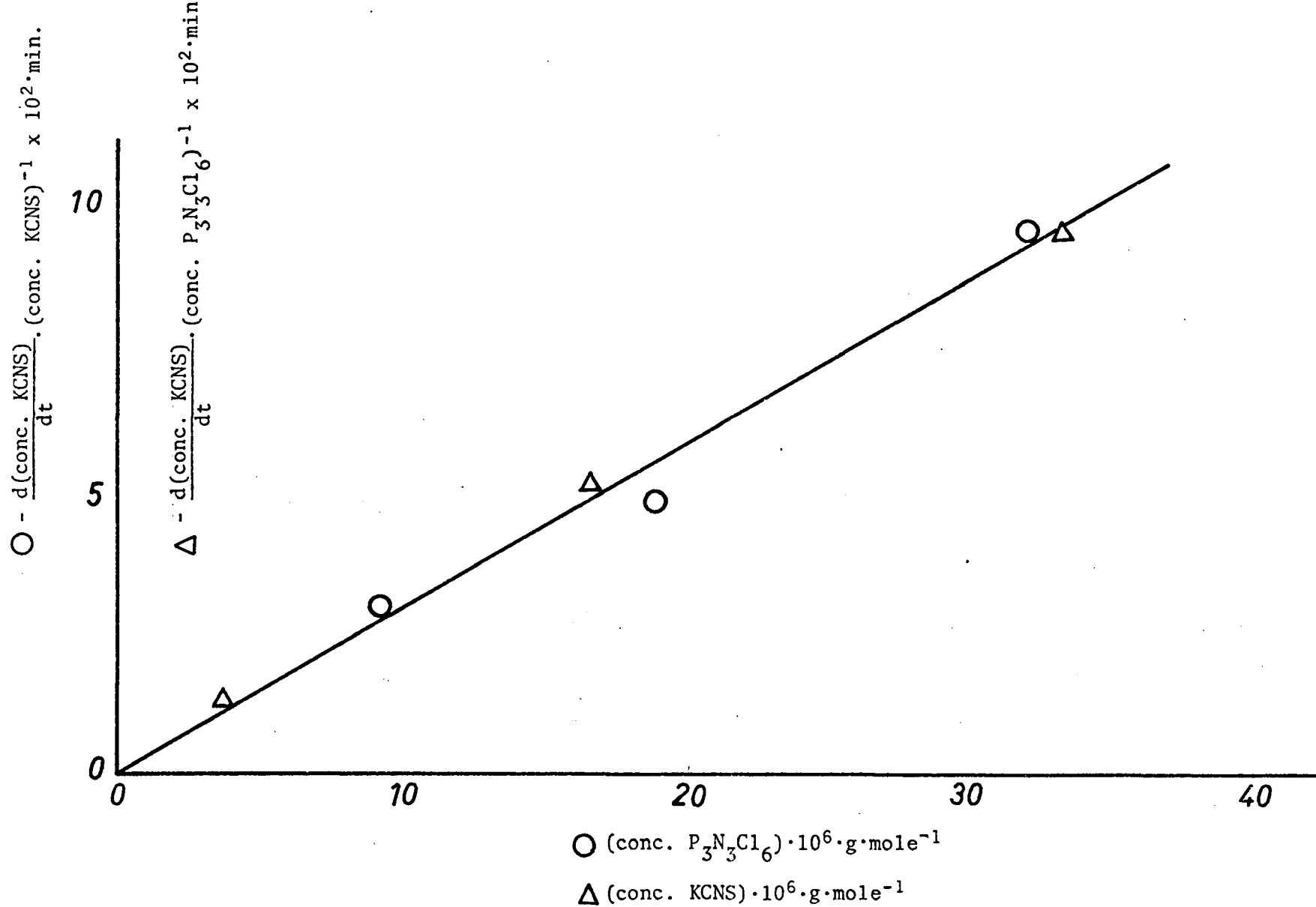


Figure 13. Graph for calculation of substitution rate constant at 0.9°C

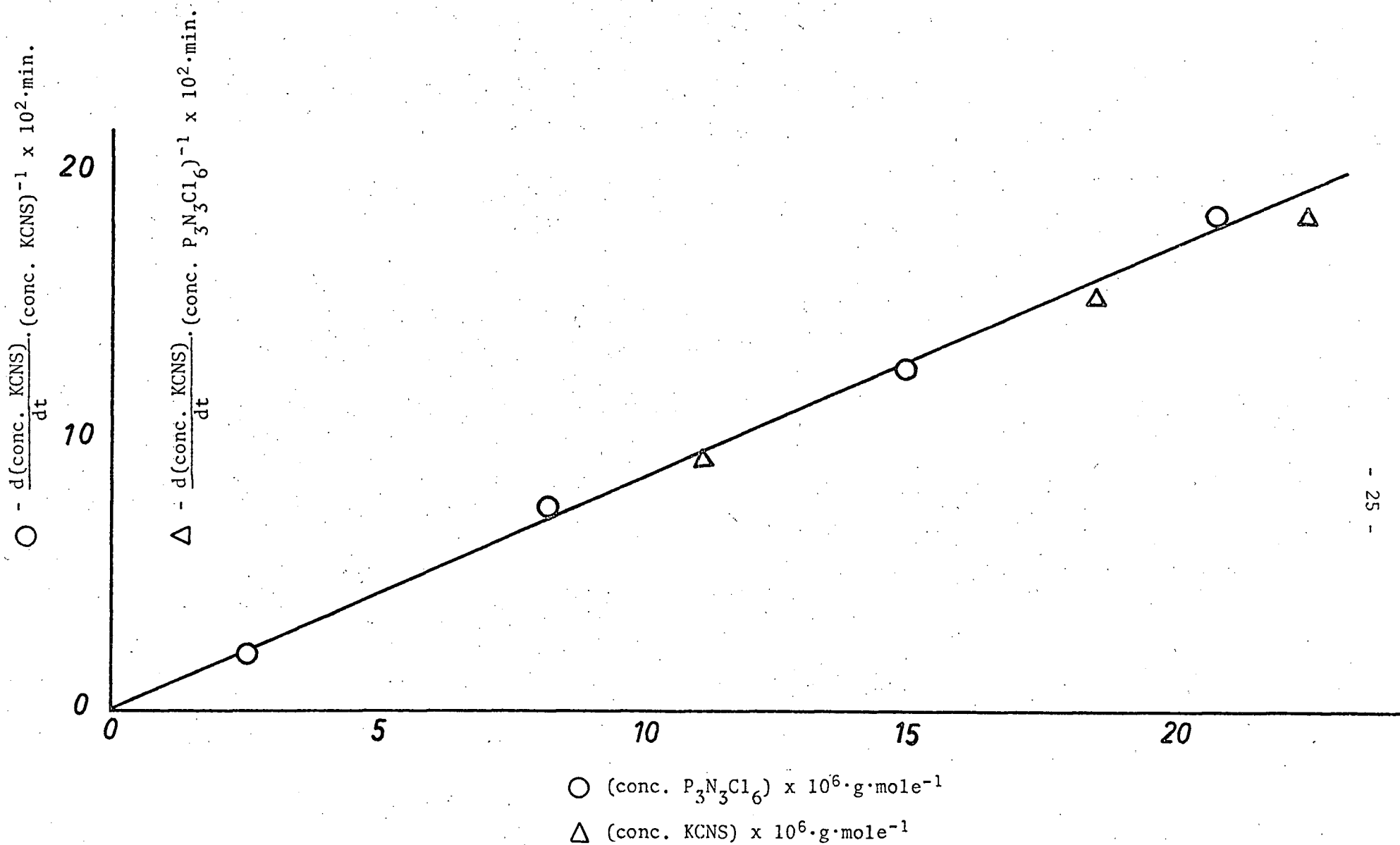


Figure 14. Graph for calculation of substitution rate constant at 40.2°C

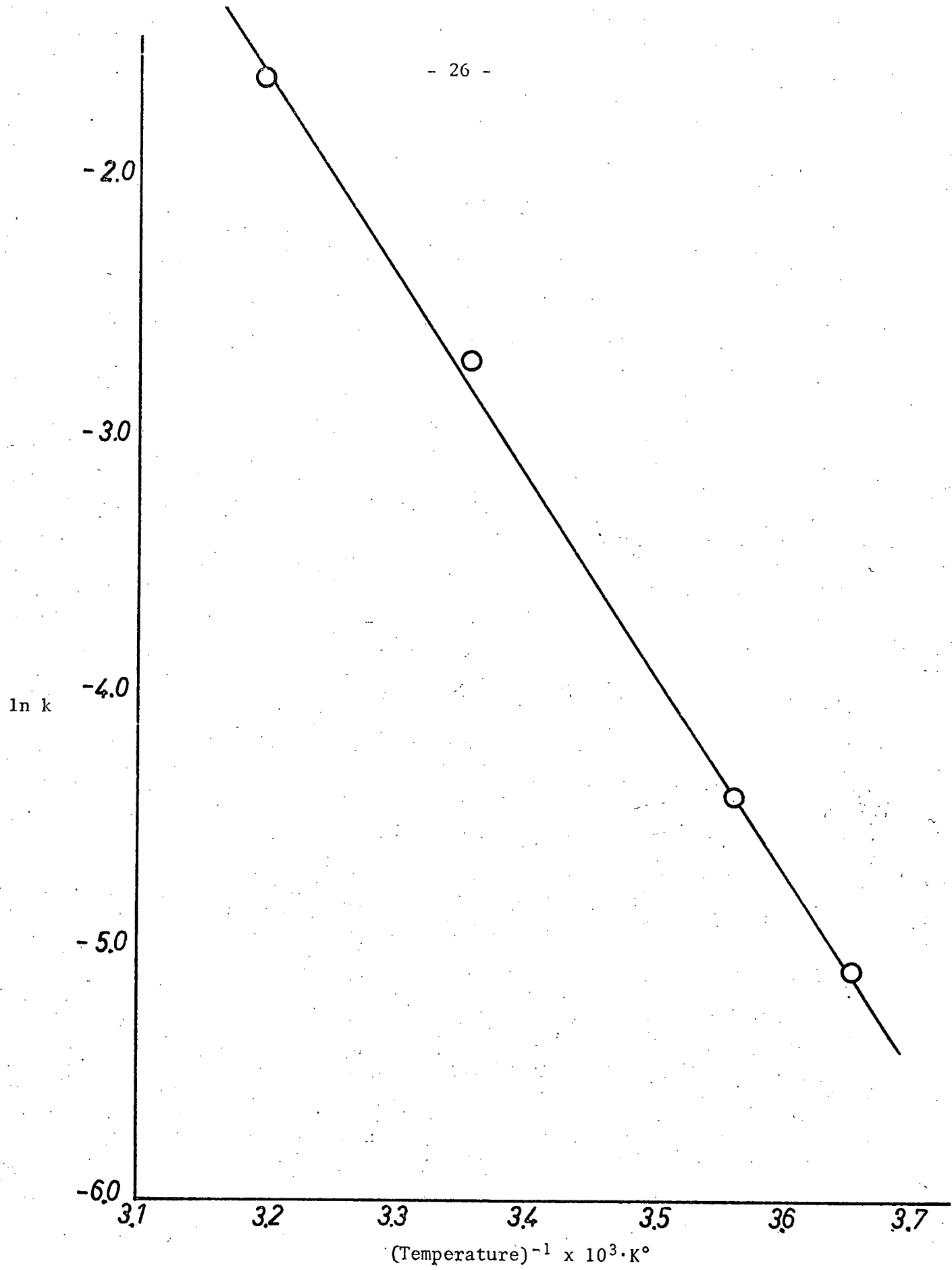


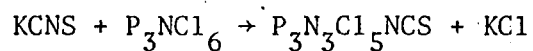
Figure 15. Arrhenius activation energy graph

activation energy, E_a , can be calculated from equation (2-8).

$$\ln k = - \frac{E_a}{RT} + \ln A \quad (2-8)$$

where A is the frequency or pre-exponential factor.

Equations (2-6) and (2-7) were thoroughly checked at 25°C (Figure 3). This graph gave a good approximation to a straight line beginning at the origin. This proves that the reaction:



is second order in both reagents and, therefore, that:

$$\frac{-d[\text{KCNS}]}{dt} = k[\text{KCNS}][\text{P}_3\text{N}_3\text{Cl}_6] \quad (2-4)$$

Characteristic plots of thiocyanate ion concentration against time in minutes are shown in Figures 4 - 11. At small time, a straight line approximation was found which was used to calculate $\frac{-d[\text{KCNS}]}{dt}$.

A plot of $\frac{-d[\text{KCNS}]}{dt}$ against $[\text{P}_3\text{N}_3\text{Cl}_6][\text{KCNS}]$ is shown on Figure 12 for the reaction at 8.8°C. Figures 3, 13 and 14 are plots of equations (2-6) and (2-7) for 25°, 0.9° and 40.2°C.

The study showed the reaction to be second order, being first order in each reagent. Its second order rate constant (k) at various temperatures is given in Table II. The Arrhenius activation energy was 15.5 ± 0.5 Kcal/mole and the \log_{10} of the pre-exponential factor was 10.2 ± 0.3 (Figure 15).

TABLE II THE SECOND ORDER RATE
CONSTANTS AT VARIOUS TEMPERATURES

<u>Temperature °C⁻¹</u>	<u>k · [l/mole sec.]⁻¹</u>
0.9	6.1 ± 0.3 x 10 ⁻³
8.8	11.9 ± 0.4 x 10 ⁻³
25	67 ± 5 x 10 ⁻³
40.2	191 ± 10 x 10 ⁻³

Discussion:

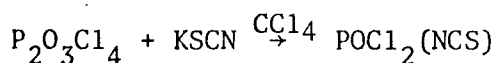
The thiocyanate group is an ambidentate ligand and can bond to an electrophile through either of its nucleophilic ends; in fact, the thiocyanate anion reacts with trimeric phosphonitrilic chloride to produce the fully substituted isothiocyanato derivative.

Several factors characteristic of the electrophile determine which atom will bond. These factors are mainly determined by the electronic environment of the electrophile, and its stereochemistry.

Two sets of antibonding π orbitals are localized on the sulphur atom⁽¹³⁾, and these can accept electrons from the electrophile. This results in additional stability of the sulphur-electrophile bond. The thiocyanate derivative is formed in groups that are able to back bond in this manner. With the metals, the second half of the second and third transition series such as Rh, Pd, Ag, Cd, Ir, Pt, Au, Hg, Te and Pb all form metal-sulphur bonds⁽¹⁴⁾. However, with smaller atoms such as the metals of the first transition series: Cr, Mn, Fe, Ni, Cu and Zn, the basicity of the nucleophile becomes increasingly important, and

they form metal-nitrogen bonds.

No nucleophilic substitution reaction of an alkyl halide with a thiocyanate has apparently ever produced an isothiocyanato derivative⁽¹⁵⁾, and so relatively small atoms can find the polarizability of sulphur more attractive than the high basicity of nitrogen. However, with penta-valent phosphorus, the bonding does occur through the nitrogen⁽¹⁶⁾.



Knowing the element and its oxidation number is not in itself sufficient information for prediction of the type of bond which will be formed. The nature of the surrounding ligands has been shown to be a determining factor⁽¹⁷⁾; π -electron withdrawing ligands reduce the electron density at the electrophile, thus making it a weaker π -electron donor.

The next determining factor has been shown to be steric. The isothiocyanato group can become linear by assuming the form $(-N^+ \equiv C-S^-)$. The thiocyanate on the other hand, is always bent $\angle S-C \equiv N$. An example of this is found when the non π -bonding ligand diethylenetriamine, $NH_2C_2H_4NHC_2H_4NH_2$, gives the S-bonded complex $[Pd(dien)SCN]^+$. The extremely bulky tetraethyl substituted ligand, $(C_2H_5)_2NC_2H_4NHC_2H_4N(C_2H_5)_2$, gives the N-bonded complex $[Pd(Et_4dien)(NCS)]^+$ ⁽¹⁸⁾. For the phosphoryl derivatives it seems unlikely that steric factors could have any effect on the substitution, and in the fully substituted isothiocyanato-phosponitrile⁽²³⁾ the substituent groups are well separated.

Kinetic studies have been done on phosphoryl compounds, but none have been reported which use the thiocyanate anion as the nucleophile. This limits the extent to which valid comparisons can be made between

the kinetics of the phosphoryl and the phosphonitrilic series of compounds. However, it is still possible to compare the base strength preferences of the phosphoryl groups with that of the phosphonitrile. Similarly, for the phosphonitriles only very limited information is available which can be used as a comparison with this work.

