

AN ABSTRACT OF THE THESIS OF

Franklin N. Russell for the Master of Science Degree in Chemistry  
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Title: A Study of the Complexation of Copper (II) Ion by N-Tetramethyl  
Substituted Diamines

Abstract approved: \_\_\_\_\_

The steric and ionic strength effects upon the chelating ability of substituted diamines with copper (II) ion was studied using N,N,N',N'-tetramethylethylenediamine and N,N,N',N'-tetramethylpropylenediamine. The stepwise formation constants of copper (II) ion with the diamines were determined at 20°, 30° and 40°C, and in aqueous .10-1.0M ClO<sub>4</sub><sup>-</sup> solutions. The Bjerrum potentiometric method was used to determine the constants.

The results indicate a general decrease in stability with increasing chain length. The N-tetramethyl substituted diamines have been determined to be less stable than the substituted diamines. Also, the acid dissociation constants indicate that the N-tetramethyl substituted diamines to be less basic than the unsubstituted diamines. Thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined for  $k_1$ .

**A Study of the Complexation of Copper (II)  
Ion by N-Tetramethyl Substituted Diamines**

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**A Thesis  
Presented to  
the Department of Chemistry  
EMPORIA STATE UNIVERSITY**

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**In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science**

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## INTRODUCTION

Many studies have been performed in the past 60 years focusing upon complex ion formation and stability. Although the available data is plentiful, there are many studies which have not been performed. Table I lists some of the available data.

This research project focused upon the complexation behavior of copper (II) ion with 1,3-propylenediamine, N,N,N',N'-tetramethylethylenediamine, and N,N,N',N'-tetramethylpropylenediamine in aqueous perchlorate ion solutions. The Bjerrum potentiometric method was used to determine the formation and stability constants. The effects of changes in ionic strength and temperature upon the formation and stability constants were studied. Also, the steric effects of methyl groups, and chelate ring size upon complex stability was investigated.

TABLE 1

## Formation Constants for Selected Copper-Diamine Systems

Ligand	Log $k_1$	Log $k_2$	Log $k_T$	Ref.
Histamine	9.60	6.49	16.09	a
trans-1,2cyclo- Heptanediamine	11.04	10.11	21.75	10
N-3'-pyridylmethyl ethylenediamine	9.0	6.90	15.9	a
cis-1,2-cyclohexane- diamine	10.72	9.40	20.12	10
2-aminoethyl pyridine	7.54	5.64	13.18	11
1-phenyl-1,2 ethylenediamine	8.72	8.36	17.08	14

a Chemical Society, London, Stability Constants of Metal Ion Complexes,  
Special Publ. No. 17, 1964



## FORMATION AND STABILITY CONSTANTS

When a metal ion coordinates to two or more ligands in the formation of a complex ion, it will do so stepwise. (1) During the stepwise process intermediate equilibria will be present. (2) The resultant stepwise formation constants indicate the degree of stability of the complexes formed in each intermediate equilibrium. The larger the formation constant, the more stable the complex.

Stability constants are indicative of the stability of the completely saturated complex ion, that is, it indicates the stability of the complex ion as a whole. The stability constant is the product of each intermediate formation constant. It is defined as

$$K_T = k_1 \cdot k_2 \cdots k_N$$

where  $K_T$  is the stability constant,  $k_1$ ,  $k_2$  and  $k_N$  the intermediate formation constants and  $N$  the maximum number of ligands complexed.

The larger the stability constant, the more stable the complex.

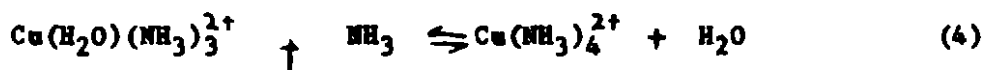
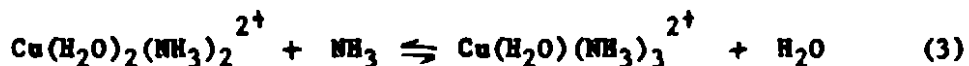
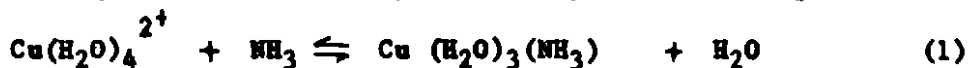
### Stepwise Formation of Complexes

The complex ion is the assembly of a metal ion, and one or more ions or molecules called ligands. Ligands are electron donors, (Lewis bases), and metal ions are electron acceptors, (Lewis acids).<sup>(3)</sup>

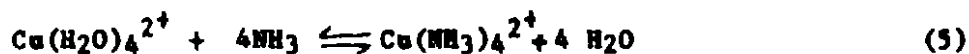
In aqueous solution, the metal ion is complexed by water molecules. The solvated metal ion is itself a complex ion. In complexation reactions water molecules are replaced by other ligands. Water replacement occurs because water complexes weakly with metal ions. Any strongly complexing molecules will replace water in the coordination sphere.