Nucleophilic reactivities are mainly determined by the electronic, steric, and solvation characteristics of the reactants. If steric and solvent effects are ignored, then the reactivity of a series of similar nucleophiles with one electrophile can be correlated from the equation:

$$\log \frac{k}{k_0} = \alpha H + \beta P \quad (2-9)$$

where: k_0 = rate constant for substitution with water

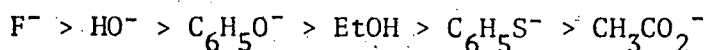
k = rate constant for substitution with the nucleophile

P = a function of the polarizability of the nucleophile

H = a function of the pK_a of the conjugate acid of the nucleophile;

α and β are parameters associated entirely with the electrophilic substrate⁽¹⁹⁾. If, as in the case of saturated carbon, polarizability is more important than basicity, then the value of β will be higher than that of α . The reactivity will then follow the polarizability function, P , of the nucleophile.

The opposite has been found for the phosphorochloridates where:⁽²⁰⁾



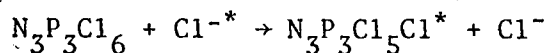
Here reactivity follows the basicity of the nucleophile, and β can be assumed to be small. The base preference of the phosphorochloridates is

also evident in the formation of the isothiocyanato derivative, $\text{Cl}_2\text{P}(\text{O})\text{NCS}$, in preference to the corresponding thiocyanato derivative. This allows equation (2-9) to be expressed in the form:

$$\log k = \alpha pK_a + \text{constant} \quad (2-10)$$

Therefore, where the reactivity of the electrophile follows the polarizability of the nucleophile β is predominant in equation (2-9). On the other hand, where the base strength is followed α is predominant and equation (2-10) is the result. Furthermore, in compounds with saturated carbon, where β is important, the thiocyanato derivative is formed. Conversely, with the phosphorochloridates, where α is important, the isothiocyanato derivative is formed.

The formation of the isothiocyanato phosphonitrilic derivative is then strongly suggestive of a reactivity dependent upon α . This can be shown by a comparison of the rate constant, k_{Cl} , for the reaction⁽³⁾



with the rate constant k for the thiocyanate substitution reaction.

k_{Cl} is lower, $5.01 \times 10^{-2}^*$ than k , $6.7 \times 10^{-2}^*$. Therefore, the reactivity does follow the basicity. These two rate constants allow a value of α to be calculated:

$$\log_{10} k_{\text{Cl}} = \alpha pK_a^{\text{HCl}} + \text{constant} \quad (2-11)$$

$$\log_{10} k = \alpha pK_a^{\text{HCNS}} + \text{constant} \quad (2-12)$$

* in units of $\text{l mole}^{-1} \text{sec}^{-1}$

$$\log k - \log k_{Cl} = \alpha(pK_a^{HCNS} - pK_a^{HCl}) \quad (2-13)$$

$$\text{where } pK_s^{HCNS} - pK_a^{HCl} = 4 \quad (19) \quad (2-14)$$

$$\log \frac{k}{k_{Cl}} = 4\alpha \quad (2-15)$$

$$\frac{1}{4} \log \frac{6.71}{5.01} = \alpha \quad (2-16)$$

$$\alpha = 0.0317 \quad (2-17)$$

The pK_a^{HCl} value is an approximation, the accuracy of which determines to a large extent the accuracy of the α value. This approximation has been used to correlate base strength and reactivity in similar reactions and therefore, it would seem to be an acceptable value to use here. Furthermore, the interest in α lies not in its absolute value, but in comparisons with α values for similar compounds. Such comparisons do show a sensible difference between the α value of the phosphonitrile and α values for compounds containing penta-valent phosphorus atoms.

α Coefficients for the Reaction of Nucleophiles with Phosphoryl

Compounds ⁽²¹⁾

<u>Compound</u>	<u>α</u>
$Et_2N(OEt)P(O)CN$	0.50
$(EtO)_2P(O)OP(O)(OEt)_2$	0.70
$PrO \cdot (Me) \cdot P(O)F$	0.82

As the positive charge on the phosphorus atom increases, the rate constant and the value of α should also increase. Therefore, if all other factors are constant, the value of α should follow the electron withdrawing effect of the ligands.

The small value of α for the phosphonitrile compared with those for the phosphoryl compounds is then an indication of the low positive charge on the phosphonitrilic phosphorus atom. This would be due to electron donation from the lone pairs of the ring nitrogens to the phosphorus atom. This effect is already known; recent studies of the ionization potentials of phosphonitriles⁽²²⁾ have indicated lone pair donation.

It should be observed from equation (2-15) that any factor which would increase k would also increase α . So decreasing the positive charge on the phosphorus atom decreases α . However, other factors could be important also. In the isothiocyanate the lone pair on the nitrogen could donate to the phosphorus atom. The corresponding increase in the exocyclic P-N bond energy would be expected to decrease the activation energy and, thus, increase k . Such donation would be evident in a shortened exocyclic P-N bond length; however, recent x-ray studies⁽²³⁾ show only a relatively small shortening and therefore indicate a weak exocyclic donation.

Two types of nitrogen lone pair donation are now evident:

- (1) donation from the ring nitrogen atoms which decreases α ,
- (2) and donation from the isothiocyanate nitrogen atom which increases k by stabilizing the transition state.

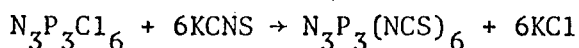
Because the α value for the phosphonitrile is smaller than the

α values for the phosphorochloridates, endocyclic donation would appear to be dominant. This is consistent with the x-ray structure of the fully substituted derivative, where the endocyclic shortening of the P-N bond is greater than the exocyclic.

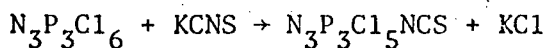
The E_a value of the thiocyanate reaction is 15.5 ± 0.5 Kcal/mole. This is lower than the value of 18.3 Kcal/mole found by Sowerby⁽³⁾ when using chlorine as the nucleophile. The $\log_{10} A$ or pre-exponential factor was 10.2 ± 0.3 compared with 12.1 for the chlorine. The difference in activation energies is compatible with the fact that substitution by isothiocyanate is faster than by chlorine. The increase in rate is then due to the stabilization of the transition step.

In conclusion it can be stated that the work in this section has provided information on several characteristics of phosphonitrile chemistry.

The reaction:



starts with the separate and individual step:



which is followed by a series of other steps to give the fully substituted derivative. The first step is second order, being first order in each reagent and is most probably bimolecular. This would involve a penta-co-ordinate phosphorus in the transition state.

Comparison of the kinetics of this first step with those of the similar chlorine exchange reaction, enables the value of the α factor to be calculated. Further comparison of this value with α factor values for phosphoryl compounds indicates that the phosphorus atom in the phosphonitrile has a higher electron density than the phosphorus atom in the phosphoryl groups.

CHAPTER THREE

METAL HALIDE DERIVATIVES OF PHOSPHONITRILES

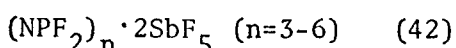
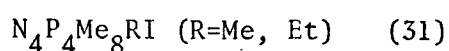
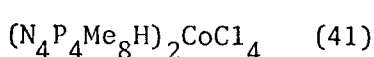
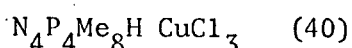
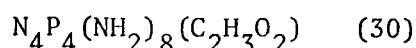
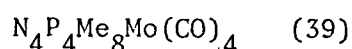
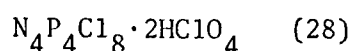
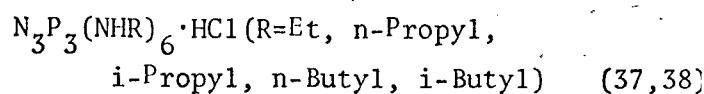
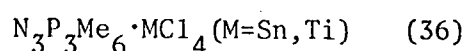
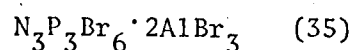
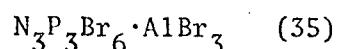
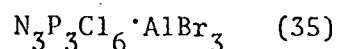
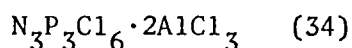
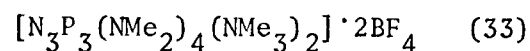
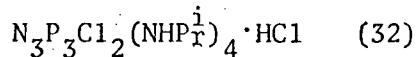
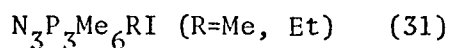
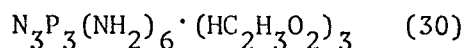
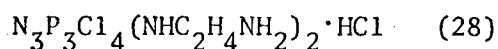
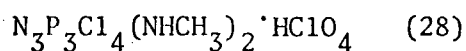
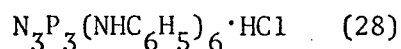
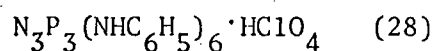
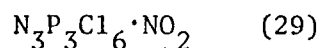
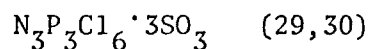
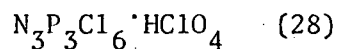
Introduction:

In the study of the chemistry of phosphonitrilic derivatives a major objective is the discovery of experimental evidence relevant to theoretical expectations. Craig and Paddock⁽²⁴⁾ and others⁽²⁵⁾ have, on the basis of Huckel M.O. theory, been able to explain many of the empirical results of such studies in terms of π -electron systems covering the whole molecule.

The structures of the tetrameric and hexameric phosphonitrilic dimethylamide derivatives are known^(26,27) and part of the object of the present work has been to make and study their complexes with metals, so as to throw more light on the factors influencing π -electron drift in the phosphonitriles. Phosphonitriles are known to form addition compounds with Lewis acids. Some of the reported compounds are listed in Table III.

Recent x-ray determination of the crystal structure of $N_4P_4Me_8H CuCl_3$ ⁽⁴⁰⁾ shows the copper bound to only one ring nitrogen, and the proton bound to the opposite nitrogen (Figure 16). In the metal carbonyl derivative, $N_4P_4Me_8Mo(Co)_4$ ⁽³⁹⁾, infra-red evidence suggests a molybdenum atom co-ordinated to two opposing ring nitrogens. However,

Table III Phosphonitric Addition Compounds



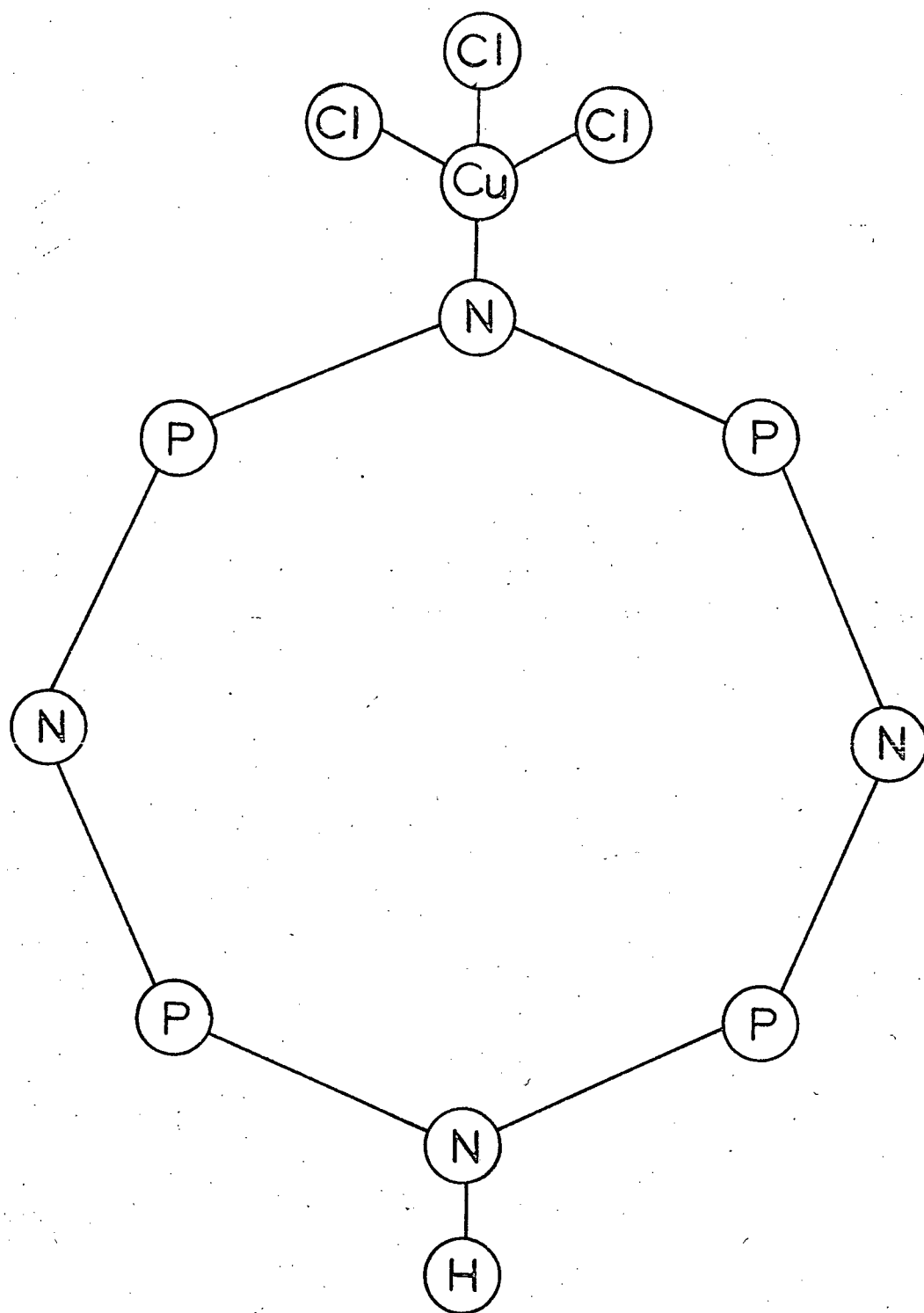


Figure 16. The Structure of $P_4N_4Me_8HCuCl_3$

(Exocyclic Groups Omitted)

since it has not been made in crystalline form, no x-ray determination of its structure is available.

$[(\text{NPMe}_2)_4\text{H}]_2\text{CoCl}_4^{(41)}$, which is stoichiometrically similar to $\text{N}_4\text{P}_4\text{Me}_8\text{CuCl}_3$, has an ionic structure composed of two sterically dissimilar $\text{N}_4\text{P}_4\text{Me}_8\text{H}^+$ cations and one CoCl_4^{2-} anion.

To date, no phosphonitrile has been bonded with a transition metal halide in such a way as to form bonds from more than one ring nitrogen. A few examples exist where the acceptor atom probably bonds to one nitrogen, e.g. $(\text{Me}_2\text{PN})_3\text{SnCl}_4$, $(\text{Me}_2\text{PN})_3\text{TiCl}_4^{(36)}$, and $\text{N}_3\text{P}_3\text{Cl}_6 \cdot 3\text{SO}_3^{(29,30)}$. The evidence for this type of bonding comes from infra-red and nuclear magnetic resonance studies.

Trimeric and tetrameric derivatives are probably too crowded to allow the metal to sit as closely to the ring plane as would be necessary in a multi-dentate ligand. Partially offsetting this, however, is the basicity of the ring nitrogens. The more basic they are, the less important will be the steric effects. The suggested structure of $\text{N}_4\text{P}_4\text{Me}_8\text{Mo}(\text{Co})_4^{(39)}$ indicates the possibility of forming an $\text{N}_4\text{P}_4\text{R}_8\text{CuCl}_2$ molecule with several ring nitrogens donating to copper. However, as this does not happen for $\text{R} = \text{Me}$, a more electron-releasing exocyclic group may be necessary.

Information on the basicity of the phosphonitrilic derivatives is available, and some is presented in Table IV.

TABLE IV pKa VALUES FOR SOME PHOSPHONITRILES*

Group	Trimer		Tetramer	
	pKa	pKa ₂ ^{**}	pKa	pKa ₂
Et (CH ₃) ^(43,44)	6.4		7.6	0.2

Group	Trimer		Tetramer	
	pKa	pKa ₂ ^{**}	pKa	pKa ₂
NMe ₂ ⁽⁴⁵⁾	7.6	-3.3	8.3	0.6

* determined in nitrobenzene

** refers to addition of a second proton

In none of the derivatives studied did the pKa values change by more than 1.2 units when varying ring size from trimer to tetramer⁽⁴⁴⁾. The effect of variation of ring size on base strength is evidently much smaller than that of variation of the exocyclic groups.

It should also be noticed that pKa values for phosphonitrilic amides are very similar to those for the free amines; dimethylamine has a pKa value of 7.5⁽⁴⁵⁾. Knowing the ease with which amines form complexes with a high copper co-ordination number, it might be expected that phosphonitriles would do the same.

The tetrameric phosphonitrilic dimethylamide derivative is more basic than the methyl derivative both to first and second protonation, and therefore, it is more likely to form a chelate complex with copper. This would involve a structure similar to that suggested for $P_4N_4(Me)_8Mo(Co)_4$ ⁽³⁹⁾.

However, steric interference would be greater for the amide groups than the methyl groups. This would offset some, if not all, of the increased basicity. Steric interactions would be reduced in the larger rings without appreciable change in base strength. In this work the reaction of copper (II) chloride with hexameric phosphonitrilic dimethylamide derivatives was investigated.

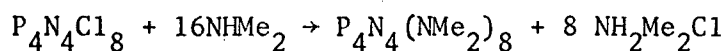
With phosphonitrilic amides, addition reactions can occur using the lone pair electrons at the ring, or exocyclic nitrogens or the molecular orbitals of the ring system. A number of articles suggest that the ring nitrogen atoms are the centres of basicity. One of these deals with the structural determination of $N_3P_3Cl_2(NHPr^i)_4HCl$ ⁽³²⁾. The proton is bonded to a ring nitrogen which indicates that this site is the centre of basicity. The structure of $[N_4P_4Me_8H]CuCl_3$ ⁽⁴⁰⁾ also supports this conclusion. Never the less, it is not inconceivable that, in hindered molecules, co-ordination of the exocyclic groups might occur, and interactions of this sort have been suggested ⁽³³⁾.

In the course of this work, the tetrameric phosphonitrilic dimethylamide derivative was made to react with copper(II) chloride in an attempt to produce a chelate complex of copper. However, the stoichiometry, $N_4P_4(NMe_2)_8HCuCl_3$, of the resulting complex and its infra-red spectra suggest a structure with only one copper-nitrogen covalent bond and one protonated ring nitrogen.

THE REACTION OF TETRAMERIC PHOSPHONITRILIC DIMETHYLAMIDE (T.P.D.) WITH COPPER (II) CHLORIDE.

The Preparation of T.P.D.:

T.P.D. is formed according to the equation:



The tetrameric phosphonitrilic chloride was prepared by the method of Stokes ⁽⁴⁷⁾ and the dimethylamine was the reagent grade chemical obtained

from Eastman Kodak.

At -78°C , 80 ml (1.21 moles) of dimethylamine in 20 ml of diethyl ether were slowly mixed with 30.2 g (0.0652 moles) of tetrameric phosphonitrilic chloride in 150 ml of diethyl ether. A dense white precipitate formed immediately. When this formation had stopped the reaction mixture was allowed to reach room temperature where it remained for two hours. The reaction mixture was then heated under reflux for nineteen hours. The white precipitate was filtered off, leaving a clear solution. Evaporation of this solution left a white hard powder (m.pt. 220°C) assumed to be the crude product (A).

The residual dimethylamine and diethyl ether were removed under vacuum from the first white residue. Co-precipitated product was then extracted from it using diethyl ether as the solvent. Evaporation of this solvent left a gummy white residue which was reacted for a further thirty-four hours with dimethylamine.

The crude product resulting from this reaction, combined with that previously obtained, (A), weighed 16 g (40% yield based on the amount of tetrameric phosphonitrilic chloride added). It was purified by repeated re-crystallization from diethyl ether to produce white crystalline needles of about 2 mm in length, m.pt. 238°C , $(\text{N}_4\text{P}_4(\text{NMe}_2)_8$ m.pt. $238^{\circ}\text{C}^{(48)})$. The infra-red spectrum of the sample in a potassium bromide pellet is shown in Table V and Figure 17(a).

A qualitative chlorine analysis showed the sample to be free from contamination by hydrogen chloride. Quantitative micro analysis gave N, 31.88; C, 35.79; H, 9.55%; (formula $\text{N}_4\text{P}_4(\text{NMe}_2)_8$ requires N, 31.60; C, 36.10; H, 9.02%.

TABLE V Infra-red Spectra* of $N_4P_4(NMe_2)_8$ and $N_4P_4(NMe_2)_8HCuCl_3$

$N_4P_4(NMe_2)_8HCuCl_3$	$N_4P_4(NMe_2)_8$
Peaks in cm^{-1}	Peaks in cm^{-1}
3100 s	3010m, 2980s, 2860s, 2780s p r
3000 - 2750 s v b	1870, 1980, 2020, 2070 p r w
2600 m	1430, 1450, 1465, 1480 p r s
1900 - 2400 p r w bands	1400 - 1230 p r s
1440, 1460, 1480, 1495 p r s	1175, 1145 s
1300, 1250, 1220, 1170 s	1060 m
1060 m	1000 - 950 b s
980 s	910 s
920 s	820 w
860 m	725 s
785 w	630 s
750s, 745m p r	520 s
660s, 665s	470 s
495 m	
450 m	

s - strong; m - medium; w - weak; v b - very broad; b - broad;
p r - poorly resolved

*Taken on a Perkin-Elmer 457 Grating Infra-Red Spectrophotometer.