As stated earlier, ligands donate electrons to metal ions. Ligands can be anions, that is, negatively charged, or ligands can be neutral molecules. Ligands that complex to metal ions through one donor atom are called monodentate ligands. Those ligands that complex through two or more donor atoms are called polydentate ligands. Bidentate ligands is a special class of polydentate ligand. Bidentate ligands complex to metal ions through two donor atoms. Ethylenediamine and all other diamines are of the bidentate class.

The formation of the tetraammine copper (II) complex ion involves four distinct equilibria.<sup>(4)</sup> Beginning with the solvated copper (II) ion, the four equilibria can be represented by the following chemical equations:



and the overall equilibrium is



Applying the law of Mass Action, the following expressions are obtained

$$k_1 = \frac{[\text{Cu}(\text{H}_2\text{O})_3(\text{NH}_3)^{2+}]}{[\text{Cu}(\text{H}_2\text{O})_4^{2+}][\text{NH}_3]} = 1.66 \times 10^4 \quad (6)$$

$$k_2 = \frac{[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_2^{2+}]}{[\text{Cu}(\text{H}_2\text{O})_3(\text{NH}_3)^{2+}][\text{NH}_3]} = 3.16 \times 10^3 \quad (7)$$

$$k_3 = \frac{[\text{Cu}(\text{H}_2\text{O})(\text{NH}_3)_3^{2+}]}{[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_2^{2+}][\text{NH}_3]} = 8.13 \times 10^2 \quad (8)$$

$$k_4 = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{H}_2\text{O})(\text{NH}_3)_3^{2+}][\text{NH}_3]} = 1.51 \times 10^2 \quad (9)$$

and the overall expression is

$$K_M = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{H}_2\text{O})_4^{2+}][\text{NH}_3]^4} = 6.58 \times 10^{12} \quad (10)$$

Expressions  $k_1$  to  $k_4$  are called concentration equilibrium constants or formation constants. The expression  $K_M$  is called the complexity or stability constant. The magnitude of each formation constant gives an indication of the degree of stability of each new complex. The greater the value of the formation constant, the more stable the complex. Thus,  $k_1 > k_2 > k_3 > k_4$ . Expression  $k_1$  indicates that the first ammonia molecule complexed is held more tightly than the three succeeding ammonia molecules.

## Copper (II) Ion

The copper (II) ion will normally coordinate four donor atoms. In exceptional cases, copper (II) ion will complex six donor atoms. Several ligands that form six-coordinate complexes with copper (II) ion are noted in the literature.<sup>(5)</sup> In the case of diamine ligands, copper (II) ion will coordinate two diamine molecules easily, and a third diamine ligand weakly.

### Monodentate vs Chelate Ligands

Complexes of chelating ligands are, in general, more stable than those of an equivalent number of monodentate ligands. (6) Chelating ligands are molecules that form rings upon complexation with metal ions. The enhanced stability of chelating ligands is called the chelate effect. The chelate effect states: The reaction of copper (II) ion with ammonia molecules should be thermodynamically less favorable than its reaction with ethylenediamine molecules.

The chelate effect is an entropy effect rather than an electronic effect. The electronic effects of ammonia and ethylenediamine are practically identical. (7) The similarity in electronic effects is due to the fact that both molecules possess the same donor atoms, the nitrogen atom.

In many cases the stability of the chelate ligand vs the monodentate ligand differ by one to two pK units. (6) Table 2 lists the formation and stability constants for ammonia and several chelating ligands. The data indicates that the ethylenediamine molecule is more stable than the non-ring forming, monodentate ammonia molecule.

The increased stability of chelate ligands is due, in part, to the ligand's ability to remain complexed to the metal ion during reaction. For example, when one of the ethylenediamine nitrogen atoms dissociates, the molecule remains attached to the metal ion through the second nitrogen atom. The dissociated nitrogen atom can only move but a few Angstroms away from the copper (II) ion, and the probability of ring reformation is good. In other words, it is thermodynamically favorable in terms of entropy effects. On the other hand, the dissociation of ammonia molecules from the copper (II) ion results in a low probability of the ammonia complex being reformed. Once dissociated ammonia molecules are swept completely into solution allowing for ligand replacement and ammonia

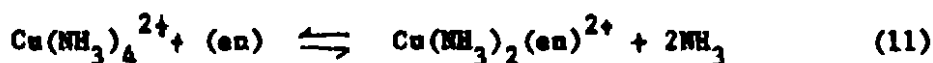
Formation Constants for Aliphatic Diamines,  
and Ammonia with Cu(II) Ion

Ligand	Log $k_1$	Log $k_2$	Log $k_3$	Log $k_4$	Log $k_T$	Ref.
Ammonia	4.15	3.50	2.89	2.13	12.66	7
1,2-ethylenediamine	10.72	9.31			20.03	17
1,3-propylenediamine	9.62	7.00			16.62	9
1,2-propylenediamine	10.58	9.08			19.66	2

instability.