Absorbance

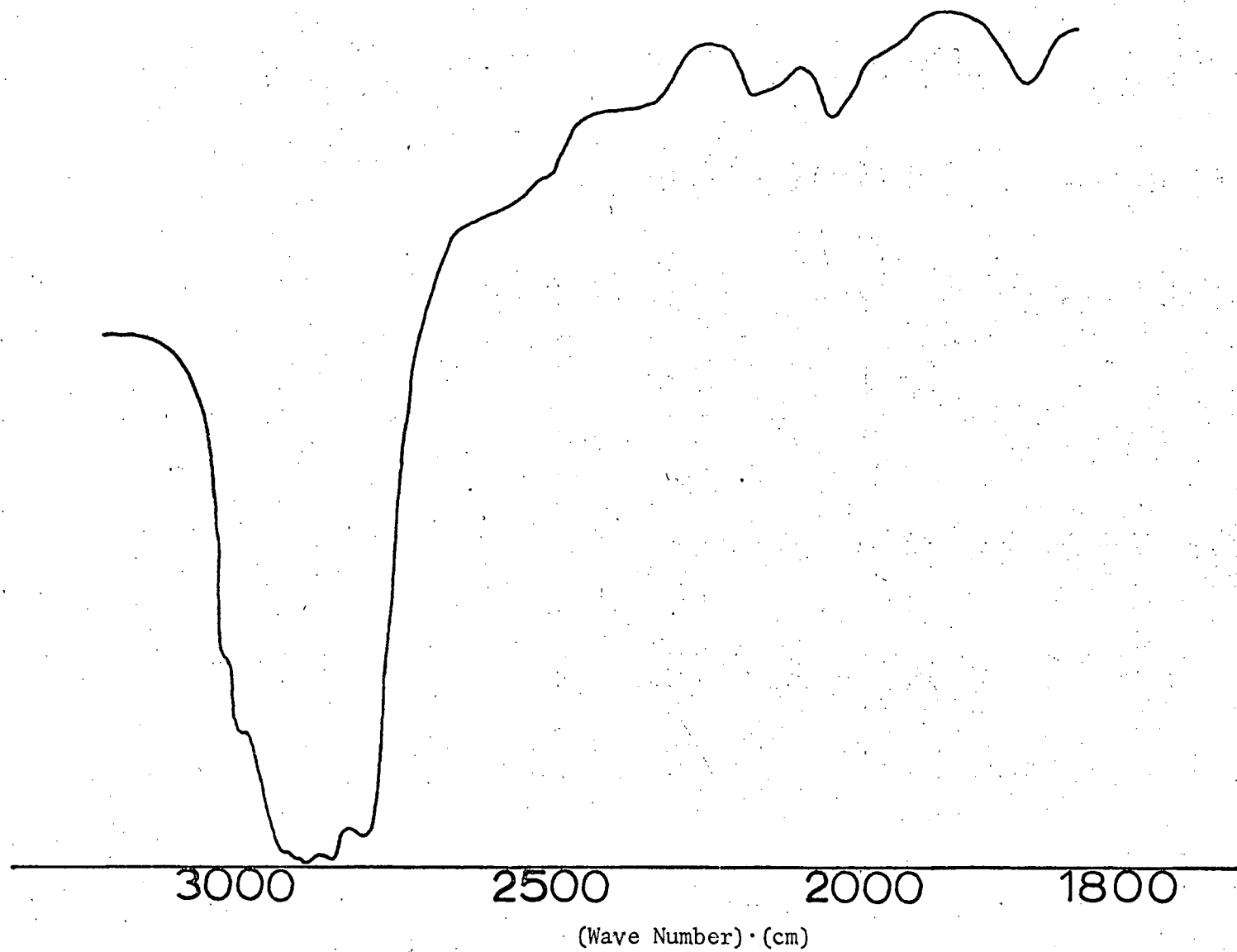


Figure 17(a). Infra-red Spectrum of $N_4P_4(NMe_2)_8$

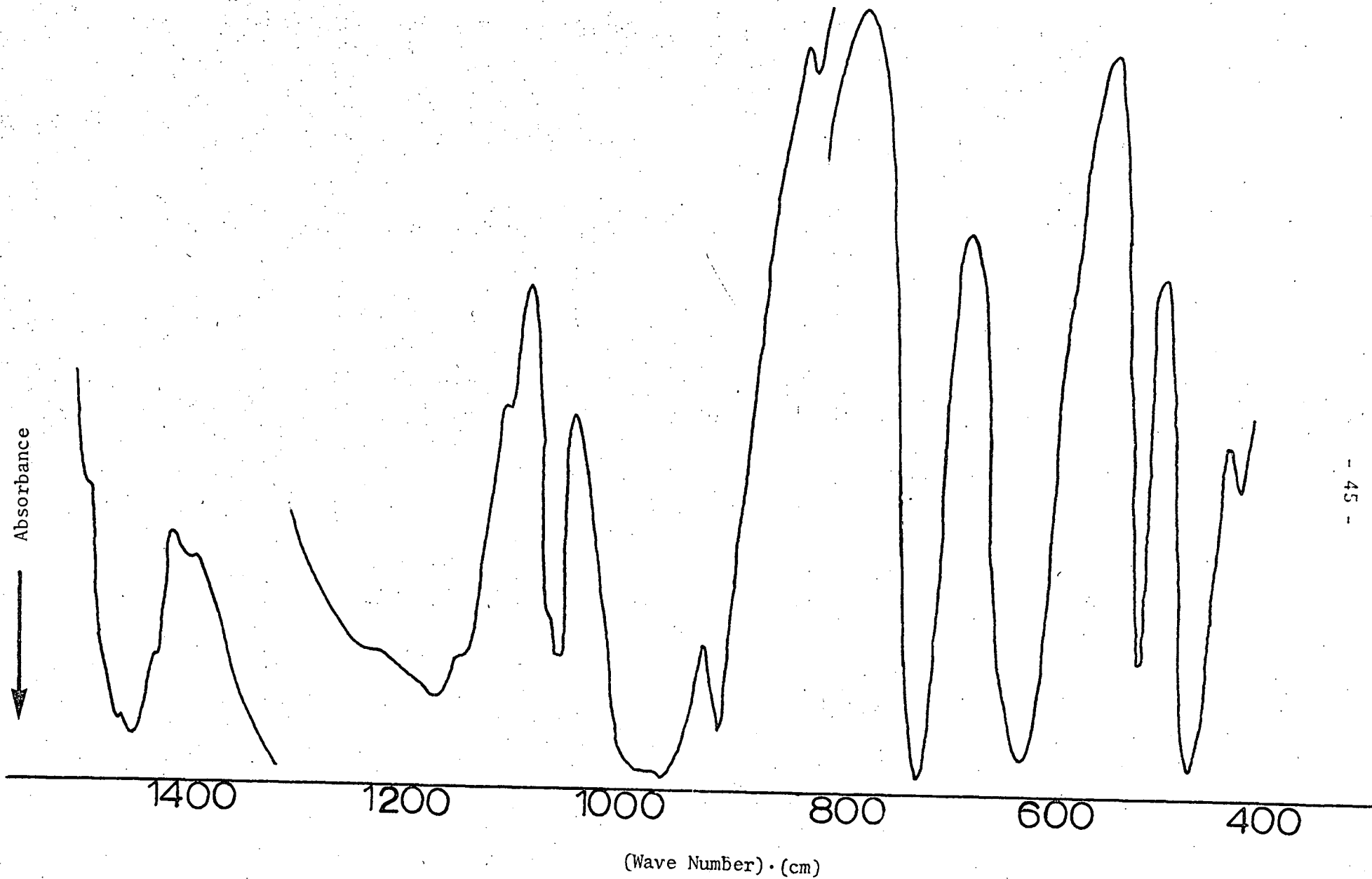


Figure 17(a). Continued

Absorbance

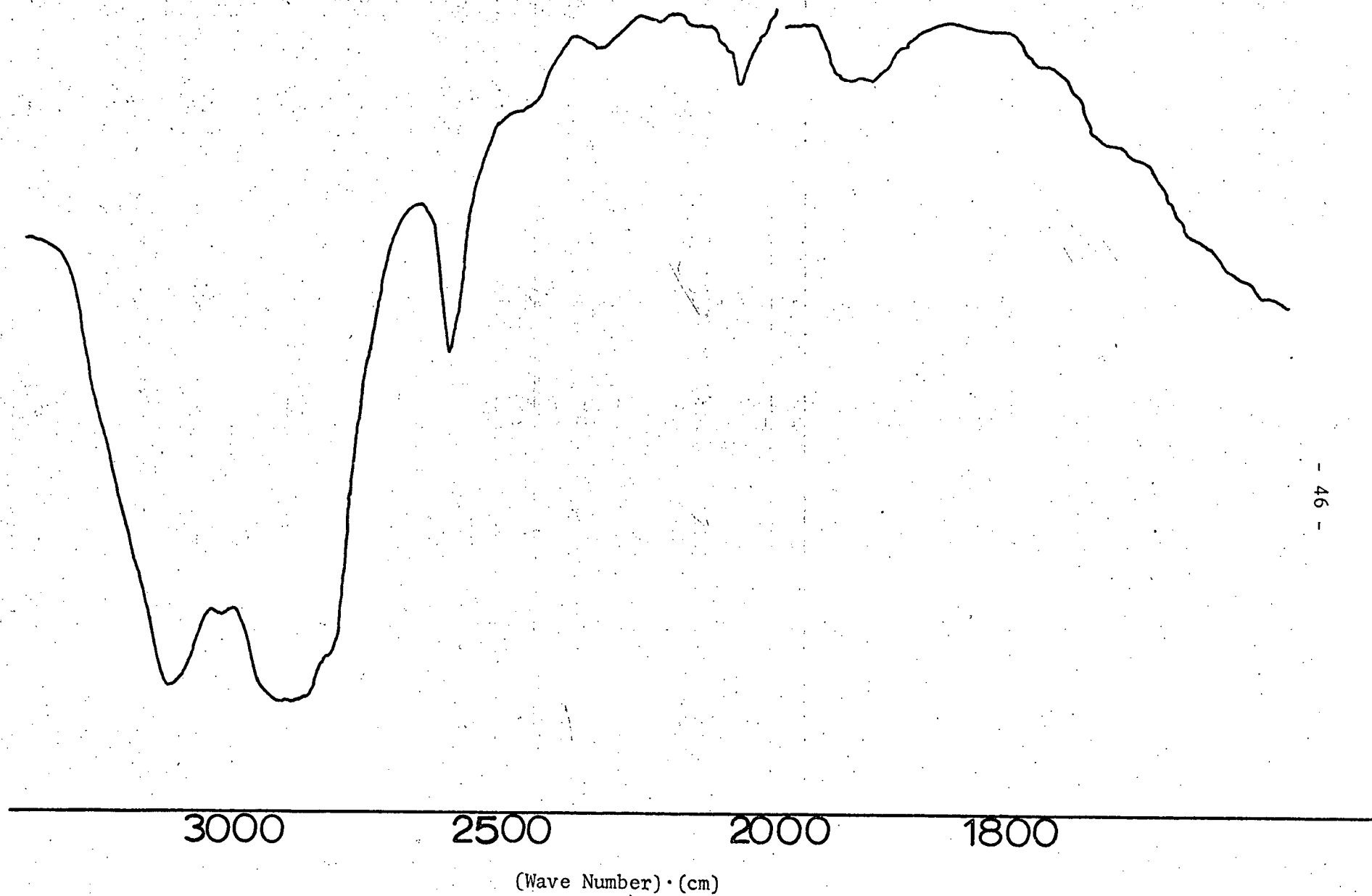


Figure 17(b). Infra-red Spectrum of $N_4P_4(NMe_2)_8HCl_3$

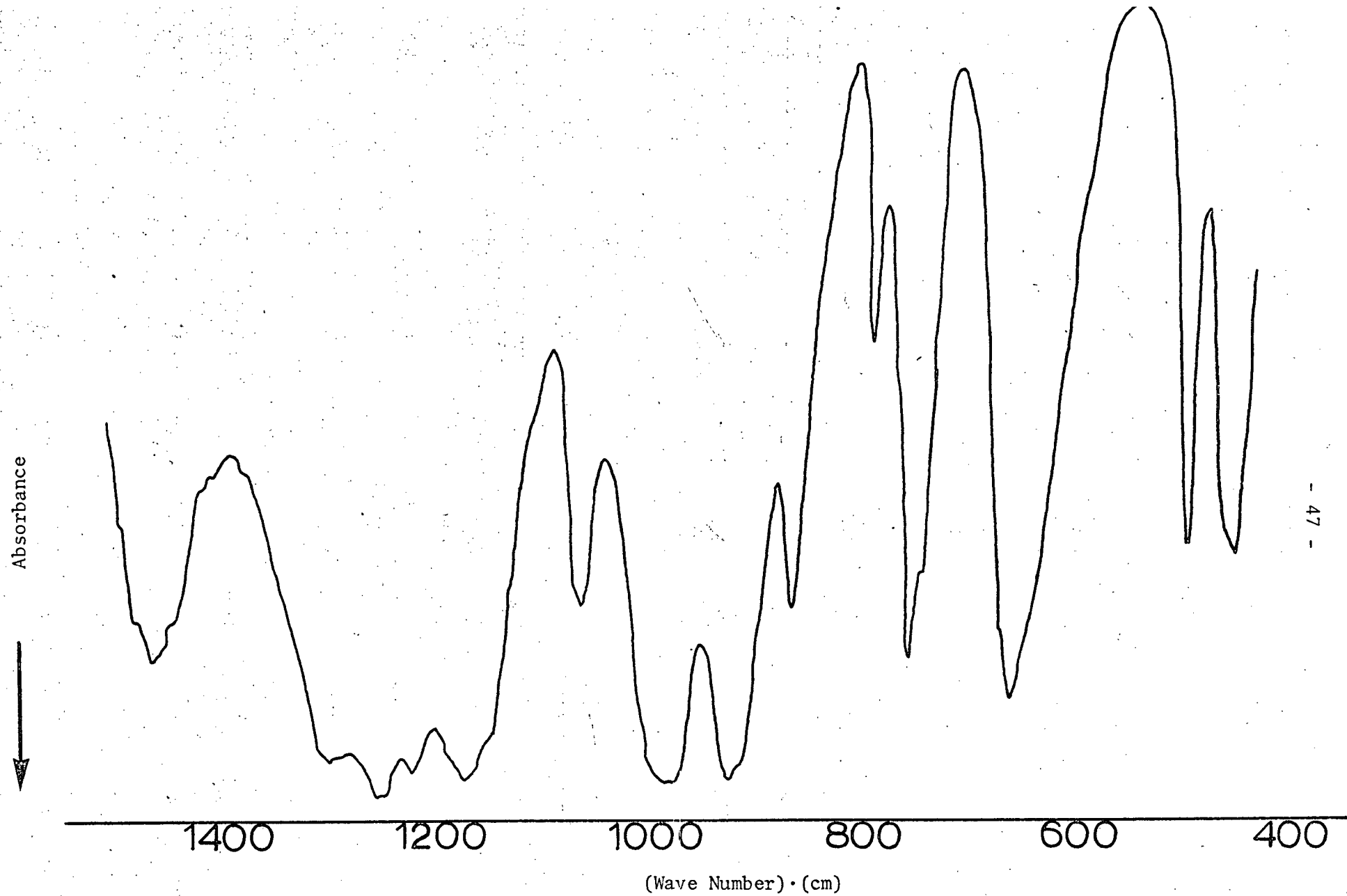


Figure 17(b). Continued

The Preparation of $N_4P_4(NMe_2)_8HCuCl_3$:

Anhydrous copper (II) chloride was obtained by dehydrating the hydrate in boiling butanone⁽⁴⁹⁾.

0.3306 g (4.3×10^{-4} moles) of T.P.D. in 100 ml of acetonitrile were added to 0.0743 g (5.53×10^{-4} moles) of copper (II) chloride in 200 ml of acetonitrile. The brown colour of the copper (II) chloride solution immediately changed to a red-brown tea colour. The reaction mixture was then heated under reflux for thirty minutes, cooled to -4°C , and left for fourteen hours.

Flash evaporation of the solution left a yellow-brown residue. This was dissolved in diethyl ether [copper (II) chloride is insoluble in this solvent] and filtered to give a golden wheat-coloured solution. Upon concentration of the solution and standing, there formed 0.0872 g of non-homogeneous primrose-yellow crystals, (m.pt. $103 - 105^\circ\text{C}$, 112°C).

The previous reaction was repeated using 3.4889 g (4.55×10^{-3} moles) of T.P.D. and 0.6679 g (4.97×10^{-3} moles) of copper (II) chloride. However, this time the yellow-brown residue was washed in 200 ml of diethyl ether and filtered. The undissolved product was extracted with diethyl ether in a Soxhlet extractor for two days. During the extraction, yellow rhombohedral needles formed in the flask. These were separated from the solvent and dried (m.pt. 114°C).

The amount of product recovered was:

rhombohedral needles from extraction	0.6980 g
material dissolved in solvent	0.1557 g
residue left in thimble after extraction of main product	<u>1.2006 g</u>
Total	1.9543 g

The yellow product in the thimble was unstable to the atmosphere, turning green upon prolonged exposure. Except for a small amount of insoluble red gum the yellow product was dissolved in benzene. This was filtered and evaporated to give a brown oil containing some benzene and some seemingly colourless crystals. The oil was diluted with 150 ml of carbon tetrachloride and the crystals filtered off as a gummy yellow powder.

The crystals formed in the flask during extraction (m.pt. 114°C) were re-crystallized from diethyl ether forming yellow rhombohedral crystals, (m.pt. 114 - 116°C); micro-analysis found N, 23.94; H, 7.04; C, 27.3; Cl, 15.45%. Formula $(P_4N_4(NMe_2)_8H)CuCl_3$ requires N, 23.8; H, 6.95; C, 27.3; Cl, 15.1%. The infra-red spectrum in potassium bromide is shown in Table V and Figure 17(b).

Discussion:

$N_4P_4(NMe_2)_8HCuCl_3$ bears an obvious stoichiometric similarity to $N_4P_4Me_8HCuCl_3$, both ligands being tetrameric rings with bulky electron-releasing groups attached and each molecule having three chlorine atoms and one copper atom. A corresponding structural similarity might therefore be expected.

The structure of $N_4P_4Me_8HCuCl_3$ has been determined by x-ray diffraction⁽⁴⁰⁾ and the ring shown to be covalently bonded through one nitrogen to the copper atom of the $CuCl_3^-$ group, and through the opposing nitrogen to the proton (Figure 16). A similar position for the proton in the amide derivative is suggested by the infra-red spectrum.

Therefore, CuCl_3^- is most probably bound to the opposing ring nitrogen.

The main differences in the spectra between the octa-amino derivative and its copper complex are the appearance of new bands at 3100, 2600, and 920 cm^{-1} , and the hypsochromic shift of the peaks at 725 and 630 cm^{-1} to 750 and 660 cm^{-1} , and the peaks at 1175 and 1145 cm^{-1} to 1220 and 1170 cm^{-1} .

Moeller and Kokalis⁽⁵⁰⁾ observed new bands at 2300 - 2650 cm^{-1} on going from the hexa-amino derivatives to their hydrochlorides. On the basis of similar results found upon the hydrohalogenation of pyridine derivatives^(51,53), he assigned these bands to N^+-H stretching modes. In several pyridinium derivatives Evans⁽⁵²⁾ assigned peaks at 3100 - 3374 cm^{-1} and 2800 - 2273 cm^{-1} to the same stretching modes. Similar bands (at 2660 and 3080 cm^{-1}) are found in the infra-red spectrum of $\text{N}_4\text{P}_4\text{Me}_8\text{HCuCl}_3$, which is known to be protonated on the nitrogen atom⁽⁴⁰⁾. Peaks at 3100 and 2600 cm^{-1} in the spectrum of $\text{N}_4\text{P}_4(\text{NMe}_2)_8\text{HCuCl}_3$ are most probably due to a similar protonation of one of the nitrogens. However, whether protonation is exocyclic or endocyclic cannot be determined from these bands.

Stahlberg⁽⁵⁴⁾ studied the spectrum of $\text{N}_3\text{P}_3\text{Cl}_2[\text{N}(\text{CH}_3)_2]_4$ and assigned peaks at 686 and 684 cm^{-1} to symmetric $\text{PN}_2(\text{exo})$ stretching modes, and peaks at 755 and 751 cm^{-1} to asymmetric $\text{PN}_2(\text{exo})$ stretching modes. Similar peaks at 630 and 725 cm^{-1} are found with $\text{N}_4\text{P}_4(\text{NMe}_2)_8$ and may be assigned to the analogous stretching modes (these may be unresolved doublets).

The spectrum of $\text{N}_4\text{P}_4(\text{NMe}_2)_8\text{HCuCl}_3$ shows a hypsochromic shift of these peaks to 665, 660 cm^{-1} and 750, 740 cm^{-1} . This is consistent

with the presence of π -electron withdrawing groups bonded to the ring. The P-N(exo) bond in $N_4P_4(NMe_2)_8$ has considerable double bond character caused by the delocalization of the lone pair electrons on nitrogen into the π -ring bonding system⁽²⁶⁾. Any bonding of the ring through its nitrogen lone pairs to an electron withdrawing group would cause an increase in the double bond character of the P-N(exo) bond and a resulting hypsochromic shift of the frequency of the vibrational modes.

Furthermore, no difference is noticed in the frequency of the N-C stretching mode (1060 cm^{-1}) between the two compounds. The bonding of an acceptor to an exocyclic group would have been expected to change this frequency; particularly if the acceptor had been a bulky copper anion. The proton and the copper atom must, therefore, be bound to the ring nitrogens.

It seems likely that, analogous to the case of $N_4P_4(NMe_2)_8H\text{CuCl}_3$, the anion is the group CuCl_3^- . This would be expected on electrostatic grounds to have an antipodal orientation relative to the proton. Evidence for this is found in the structure of $N_4P_4Me_8H\text{CuCl}_3$.

Because protonation of the ring reduces the basicity of the nitrogen atoms, this orientation would eliminate any chelation. So the copper is most probably bound to only one ring nitrogen. This would involve a structure analogous to that of $N_4P_4Me_8H\cdot\text{CuCl}_3$.

CHAPTER FOUR

THE PREPARATION OF A PHOSPHONITRILIC COMPLEX CONTAINING A CHELATED COPPER

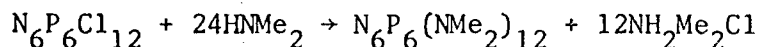
Both size and base strength should determine whether or not a phosphonitrile can act as a multidentate ligand. The failure of tetrameric phosphonitrilic dimethylamide to act as such a ligand indicates that a phosphonitrile with a larger ring and high basicity is necessary for chelation. The hexameric phosphonitrilic dimethylamide meets both these requirements^(45,55) and, therefore, its reactions under varying conditions with copper (I) chloride and copper (II) chloride have been studied.

In the course of this work the complex $N_6P_6(NMe_2)_{12}Cu(II)Cl Cu(I)Cl_2$ has been prepared and characterized. It is the first phosphonitrilic derivative to be shown to have a chelated metal atom, and also the first compound to contain the $CuCl_2^-$ ion⁽⁵⁶⁾.

Several attempts were made to produce complexes containing copper in only one oxidation state. However, only poorly defined solids were obtained.

THE PREPARATION OF HEXAMERIC PHOSPHONITRILIC DIMETHYLAMIDE (H.P.D.)

H.P.D. is produced according to the equation:



The hexameric phosphonitrilic chloride was already available and the dimethylamine was the reagent grade chemical obtained from Eastman Kodak.

At -78°C 50 ml (0.75 moles) of dimethylamine were slowly added to 11.9 g (0.0171 moles) of hexameric phosphonitrilic chloride in 75 ml of benzene. Upon warming to room temperature, the reaction mixture produced a dense white precipitate. After several hours at this temperature, the mixture was heated to reflux and kept there for ten hours.

Filtration and evaporation of the reaction mixture left 7 g of a sticky white powder which was assumed to be the desired product. Washing the filtrate with hot benzene removed several more grams of co-precipitated product. The product was re-crystallized repeatedly from benzene to give 6.5 g (48% of theory) of white powder, m.pt. 260°C (literature 256°C ⁽⁷⁸⁾). A qualitative chlorine analysis was negative, indicating complete substitution and the absence of the hydrochloride, $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{H Cl}$. The infra-red spectrum, which has not as yet been published, is given in Table VI and Figure 18(a).

THE REACTION OF H.P.D. WITH COPPER (II) CHLORIDE

Reactions in Butanone:

The butanone used was distilled and the fraction boiling between $79 - 81^{\circ}\text{C}$ was collected and passed through a column containing 400 mm of alumina and 200 mm of silica gel.

Anhydrous copper (II) chloride was obtained from the Fisher Scientific Company.

TABLE VI Infra-red Spectra* of H.P.D. and $N_6P_6(NMe_2)_{12}Cu_2Cl_3$

3010m, 2970m, 2860bs, 2790s; p r†	3010m, 2890s, 2850s, 2800s; p r
2150 b w	1490w, 1480m, 1460m, 1455m, 1440w, 1425w; p r
1480s, 1460, 1450; s	1290 s
1400 - 1250 v b s	1250 s
1183 s	1200, 1175; p r s
1145 m	1135 s
1070, 1063; p r m	1062 m
990, 970; p r s	980 s
890 m	859 m
780 m	795 m
718, 708; p r s	768 m
650 m	743m, 730m
590 s	568 m
	545 m
	515w, 509m, 490m; p r

* Taken on a Perkin-Elmer 457 Grating Infra-Red Spectrophotometer

† Symbols Defined on TABLE V

Absorbance
↓

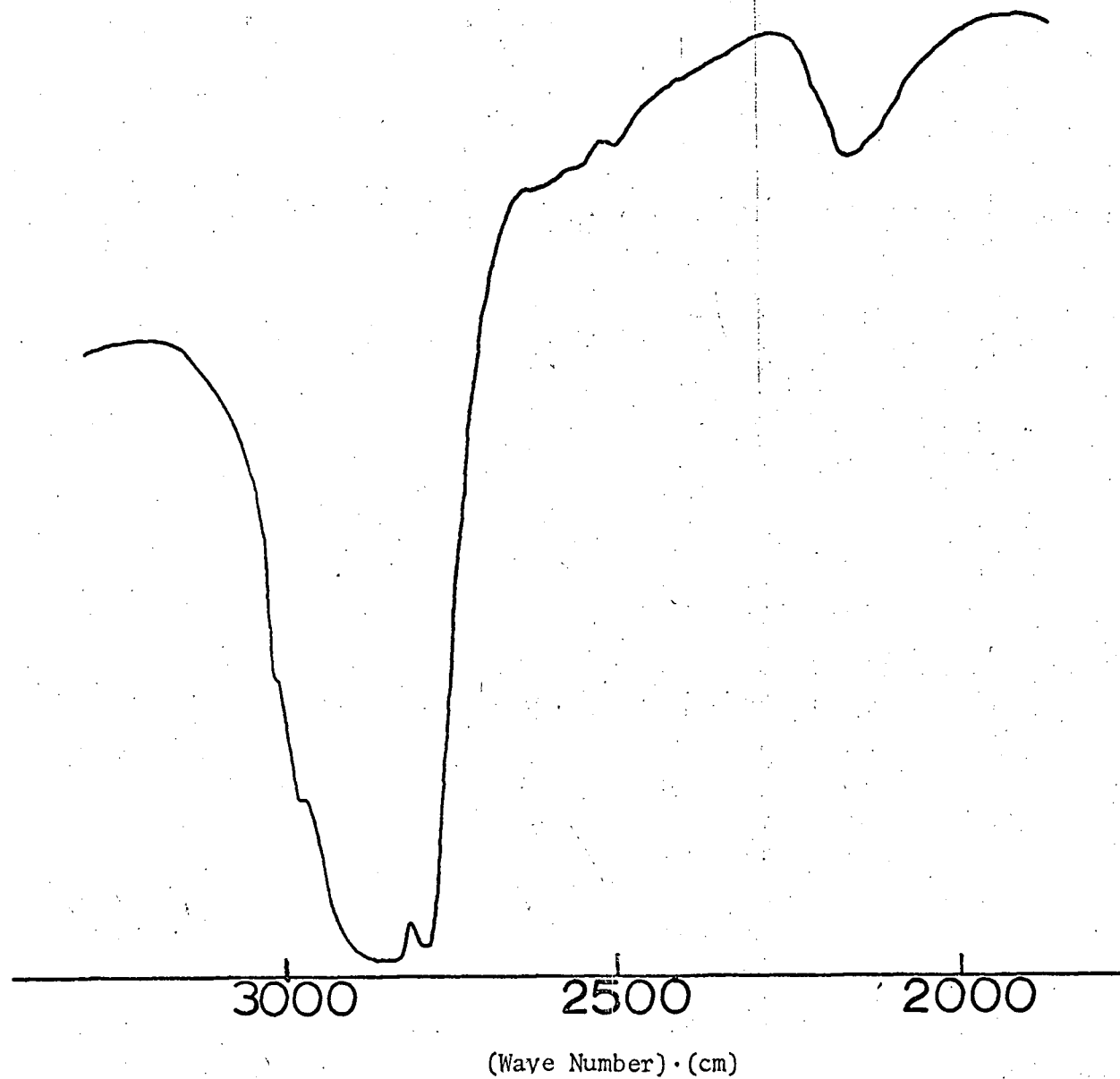


Figure 18(a). Infra-red Spectrum of $N_6P_6(NMe_2)_{12}$

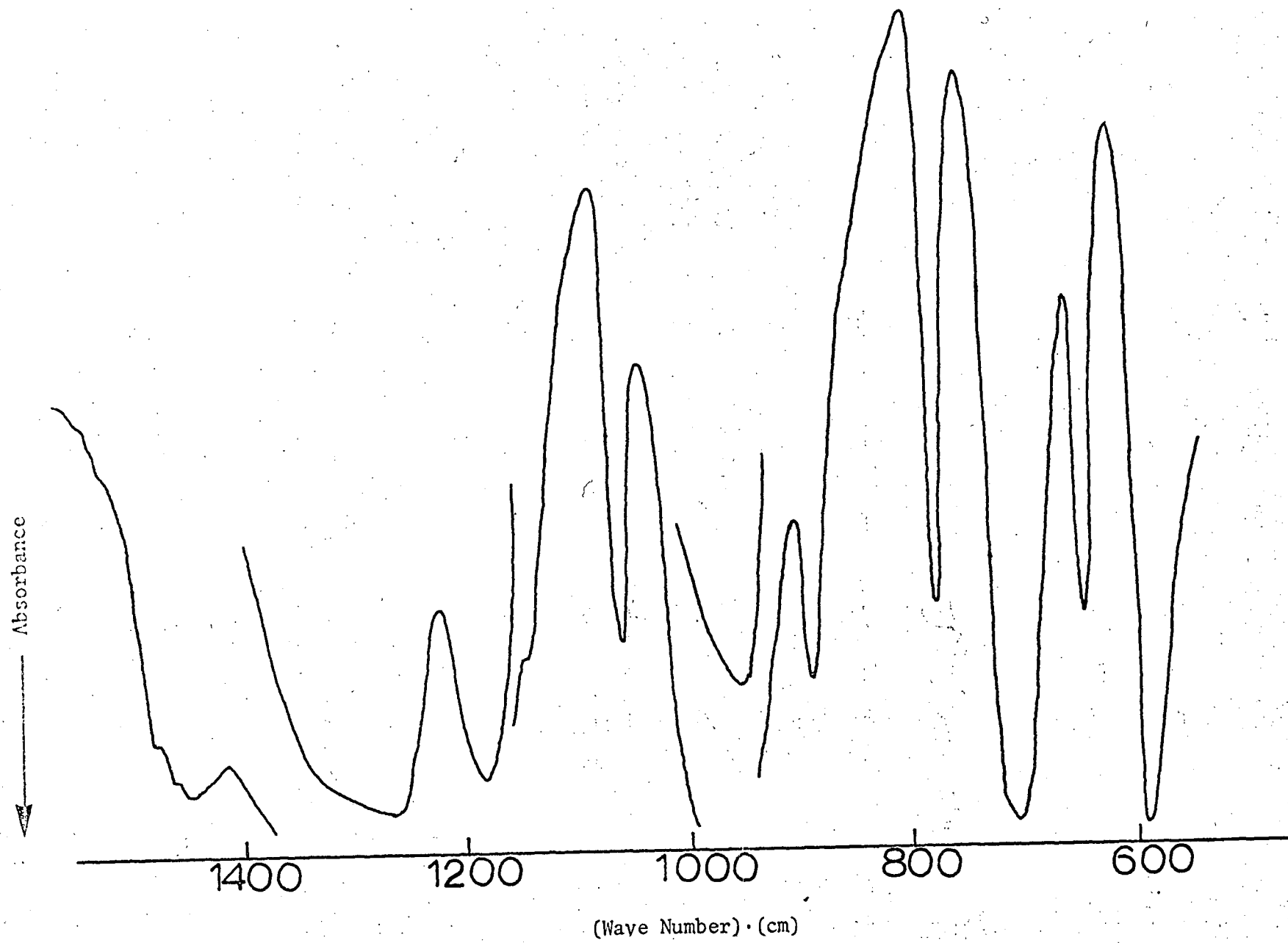


Figure 18(a). Continued

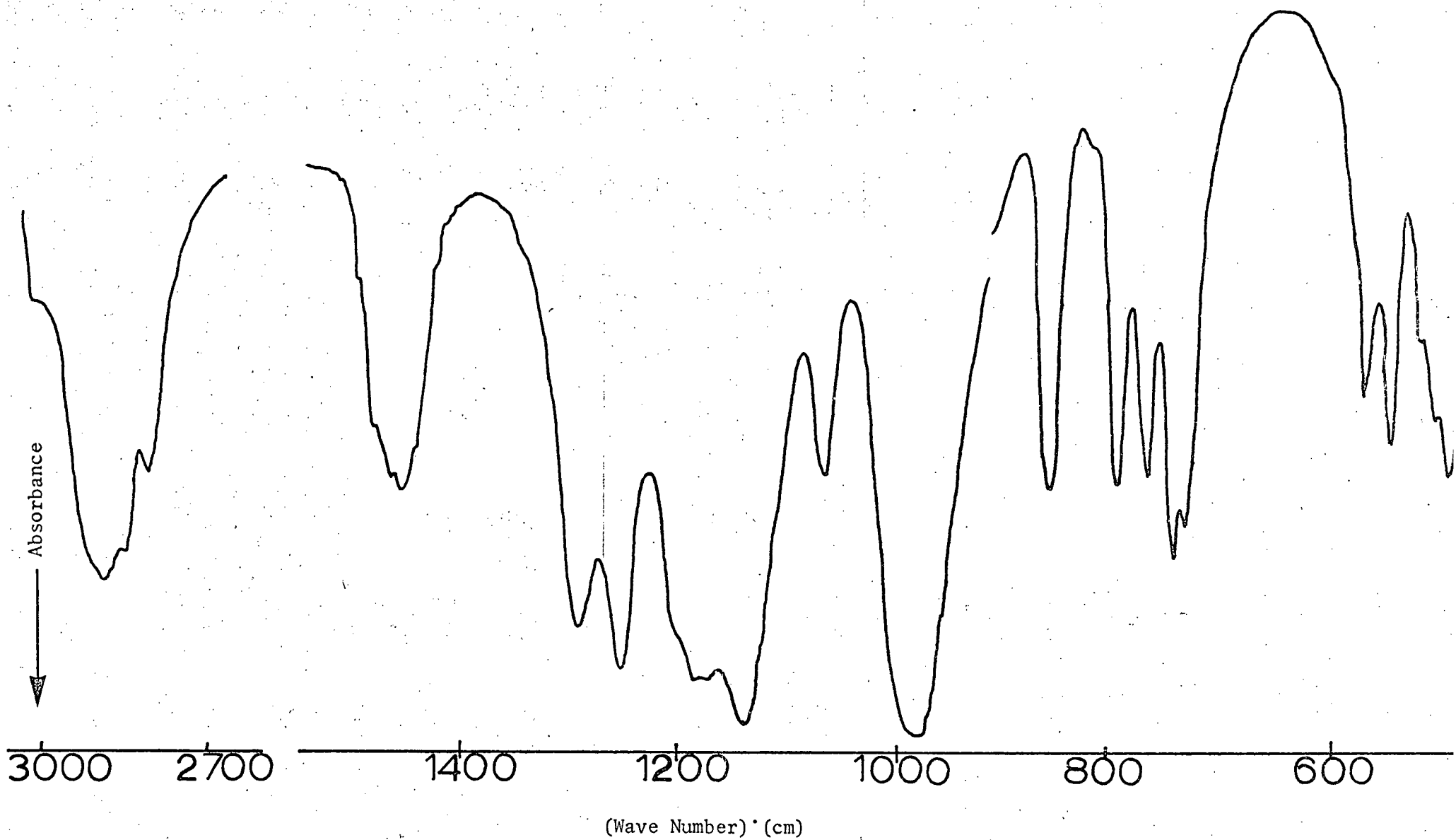


Figure 18(b). Infra-red Spectrum of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$

A clear solution of 3.0054 g (3.76×10^{-3} moles) of H.P.D. partially dissolved in 325 ml of butanone was added to a brown solution of 1.0306 g (7.66×10^{-3} moles) of copper (II) chloride. A bright red colour was instantaneously formed. Shaking the reaction vessel for several seconds dissolved the H.P.D. leaving a clear red solution with approximately 30 mg of high density dark powder. Upon standing for an hour, none of the powder visibly went into solution, though some of it dissolved on boiling.

Concentrating, filtering, and cooling the solution gave 2.6758 g of rust-red flakes, m.pt. 174°C . Further crystallization from butanone yielded 2 g of flakes (m.pt. 175°C) and some insoluble brown powder. A second crop of crystals was recovered from the mother liquor of the second crystallization.

A final re-crystallization was accomplished by slow evaporation of a butanone solution with purified nitrogen, (obtained from the Canadian Liquid Air Co.), and 0.79 g of small red-brown flakes (m.pt. 180°C) were obtained. After drying in vacuo these crystals were analyzed; the results are shown in Table VII.

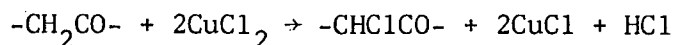
TABLE VII Elemental Analysis of Copper Complex

	%N	%Cu	%C	%H	%Cl
Obtained	23.3	11.40	26.8	6.80	13.21 13.25
Calculated for $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_4$	23.62	11.90	26.99	6.75	13.29
Calculated for $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3\cdot\text{HCl}$	23.59	11.88	26.96	6.83	13.28

The infra-red spectrum is: 2900*, 2800*, 2750*, p.r.s.; 1725* v.w.; 1485*, 1460*, 1450*, p.r.s.; 1420* w.; 1280[†]s; 1250^{*}s; 1185[†], 1170[†], 1145[†], p.r.s.; 1050[†]m; 850[†]m; 795[†]m; 766[†]m; 745[†]m; 725[†]m in units of cm⁻¹, (abbreviations defined in Table V.) The absence of any peaks in the N-H stretching region is not conclusive evidence for the absence either of the hydrochloride, N₆P₆(NMe₂)₁₂ Cu₂Cl₃·HCl, or of free hydrogen chloride.

The formula, N₆P₆(NMe₂)₁₂ Cu₂Cl₄ was not consistent with the properties of the compound. When a small sample was heated to 153°C in vacuo the chlorine analysis dropped to 10.5%, indicating a loss of one chlorine atom per molecule. This could be due to the loss of easily removable hydrogen chloride from a complex having the formula, N₆P₆(NMe₂)₁₂ Cu₂Cl₃·HCl. Table VII shows that the two formulas have almost identical percentage compositions and are both consistent with the analytical results.

The hydrogen chloride could come from the oxidation of the solvent by the copper (II) chloride, e.g.:



It is important to note that the formula, N₆P₆(NMe₂)₁₂ Cu₂Cl₃·HCl, requires the presence of a copper (I) atom which is also produced in the redox reaction. Succeeding work showed that the complex does in fact contain two oxidation states of copper. It might, therefore, be expected that copper (II) chloride and H.P.D. would react differently in a non-reducing solvent, acetonitrile, than in the reducing solvent

* Taken from halocarbon oil mull

† Taken from nujol mull

butanone. This reaction and others similar to it are studied next.

REACTIONS IN ACETONITRILE

Reaction of Copper (II) Chloride with H.P.D.:

0.98909 g (1.24×10^{-3} moles) H.P.D. partially dissolved in 200 ml of acetonitrile, were added to a murky green solution of 0.3356 g (2.49×10^{-3} moles) of copper (II) chloride in 200 ml of acetonitrile. One minute after mixing, a red-tea colour appeared and all but a small amount of H.P.D. went into solution. After standing for ten hours, the reaction mixture was filtered to give a clear red solution.

Removing the solvent under reduced pressure at 50°C left 1.2 g of a dark red powder, m.pt. 169°C. This was crystallized from an acetonitrile-benzene mixture to produce 0.6932 g of brown crystalloid needles, m.pt. 170°C. The infra-red spectrum taken in potassium bromide wafer was: 2950, 2900, 2850, 2825, p.r.s.; 1500 b.m.; 1300s; 1260; 1190, 1170, 1130 p.r.m.; 1065m; 985 b.s.; 860s; 800m; 750m; 730m; in units of cm^{-1} , (Abbreviations defined in Table V.), and is different from that of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$.

Microscopic examination showed the crystals to be of two types, transparent, ruby red needles and opalescent brown needles. The former were mechanically separated and then analyzed; (N, 22.51; H, 6.96; C, 29.42%).

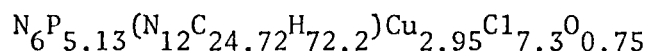
Further attempts at re-crystallization from acetonitrile failed, and produced a decomposition of the product, evident by a depressed melting point of 153 - 156°C. Under vacuum at 92°C, this material

decomposed into a white sublimate and a dark red powder.

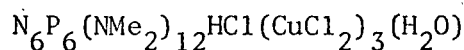
Repeated re-crystallization from chloroform and carbon tetrachloride solutions gave a golden-yellow powder, m.pt. 171 - 173°C. The infra-red spectrum was identical to that previously obtained.

Analysis of this material gave: N, 20.29; P, 12.81; C, 23.88; H, 5.82; Cl, 20.97; Cu, 15.09; O, 0.96%.

Assuming a molecule having eighteen nitrogen atoms, this analysis corresponds to:



which is most probably:



Further purification by thin layer chromatography failed owing to the decomposition of the sample. No further purification was attempted.

Reaction of Copper (I) Chloride with H.P.D.:

Copper (I) chloride was prepared by the reduction of an aqueous solution of copper (II) chloride with sulphur dioxide⁽⁵⁷⁾. The product was washed with sulphurous acid and glacial acetic acid, then dried in vacuo at 100°C. The pure white powder produced by this method was stored under nitrogen in a stoppered and wax sealed vial.

The acetonitrile used in this experiment was dried by the method described in Chapter 2. All oxygen was removed by heating the

solution under reflux and bubbling in purified nitrogen for two hours.

The H.P.D. was heated at 90°C in vacuo for two hours. The melting point was then 260°C.

All reactions were carried out under purified nitrogen.

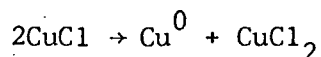
A clear, colourless solution of 1.98 g (20.0×10^{-3} moles) of copper (I) chloride in 500 ml of acetonitrile was added to a clear, colourless solution of 4.65 g (5.82×10^{-3} moles) of H.P.D. partly dissolved in 100 ml of acetonitrile. A further 5.2 g (6.5×10^{-3} moles) of H.P.D. was added to the reaction mixture. No colour change was noticed during either addition.

Warming of the reaction mixture dissolved all the remaining H.P.D. During this warming, the solution turned a pale yellow. Concentration of the solution produced a dark yellow solution and a brown-white precipitate. Flash evaporation revealed 5.41 g of dark powder. Extracting this powder with benzene for eight hours gave a clear solution and left insoluble brown powder in the Soxhlet thimble. Flash evaporation of the solution gave 0.3331 g of H.P.D. (m.pt. 243°C; infra-red spectrum as in Table VI).

The benzene insoluble material was washed with dry chloroform to produce a red solution with a green reflex and leaving an insoluble black powder.

The black powder was insoluble in all the common organic solvents, but dissolved in sulphuric and hydrochloric acids, as well as ammonium hydroxide. Its infra-red spectrum was a blank; a qualitative copper test performed on it was positive; and its melting point was in excess of 320°C. All of this is consistent with the black powder being

metallic copper. This, in turn suggests disproportionation during the reaction according to the equation:



Because copper (II), unlike copper (I), forms coloured compounds, disproportionation would also explain the presence of a coloured product.

When it was cooled to -4°C , the chloroform solution formed 1.19 g of crystals having the appearance of clotted blood. These were air sensitive, turning green upon prolonged exposure to the atmosphere.

Upon drying in vacuo, the compound had a melting point of $191 - 193^{\circ}\text{C}$ and in nujol and halocarbon oil mulls, its infra-red spectrum was: 3012^*m , 2930^*s , 2900^*s , 2850^*s , 2810^*s , 1835^*w , 1800^*m , 147^*s , 1465^*s , 1455^*s , 1445^*s , 1435^*m , 1300^+s , 1255^+s , 1210^+s , 1190^+s , 1175^+s , 1150^+s , 1070^+m , 980^+s , 863^+m , 800^+m , 773^+m , 750^+s , 735^+s , in units of cm^{-1} , (abbreviations defined in Table V). They were soluble in chloroform and acetonitrile, but insoluble in petrol ether, carbon tetrachloride and benzene.

Further attempts at re-crystallization from acetonitrile and chloroform resulted in adulteration of the product evident by a depressed melting point, $190 - 191^{\circ}\text{C}$. Attempted purification by thin layer chromatography was similarly unsuccessful.

* Taken from halocarbon oil mull

† Taken from nujol mull

Reaction of Copper (I) Chloride and Copper (II) Chloride with H.P.D.:

The H.P.D., copper (I) chloride and anhydrous, oxygen free acetonitrile used in this experiment were prepared in an identical manner to those used in the previous experiment. The anhydrous copper chloride was obtained from the Fisher Scientific Company.

0.1761 g (1.31×10^{-3} moles) of copper (II) chloride were added to 300 ml of warm acetonitrile under purified nitrogen. There was an immediate colour change, giving a yellow solution. To this solution 0.1335 g (1.34×10^{-3} moles) of copper (I) chloride powder was added. Finally, 300 ml of acetonitrile containing 1.0235 g (1.28×10^{-3} moles) of partially dissolved H.P.D. was added. There was an immediate colour change after the final addition resulting in a weak tea-coloured solution.

The H.P.D. dissolved completely upon boiling the reaction mixture. During this heating, the solution became appreciably darker and assumed a dark red colour .

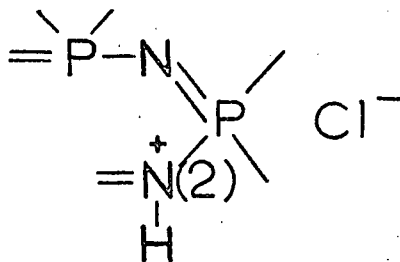
Concentration of the solution yielded 0.8 g of yellow flakes, m.pt. 179 - 181°C. The crystals were reported to be crystallographically identical to those of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ as prepared by the dehydro-halogenation of the product prepared previously in butanone⁽⁵⁸⁾. The analysis was: N, 24.15; P, 18.22; C, 28.18; H, 6.86; Cu, 12.33; Cl, 10.28% calculated for $N_6P_6(NMe_2)_{12}Cu_2Cl_3$: N, 24.4; P, 18.05; C, 27.9; H, 6.96; Cu, 12.3; Cl, 10.2%.

The infra-red spectrum taken in a potassium bromide wafer is identical to the spectrum of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ as shown in Table VI.

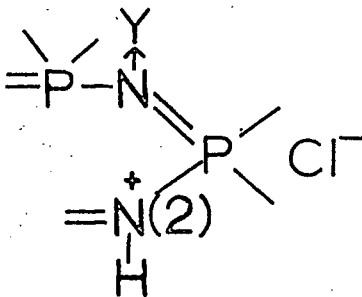
Discussion:

The reaction between hexameric phosphonitrilic dimethylamide and copper (II) chloride in butanone produces crystals of $N_6P_6(NMe_2)_{12} Cu_2Cl_3 \cdot HCl$ which dehydrohalogenates upon warming to form the compound, $N_6P_6(NMe_2)_{12} Cu_2Cl_3$. This contains two oxidation states of copper and can be produced by the reaction of H.P.D. with a mixture of copper (II) chloride and copper (I) chloride in the non-reducing solvent, acetonitrile.

Phosphonitrilic amides are such strong bases that they often form hydrochlorides in the presence of secondary amines. However, if a π -electron withdrawing group were to complex strongly to the ring nitrogens of such a hydrochloride, there would be a considerable weakening of the forces holding the hydrogen chloride to the molecule. For example, if the system:

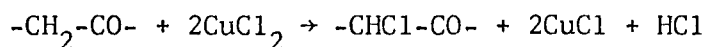


complexes with a π -electron withdrawing group Y to form:



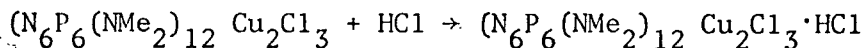
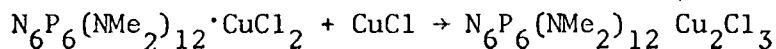
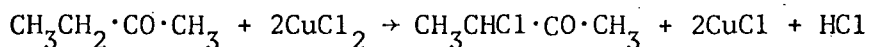
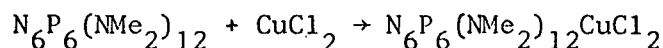
there would be a reduction in density of the lone pair on N(2). The N(2)-H bond would be weakened and hydrogen chloride could be more readily removed from the molecule. If the complexing were strong enough, hydrogen chloride could be readily removed.

Hydrogen chloride must, therefore, have been present at some time during the reaction. This would occur if copper (II) chloride were reduced by the solvent. Ketones are known reducing agents, the following reaction occurring for acetone:



Similar reduction could also explain the presence of hydrogen chloride in $\text{N}_4\text{P}_4\text{Me}_8\text{HCuCl}_3^{(49)}$, $(\text{N}_4\text{P}_4\text{Me}_8\text{H})_2\text{CoCl}_4^{(49)}$, and $\text{N}_4\text{P}_4(\text{NMe}_2)_8\text{HCuCl}_3$. Each of these complexes was prepared using metal chlorides previously dehydrated in butanone.

The formula, $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3 \cdot \text{HCl}$ suggests that copper is present as copper (I) and copper (II). This, and the presence of hydrogen chloride could be explained by a reaction path similar to:



However, it remains to be shown that the complex does in fact contain copper (I) and copper (II) atoms. To do this, purely chemical evidence

is the most satisfying.

Acetonitrile is a non-reducing solvent, therefore, copper (II) chloride will not be reduced if dissolved in it. If $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ could be produced by the reaction of copper (II) chloride with H.P.D. in acetonitrile, then it must contain only copper (II). On the other hand, if it contains both oxidation states, then it cannot be produced by this reaction. The reaction was investigated, and while an unstable product was isolated, infra-red spectroscopy and chemical analysis showed it was not $N_6P_6(NMe_2)_{12}Cu_2Cl_3$.

Similarly if the complex could be produced by the reaction of copper (I) chloride with H.P.D. it would be positive evidence that it contained only copper (I). This reaction was investigated, and did not produce the required product. Furthermore, $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ is a coloured compound and there is no known coloured complex containing only copper (I) as an acceptor, (except when the colour results from charge transfer bands)⁽⁵⁶⁾.

These experiments showed that $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ cannot be produced from the reaction of H.P.D. with either copper (I) chloride or copper (II) chloride in a non reducing solvent such as acetonitrile. This indicates that the metal in the complex does not belong exclusively to one oxidation state. And the presence of one atom each of copper (I) and copper (II) in the complex was proven by the reaction of H.P.D. with an equimolar mixture of copper (I) chloride and copper (II) chloride in acetonitrile which produces $N_6P_6(NMe_2)_{12}Cu_2Cl_3$. Because no reduction of the copper (II) chloride could have occurred, and because similar solutions containing either of the copper chlorides do not produce the

desired product, $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ must, therefore, contain both oxidation states of copper.

The absence of hydrogen chloride from the product obtained from the acetonitrile solution shows that its presence on the product from the butanone solution is a result of a redox reaction and is not a necessary part of the copper complexing process. If it were, then $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ could not be produced except through the hydrochloride intermediate.

In conclusion, the following facts are now known about $N_6P_6(NMe_2)_{12}Cu_2Cl_3$. It can be produced by the reaction of H.P.D. with either copper (II) chloride in butanone or with a mixture of copper (I) chloride and copper (II) chloride in acetonitrile. The mono-hydrochloride of the complex is readily made and loses hydrogen chloride upon heating. Finally, the complex contains both copper (I) and copper (II).

The actual formation of the $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ is, however, still unknown, although many possibilities are evident. The number of these is somewhat limited by the known co-ordination numbers of copper (I) and (II) (56,59).

If the compound is a true complex, then it can only be:

$N_6P_6(NMe_2)_{12}Cu(I)Cu(II)Cl_3$, $N_6P_6(NMe_2)_{12}Cu(I)ClCu(II)Cl_2$, or $N_6P_6(NMe_2)_{12}Cu(I)Cl_2Cu(II)Cl$. On the other hand, if it is in fact a salt then it can only be: $N_6P_6(NMe_2)_{12}Cu^{+2}CuCl_3^{-2}$, or $N_6P_6(NMe_2)_{12}CuCl^+CuCl_2^-$. The choice waits upon evidence presented in the following chapter and here no decision regarding the true formation of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ can be made.

CHAPTER FIVE

PHYSICAL STUDIES OF $N_6P_6(NMe_2)_{12}Cu_2Cl_3$

Introduction and Summary:

An x-ray crystal structure determination done on the complex shows that of the possibilities referred to in the previous chapter, the structure in the solid is ionic being $N_6P_6(NMe_2)_{12}CuCl^+CuCl_2^-$. The cation is the only example of a phosphonitrilic derivative which forms a chelate complex with a transition metal. The detailed structure found in the crystal does not persist in solution.

The existence in solution of the cation, $N_6P_6(NMe_2)_{12}Cu^{++}$ is suggested by evidence obtained from the reaction of the complex with silver nitrate. This cation would have less internal crowding than the corresponding $N_6P_6(NMe_2)_{12}CuCl^+$ cation and might, therefore, be favoured in solution.

Electrochemical measurements support this supposition. The salt is not a 1:1 electrolyte in acetonitrile solution, the limiting conductance being higher than has been reported for any such electrolyte.

The existence of the anion, $CuCl_2^-$ is proven by the molecular structure. $CuCl_2^-$ is linear and has bond lengths corresponding to the sum of the covalent radii for Cu (I) and Cl atoms. A possible path for producing anions of the type $Cu(NO_3)_2^-$ is suggested by the silver nitrate

experiment.

Magnetochemical studies on the solid complex showed that it contained only one copper (II) atom per molecule.

The infra-red spectrum of the complex is very similar to that of the parent H.P.D. This is attributed to the basic similarity of the two molecules. Due to the lack of information concerning the infra-red spectra of phosphonitric derivatives, very few assignments of the peaks in either spectrum could be made.

The Crystal Structure of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$:

The crystal structure of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ was determined in this department⁽⁵⁸⁾ and shown to be formed from two discrete ions, $N_6P_6(NMe_2)_{12}CuCl^+$ and $CuCl_2^-$. The cation contains a chelated copper with a distorted square pyramidal environment. The anion is linear.

The formula $N_6P_6(NMe_2)_{12}CuCl^+CuCl_2^-$ can be proven by consideration of structural evidence alone, (Figures 19,20; Table VIII). The chelated copper, Cu(2), is penta co-ordinate, and while such co-ordination is well known for copper (II) atoms⁽⁵⁶⁾, (for example, dimethylglyoximatocopper (II)^(60,61)), tetra co-ordination is the highest observed for copper (I), silver (I), or gold (I) atoms⁽⁶²⁾. Thus, it can be presumed that this copper atom is divalent.

Furthermore, the Cu(2)-Cl(2) bond length (2.28Å) is better approximated by the sum of the covalent radii⁽⁶³⁾ for Cu (II) and Cl, (2.34Å), than for Cu(I) and Cl, (2.17Å). Thus, the phosphonitric derivative is far more likely to be the cation, $N_6P_6(NMe_2)_{12}Cu(II)Cl^+$

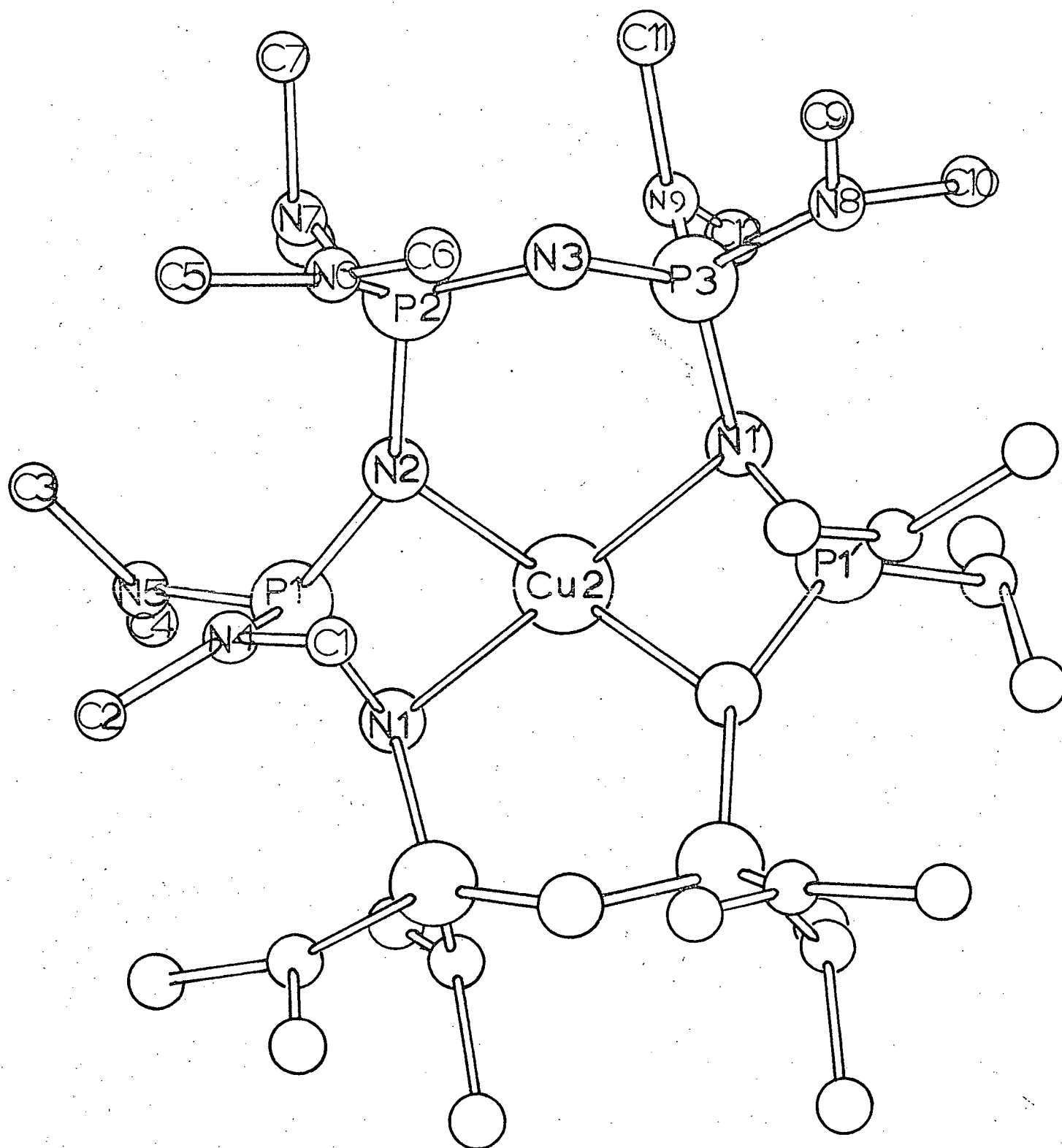


Figure 19. Phosphonitrilic Ring of $N_6P_6(NMe_2)_{12}CuCl^+$ Anion

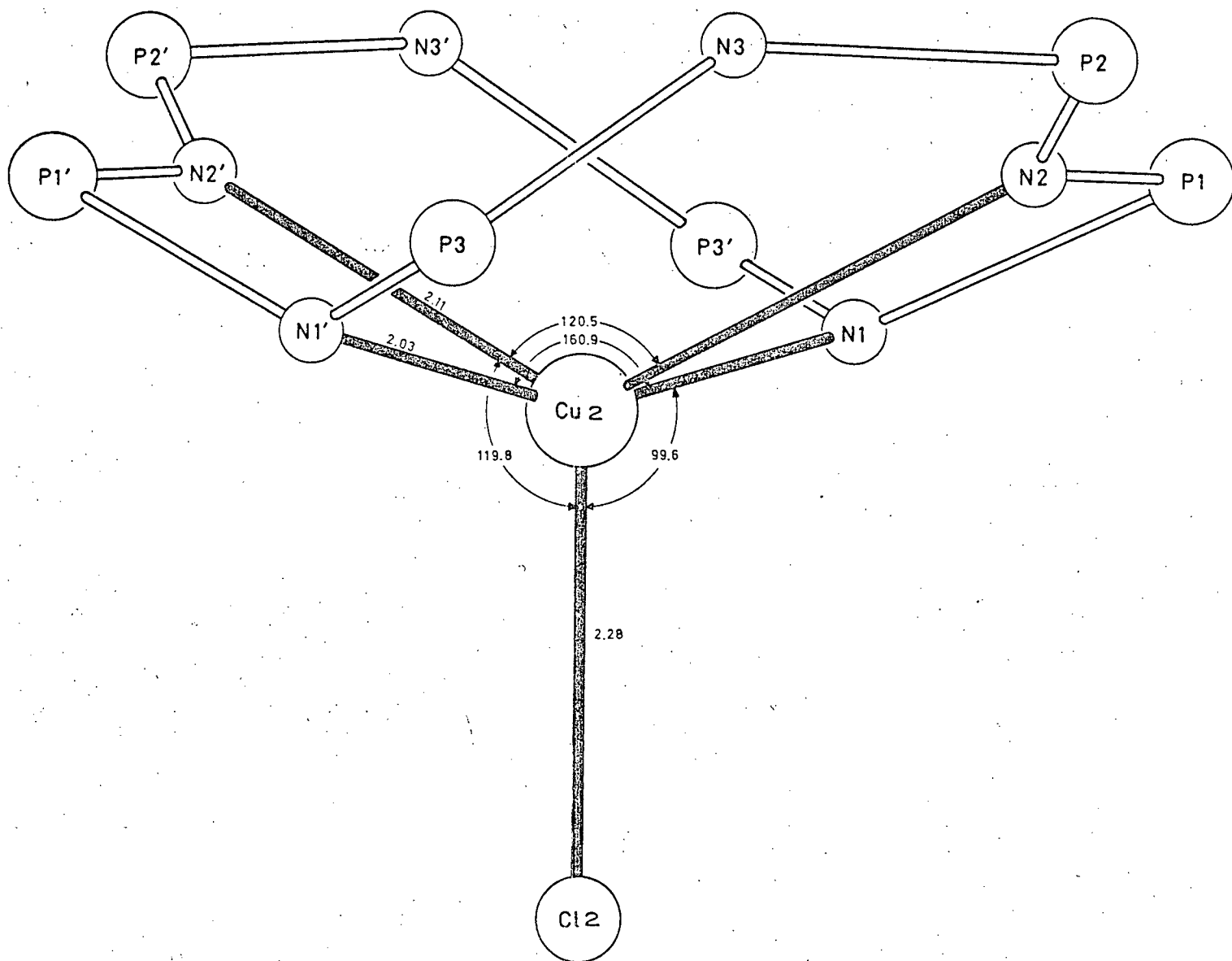


Figure 20. General view of the $N_6P_6(NMe_2)_{12}CuCl^+$ ion, showing the copper (II) atom coordination (NMe₂ groups omitted for clarity).⁽⁷⁹⁾

TABLE VIII

Bond lengths (\AA) and valency angles (degrees), with standard deviations in parentheses.⁽⁷⁹⁾

Cu(2)-N(1)	2.03(2)	Cu(1)-Cl(1)	2.06(1)
Cu(2)-N(2)	2.11(2)	[2.11(1) corrected for libratic	
Cu(2)-Cl(2)	2.28(1)		
N(1)-P(1)	1.62(2)	N(4)-C(1)	1.46(3)
N(1)-P(3')	1.65(2)	N(4)-C(2)	1.48(3)
N(2)-P(1)	1.60(2)	N(5)-C(3)	1.45(3)
N(2)-P(2)	1.61(2)	N(5)-C(4)	1.45(3)
N(3)-P(2)	1.53(2)	N(6)-C(5)	1.46(3)
N(3)-P(3)	1.57(2)	N(6)-C(6)	1.49(3)
P(1)-N(4)	1.62(2)	N(7)-C(7)	1.55(3)
P(1)-N(5)	1.64(2)	N(7)-C(8)	1.44(3)
P(2)-N(6)	1.65(2)	N(8)-C(9)	1.46(3)
P(2)-N(7)	1.67(2)	N(8)-C(10)	1.50(3)
P(3)-N(8)	1.67(2)	N(9)-C(11)	1.50(3)
P(3)-N(9)	1.68(2)	N(9)-C(12)	1.47(3)
N(2)-Cu(2)-N(1)	71.2(7)	N(1)-P(1)-N(2)	97.2(10)
N(2)-Cu(2)-N(1')	99.1(8)	N(1)-P(1)-N(4)	118.2(11)
N(2)-Cu(2)-N(2')	120.5(11)	N(1)-P(1)-N(5)	108.2(12)
N(1)-Cu(2)-N(1')	160.9(12)	N(2)-P(1)-N(4)	111.3(11)
Cl(2)-Cu(2)-N(2)	119.8(5)	N(2)-P(1)-N(5)	117.9(11)
Cl(2)-Cu(2)-N(1)	99.6(6)	N(4)-P(1)-N(5)	104.5(12)
Cl(1)-Cu(1)-Cl(1')	179.5(9)	N(2)-P(2)-N(3)	110.0(10)
		N(2)-P(2)-N(6)	118.5(12)
		N(2)-P(2)-N(7)	104.3(11)
P(1)-N(1)-P(3')	130.7(13)	N(3)-P(2)-N(6)	103.8(12)
P(1)-N(1)-Cu(2)	96.9(10)	N(3)-P(2)-N(7)	115.5(12)
P(3')-N(1)-Cu(2)	118.4(11)	N(6)-P(2)-N(7)	105.2(12)
P(1)-N(2)-P(2)	137.6(13)	N(3)-P(3)-N(1')	115.4(10)
P(1)-N(2)-Cu(2)	94.5(9)	N(3)-P(3)-N(8)	106.0(11)
P(2)-N(2)-Cu(2)	127.9(11)	N(3)-P(3)-N(9)	109.6(11)
P(2)-N(3)-P(3)	132.4(13)	N(1')-P(3)-N(8)	110.7(10)
		N(1')-P(3)-N(9)	105.3(11)
		N(8)-P(3)-N(9)	109.8(10)
C-N-C	111-118, mean 114		
P-N-C	114-127, mean 120		

than the uncharged species, $N_6P_6(NMe_2)_{12}Cu(I)Cl$.


The second group found in the crystal structure is then the anion $CuCl_2^-$. This anion has been postulated to exist in solution^(64,65) but the evidence has been mainly electrochemical and its validity has been seriously questioned⁽⁶²⁾. Suitable analogues for $CuCl_2^-$ do exist, however, in the anions $AgCl_2^-$, $AuCl_2^-$ ⁽⁶⁶⁾, and $AuBr_2^-$ ⁽⁶⁷⁾. All of these are linear, as is the postulated $CuCl_2^-$ anion. Furthermore, a co-ordination number of two has never been found for either Cu (II) or Ag (II) atoms. It should also be noted that the difference between the observed Cu(1)-Cl(1) bond length, and that predicted from the sums of the covalent radii of the atoms^(63,68), is 0.06Å. This difference is of the same order as those found for $AgCl_2^-$, $AuCl_2^-$ and $AuBr_2^-$ (Table IX).


TABLE IX ACTUAL AND PREDICTED BOND LENGTH

ANION	$CuCl_2^-$	$AgCl_2^-$	$AuCl_2^-$	$AuBr_2^-$
sum of co-valent radii (Å)	2.17	2.38	2.33	2.45
bond length (Å)	2.11	2.36	2.31	2.35
difference (Å)	.06	.02	.01	.10

All of these facts point to the existence of the anion, $CuCl_2^-$. This, together with the evidence for the cation, $N_6P_6(NMe_2)_{12}CuCl^+$, is sufficient proof that the complex, $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ is in fact the salt, $N_6P_6(NMe_2)_{12}CuCl^+CuCl_2^-$. It should be noticed in passing that except for the structure of copper (I) oxide⁽⁶²⁾, there is almost no other

structural evidence for the existence of the two co-ordinate copper (I) atom.

The structure and the conformation of the $N_6P_6(NMe_2)_{12}CuCl^+$ cation are interesting, especially when compared to those of the parent $N_6P_6(NMe_2)_{12}$ ⁽²⁷⁾. One of the interesting features of the H.P.D. structure is the effect π -bonding has on the exocyclic P-N bond lengths and on the planarity of the P-N  system.

The dimethylamide group formally has a lone pair of electrons on the nitrogen atom which in the phosphonitric system is donated to the adjacent phosphorus atom. This causes a shortening of the exocyclic P-N bond length from a calculated single bond length value of 1.74\AA ⁽²⁶⁾ to 1.675 and 1.663\AA ⁽²⁷⁾. The most obvious effect of this delocalization is seen in the sums of the angles around the exocyclic nitrogen atom. In the H.P.D. molecule, they are 357.5° and 348.7° , indicating a flattening of the P-N  group. This is the result of the loss of lone pair electron density on the nitrogen atom which allows the methyl groups and the phosphorus atom to move away from each other in the direction of the lone pair.

The ring π -bonding system involves the donation of the lone pair on the endocyclic nitrogen atom to a suitable, vacant d-orbital on the phosphorus atom. However, back bonding from the exocyclic nitrogen increases the π -electron density of the phosphorus atom. As it does so, lone pair electrons are increasingly localized on the ring nitrogen atoms, so lengthening the endocyclic P-N bond length.

When the lone pair on an exocyclic nitrogen donates to the adjacent phosphorus atom, the following effects occur:

- 1) the exocyclic P-N bond length is shortened,
- 2) the sum of the angles around the exocyclic nitrogen atom increases,
- 3) the endocyclic P-N bond length increases.

Identical effects would be noticed if the ring nitrogen lone pairs were removed from the π -bonding system by complexing, i.e. the resulting decrease in the π -electron density on the phosphorus atom would result in a larger π -electron donation from the exocyclic nitrogen atoms.

In $N_6P_6(NMe_2)_{12}CuCl^+$ the copper atom removes π -electron density from four ring nitrogen atoms, and the expected effects are all observed. The average endocyclic P-N bond length is $1.60\overset{\circ}{\text{\AA}}$ compared to $1.563\overset{\circ}{\text{\AA}}$ for the parent, and the average exocyclic P-N bond length is $1.652\overset{\circ}{\text{\AA}}$ as compared with $1.669\overset{\circ}{\text{\AA}}$ for the parent. While these differences are not large in themselves, they are in the correct direction.

Comparisons between the individual bond lengths within the cation are also interesting. There are two Cu-N bond lengths, one of $2.03\overset{\circ}{\text{\AA}}$ and one of $2.11\overset{\circ}{\text{\AA}}$. This difference could easily be due to the effect of steric factors on the alignment of the nitrogen atom lone pairs, i.e. as the cation is very crowded, optimum bonding overlap cannot be expected for all the Cu-N bonds.

The π -electron donation from N(1) and N(2) atoms to the central copper atom lowers the bond order of the corresponding N-P bonds. This is evident in the increased bond lengths of the cation, (P(3')-N(1), $1.65\overset{\circ}{\text{\AA}}$; N(1)-P(1), $1.62\overset{\circ}{\text{\AA}}$; N(2)-P(1), $1.60\overset{\circ}{\text{\AA}}$; N(2)-P(2), $1.61\overset{\circ}{\text{\AA}}$), compared to the parent $N_6P_6(NMe_2)_{12}$, ($1.563\overset{\circ}{\text{\AA}}$). The least affected are the N(3)-P(3) bond length, ($1.57\overset{\circ}{\text{\AA}}$), and the N(3)-P(2) bond length, ($1.53\overset{\circ}{\text{\AA}}$). In both cases, the nitrogen lone pair electrons donate fully into the ring

π -system. It would be expected that P(1) have a lower π -electron density than either P(3') or P(2). In other words, P(1) is joined to two complexing nitrogen atoms and P(3') and P(2) to only one. This results in the shortest exocyclic bond lengths occurring at P(1)-N(4) and P(1)-N(5), (mean, 1.63(1)Å).

Because the Cu(2)-N(1) bond is shorter than the Cu(2)-N(2) bond, it would be reasonable to assume that the lone pair density would be lower on N(1) than on N(2). However, the sum of the angles around N(1) is 346°, while around N(2) it is 360°. This apparent anomaly can be explained by assuming that steric factors have caused a difference in the effectiveness of the π -system at N(1) and N(2). Therefore, N(2) lone pair electrons are more likely to form bonds to phosphorus than are those of N(1). This is evident in the shortness of the N(2)-P(1) and N(2)-P(2) bonds, (1.60Å and 1.61Å respectively), compared to the N(1)-P(1) and N(1)-P(3') bonds, (1.62Å and 1.65Å respectively). Again, the difference is small but in the correct direction.

The configuration of the ring is mainly caused by chelation which restricts the size of the ring, pulling atoms N(1), N(2), N(1') and N(2') towards the centre, so giving an average endocyclic PNP angle of 134° compared to 147.5° for the parent phosphonitrile⁽²⁷⁾. The strain resulting from this crowding is partially offset by chelation itself which lowers the electron density of the ring bonds. An illustration of this is the N(1)-P(1) and P(1)-N(2) bonds which are the most affected by electron withdrawal, and the N(1)P(1)N(2) angle which is the lowest of this type found in phosphonitriles. The angles at P(2) and P(3), (110.0° and 115.4°), are also smaller than that found for the parent, (120°).

The angle $P(3)N(3)P(2)$ is 132.4° which is similar to the same type of angle in $N_4P_4(NMe)_8$, 133° ⁽²⁶⁾; and $N_4P_4Me_8$, 132° ⁽²⁶⁾, but significantly smaller than that in $N_6P_6(NMe_2)_{12}$, 147.5° ⁽²⁷⁾. This large angle is an outstanding feature of the parent and is attributed to steric effects. Wagner and Vos suggest that for $N_6P_6(NMe_2)_{12}$, no angle less than 148° could accomodate the bulky dimethylamide groups without at least one unacceptably short C...C distance. Because a smaller angle is found for the $N_6P_6(NMe_2)_{12}CuCl^+$ cation, high steric crowding should be evident in the intramolecular distances.

In the $N_6P_6(NMe_2)_{12}CuCl^+$ cation, there are three types of intramolecular distances of interest. These are:

- 1) the distance between the carbon atoms of the lower exocyclic groups and the chlorine atom, Cl(2);
- 2) the distance between the carbons of the upper and lower exocyclic group on the same phosphorus atom; and
- 3) the distance between the carbon atoms of the upper exocyclic group on different phosphorus atoms.

Some of these distances are shown in Table X for $N_6P_6(NMe_2)_{12}$ and $N_6P_6(NMe_2)_{12}CuCl^+$.

TABLE X INTRAMOLECULAR DISTANCES

Type of Distance	Species	Distance in $N_6P_6(NMe_2)_{12}$	Distance in $N_6P_6(NMe_2)_{12}CuCl^+$	Sum of Van der Waals Radii
1)	Smallest		3.56Å	3.8Å
2)	Smallest	3.52Å	3.23Å	3.8Å
3)	Smallest	3.77Å	3.689Å	3.8Å

In each of these types of intramolecular distances, there are distances smaller than the sum of the individual Van der Waals radii, which is a direct indication of steric crowding due to the position of the chlorine atom. This atom forces the lower exocyclic methyl groups to bend upwards, thus increasing the crowding of the exocyclic group on the same phosphorus atom, which in turn, increases the crowding of the methyl groups on different phosphorus atoms. The chlorine has therefore pushed all the methyl groups up and away from itself, thus the smallest C...C bond distances are found in the $N_6P_6(NMe_2)_{12}CuCl^+$ ion and not in the parent $N_6P_6(NMe_2)_{12}$.

A further effect of crowding is the distortion of the Cu(2) atom from square pyramidal towards a trigonal bipyramidal environment. Distortion raises the four ring nitrogens out of a planar environment, pushing up the whole ring and the exocyclic methyl groups with it, and is so obvious it becomes unlikely that any smaller phosphonitrilic amide could chelate in the same manner; a further indication that $N_4P_4(NMe_2)_8$ would not chelate with copper.

The Infra-Red Spectrum of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$:

The infra-red spectra of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ and the parent $N_6P_6(NMe_2)_{12}$ are very similar (Figure 18, Table VI). This is reasonable because the complex has retained both the phosphonitrilic ring and the exocyclic groups of the parent. Moreover, the spectra were taken in a region where Cu-N or Cu-Cl vibrational modes would not produce peaks, so only the ring and exocyclic groups would contribute to the spectrum. However, differences between spectra would be expected due to electron

withdrawal from the ring in the complex and changes in symmetry.

Unfortunately, very little information exists about the assignment of bands in the spectra of phosphonitrilic derivatives, so that a complete interpretation of the spectrum of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ must await a better understanding of the entire field. However, previous work^(50,54) does allow some tentative assignments.

The peaks between 3010 and 2790 cm^{-1} in both spectra may safely be assigned to asymmetric and symmetric C-H stretching modes and overtones of CH_3 bonding vibrations. The similarity of the spectra in this region indicates that there is little difference between the environments of the CH_3 groups in the complex and the parent. This, in turn, is consistent with co-ordination through the rings rather than the exocyclic groups.

The peak at 2150 cm^{-1} present in the parent, yet absent in the complex, is most probably an overtone of the peak at 1070 cm^{-1} .

The peaks between $1490 - 1425\text{ cm}^{-1}$ for the complex and between $1480 - 1450\text{ cm}^{-1}$ for the parent can be assigned to asymmetric C-H bending vibrations. These are essentially similar in both compounds; again indicative of bonding between the copper and the endocyclic nitrogen atoms.

There is no doubt that the main ν_{as} (P-N-P) band is centered near 1270 cm^{-1} in the parent, but extensive splitting and reduction of frequency occurs in the complex indicating strong interaction with the copper atom. It should be noticed that chelation of the copper will have greatly increased the rigidity of the ring resulting in a more complex vibrational pattern.

The doublet at 1070 and 1063 cm^{-1} in the spectrum of the parent molecule corresponds to the asymmetric band at 1062 cm^{-1} in the spectrum of the complex, and is to be attributed to C-N stretching.

Any further interpretation of the spectra past this point becomes futile because of the increasing number and complexity of the peaks.

The main point of interest in the spectra is the similarity between the spectrum of the complex and that of the parent. This is consistent with all the known structural information on the two molecules. Complexing does, however, have a large effect on the ν_{as} (P-N-P) bands, causing them to split.

Therefore, the dominant features of the spectra are due to the various modes of the phosphonitric system; only as copper chelation affects these does it have any effect on the spectra. Finally, the fact that only the ν_{as} (P-N-P) bands are affected is then characteristic of endocyclic bonding to copper.

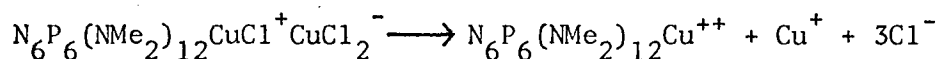
Studies of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$ in Solution:

The steric interference evident in the structure of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$ could be relieved by the loss of the Cl(2) atom from the cation. This would change the environment of Cu(2) from distorted square pyramidal to square planar. The latter is a well known type of environment for Cu(II) atoms, e.g. CuO, $[\text{Cu}(\text{Py})_4]^{2+}$ (56).

If the chlorine were lost as the anion Cl^- , than the double charged cation, $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}^{2+}$ would be left in solution. The other

species, CuCl_2^- could also break down, though no information exists concerning its behaviour in solution. Nyholm⁽⁶⁵⁾ used preparative evidence to suggest the existence of the salts $[\text{Cu}(\text{AsMe}_2)_4][\text{CuX}_2]$. These, however, were non electrolytes of undetermined molecular weight and probably do not contain the anion CuCl_2^- . No work has been done on a salt definitely known to contain the anion CuCl_2^- .

With maximum ionization this anion would produce one Cu^+ cation and two Cl^- anions, so that the highest possible degree of dissociation which can be envisaged for $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$ is:



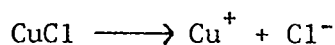
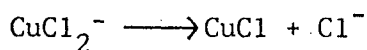
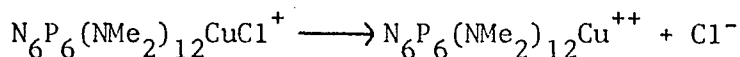
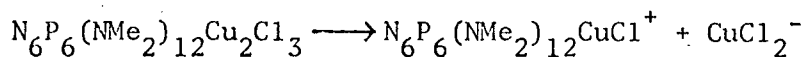
If dissociation occurs in solution, then an analysis for ionic chlorine will show three chlorines per molecule.

Quantitative Ionic Chlorine Analysis:

A gravimetric chlorine analysis with silver nitrate was employed. The complex was dissolved in pure, dry acetonitrile and a solution of silver nitrate added. The resulting dense white precipitate was filtered off in a tared sintered glass filter, dried, and weighed. 90.1 mg of the complex gave 0.0381 g of silver chloride: three chlorine ions would give 0.0376 g. Thus, under the conditions employed, both cation and anion dissociate completely.

Conductance Studies:

The possible ionization path of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$ in solution is:



The ionic chlorine analysis showed that all of these steps do occur, but did not show their relative importance.

Electrochemical measurements were done on a Wayne-Kerr Universal Bridge B221A. The solvent used was acetonitrile dried by the method outlined in Chapter 2. The cell used (Figure 1) had a constant, 0.19249, determined using an aqueous solution with a known concentration of potassium chloride. The complex studied had been analyzed previously as $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$. The constant temperature bath was held at $25^\circ\text{C} \pm 0.02^\circ\text{C}$.

A standard solution of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$ in 9 ml of acetonitrile was transferred in 1 ml quantities into the cell containing 25 ml of acetonitrile. After each addition conductance readings were taken. The molecular conductance was then calculated using the formula weight of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$.

All simple electrolytes⁽⁶⁹⁾ in acetonitrile and similar solvents obey the equation:

$$\Lambda = \Lambda_o \sqrt{C} \quad (5-1)$$

where: Λ = molecular conductance

Λ_o = limiting molecular conductance

TABLE XI Limiting Molecular Conductances
of Some Salts in Acetonitrile at 25°C

Salt	Λ_o (Ohms)	Reference
LiClO_4	183.25	(70)
NaClO_4	192.40	"
KClO_4	208.92	"
RbClO_4	203.24	"
CsClO_4	207.63	"
$\text{BuNH}_3\text{ClO}_4$	194	(71)
$\text{BuNH}_3\text{Pic.}$	167	"
$\text{Bu}_2\text{NH}_2\text{ClO}_4$	185	"
$\text{Bu}_2\text{NH}_2\text{Pic.}$	158	"
$\text{Bu}_3\text{NHCLO}_4$	177	"
$\text{Bu}_3\text{NHPic.}$	149	"
Et_4NClO_4	189	"
$\text{Et}_4\text{N Salicylate}$	176	"
PyHClO_4	202	"
Et_4NCl	176.6	"
Et_4ClO_4	188.9	"
Et_4NBCl_4	180.9	"
$(\text{C}_6\text{H}_5)_4\text{P}_2\text{N}_3\text{H}_4\text{SbCl}_6$	162.5	"

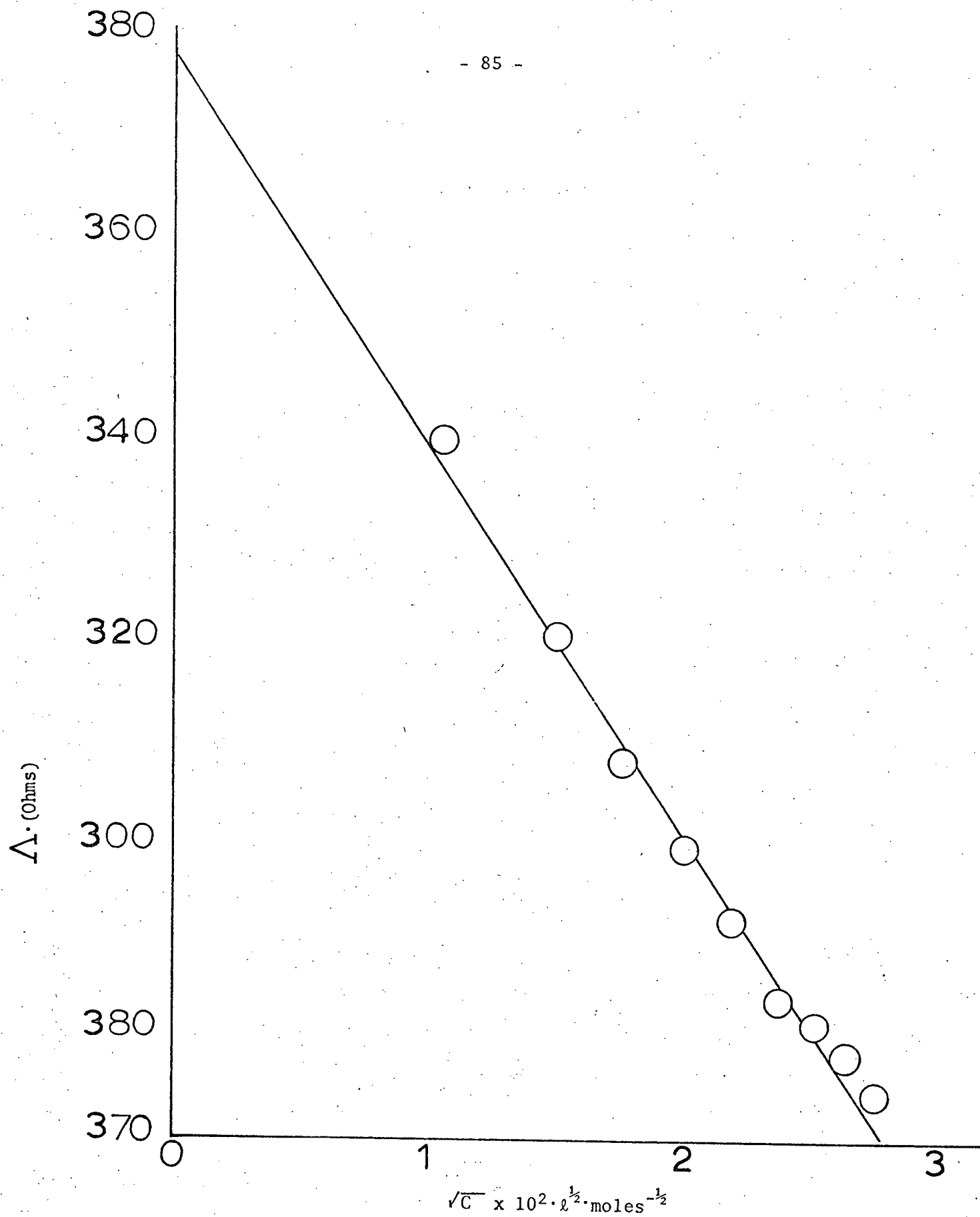


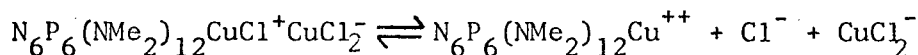
Figure 21. Conductance Plot of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$

C = molarity

A = constant dependant on solvent and Λ_o

The limiting conductance, i.e. the conductance at infinite dillution, is a function of the solvent and the number and types of ions in solution. For a given solvent the Λ_o values for any 1:1 electrolyte will all be very similar. In acetonitrile the Λ_o values for 1:1 electrolytes are between 209 - 155 Ohms⁻¹ (Table XI). Therefore, any Λ_o higher than 209 Ohms⁻¹ demonstrates the presence of an electrolyte possessing more than two univalent ions.

Figure 21 shows the plot of Λ_o against \sqrt{C} for $N_6P_6(NMe_2)_{12}Cu_2Cl_3$. The limiting conductance is 377 ± 10 Ohms⁻¹ which is much too large for a 1:1 electrolyte. The results are compatible with various dissociation patterns, typically with:



Further studies are necessary to establish this pattern definitely.

Magnetic Measurements of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$:

In the crystal structure of $N_6P_6(NMe_2)_{12}Cu_2Cl_3$ the intra-molecular distance between the two copper atoms is too large to allow any appreciable interaction. The crystal should therefore have a magnetic moment corresponding to one copper (II) ion per molecule. This is indeed the case and therefore is further evidence that the molecule contains two oxidation states of the copper atom.

The magnetic moment, μ , of a metal ion may be approximated by

a calculated value, $\mu_s^{(56)}$ obtained from.

$$\mu_s = \sqrt{4s(s+1)} \quad (5-2)$$

where s is the total spin quantum number.

In practice, however, the observed magnetic moment, μ , is usually higher than μ_s . For the copper (II) atom μ_s is 1.73 B.M. (Bohr Magnetons), but the usual experimental value is 1.7 - 2.2 B.M. ^(72,73). This is due to incomplete orbital quenching which in the extreme case would give a μ value approximated by:

$$\mu_{s+L} = \sqrt{4s(s+1) + L(L+1)} \quad (5-3)$$

where L is the total orbital quantum number.

The experimental magnetic moment, μ , is calculated from the equation:

$$\mu = 2.83\sqrt{\chi'_m T} \quad (5-4)$$

where χ'_m = molar paramagnetic susceptibility of the metal ion

T = temperature.

The molar susceptibility of the whole molecule, χ_m , is found by the Faraday method ⁽⁷⁴⁾. This value has to be corrected for the diamagnetism of every species in the molecule, which is done using the equation:

$$\chi_m = \chi'_m + \sum_A \chi_A^{dia} \quad (5-5)$$

where χ_A^{dia} = diamagnetic molar susceptibility of all species A .

Values of χ_A^{dia} can be found in the literature for various atoms and ions ^(72,73).

The magnetic susceptibility measurements were done in this

department using the Faraday method⁽⁷⁵⁾. An Alpha Model 9500 water-cooled 6 inches electromagnet equipped with pole tips of Heyding design, (1 1/2 inches in pole gap), was used. Samples, (approx. 5 mg), were suspended in a quartz bucket from a Cahn Rg electrobalance. Measurements were done under a nitrogen atmosphere at 295°K. The magnetic susceptibilities were field independent. Calibration was achieved using HgCo(CNS)_4 ⁽⁷⁶⁾.

The molar susceptibility of $\text{N}_6\text{P}_6(\text{MNe}_2)_{12}\text{Cu}_2\text{Cl}_3$, χ_m , was 845.83×10^{-6} c.g.s. units. The diamagnetic molar susceptibility of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}$ has not been determined and therefore had to be calculated. The hexameric phosphonitrilic chloride derivative has a χ_m^{dia} of -300.5×10^{-6} c.g.s. units⁽⁷⁷⁾, therefore, taking χ_m^{dia} of a chlorine atom as -20.1×10^{-6} c.g.s. units^(72,73) the χ_m^{dia} of the P_6N_6 ring is -59.3×10^{-6} c.g.s. units.

The diamagnetic correction necessary for $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$ is -573.3×10^{-6} c.g.s. units. This is calculated using the constants in Table XII^(72,73).

Table XII Diamagnetic Susceptibilities

Species	$\chi_A^{\text{dia}} \times 10^6 \cdot (\text{c.g.s. units})^{-1}$
N_6P_6 ring	-59.3
N in amine	- 5.6
C	- 6.0
H	- 2.9
Cl^-	- 2.6
Cu^{++}	-11
Cu^+	-12

Therefore, as:

$$\chi'_m = \chi_m - \sum_A \chi_A^{\text{dia}} \quad (5-6)$$

The molar susceptibility due to the paramagnetism of the Cu (II) cation is $1, 419.13 \times 10^{-6}$ c.g.s. units. Therefore, the magnetic moment is 1.83 B.M.

A magnetic moment of 1.7 - 2.2 B.M. is indicative of one copper (II) atom per molecule. The value here of 1.83 B.M. is then further proof that a molecule of $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cu}_2\text{Cl}_3$ contains one copper (II) atom and one copper (I) atom.

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