It has been reported,<sup>(8)</sup> based on enthalpic data, that the amine nitrogens on the ethylenediamine molecule form very strong bonds with hydrated copper (II) ions. In the same report, ammonia molecules were found to give noticeably smaller enthalpy values, inferring weaker bond attraction. The smaller enthalpy values for ammonia is a valid indication of high entropy effects (probability) and increased stability of ethylenediamine molecules.

Substitution of ammonia with ethylenediamine produces an increase in the reaction entropy. The replacement of ammonia (monodentated ligand) with ethylenediamine (chelate ligand) produces an increase in the number of particles in the system. In other words, two molecules react, but three molecules are produced. This phenomenon is illustrated below



where (en) is the ethylenediamine molecule.

### Ring Size of Bidentate Ligand

In general, five-membered diamine ring systems are more stable than the corresponding six-membered ring systems.<sup>(4)</sup> Several investigators<sup>(6,9)</sup> have studied and compared the stability of 1,2-ethylenediamine and 1,3-propylenediamine as ligands with copper (II) ion. Each investigation indicated that the 1,2-ethylenediamine ligand possessed greater stability. The molecule's greater stability was indicated by large formation constants,<sup>(6,9)</sup> and favorable thermodynamic parameters.<sup>(9)</sup>

Bertsch and associates<sup>(10)</sup> made an in depth comparison of 1,2-ethylenediamine and 1,3-propylenediamine at 10°, 20°, 30° and 40° c, and zero ionic strength with copper (II) ion. Their findings corresponded with those of previous researchers.

Ironically, the enthalpy values for 1,3-propylenediamine indicate that the molecule should be more stable than 1,2 ethylenediamine.<sup>(9)</sup> The larger enthalpy values are attributed to the greater basicity of the 1,3-propylenediamine.<sup>(10)</sup> Cotton and Harris found that increasing proton affinity occurred with increasing chain length.<sup>(6)</sup> The enhancement of proton affinity results in stronger acid-base interactions (Lewis acid-base interactions). Strong acid-base interactions are reflected by the magnitude of enthalpy values.

The diminished stability of 1,3-propylenediamine can, according to Schwarzenbach<sup>(7)</sup> and others, be traced to entropy differences between the two molecules. Consequently, the formation of six-membered ring systems produce increased ring strain upon chelation, and less favorable entropy effects.<sup>(10)</sup>

Holmes and Williams<sup>(11)</sup> studied the complexation behavior of 1,2-ethylenediamine and 1,3-propylenediamine in .30M perchlorate ion at 25°C. A comparison of trends in data collected by other investigations and



those of Holmes and Williams indicate greater 1,2-ethylenediamine stability. Also, Holmes and Williams' data indicated 10-20% greater bond strengths for five-membered ring systems, and that easily protonated ligands are more difficult to chelate. (12)

It has been reported (9,10) that seven-membered ring systems are less stable than six-membered ring systems with copper (II) ion. The chelation behavior of 1,4-butylenediamine has been investigated by researchers, and concrete data has been unattainable. Acid dissociation constants have been the only data collectable. The acid dissociation constants collected follow previous observations that easily protonated species (long chained diamines) are more difficult to chelate. Formation constants were unattainable due to precipitation of complexes during investigation.

Investigators have raised the question of methyl-substitution and its effect on diamine complexation with copper (II) ion. Bjerrum and Lamm<sup>(8)</sup> conducted investigations using the methyl-substituted ammonia, methylamine. Their investigation indicated that methylamine's acid dissociation constant was twenty times larger than ammonia's. This fact indicated a higher stability for ammonia. Subsequent investigations by Spike and Parry<sup>(8)</sup> using 1,2 ethylenediamine with zinc (II) and cadmium (II) ions indicate that the methyl groups had no inductive effects on their complexes. In other words, the methyl groups would tend to produce less favorable stability in terms of entropy effects and stability constant values, and the subsequent enthalpy values would be of larger magnitudes.

Basolo<sup>(13)</sup> conducted an in depth study of steric hinderance using C(1,2)-methyl substituted ethylenediamines. The data listed in Table 3 indicated that methyl substitution and the possible inductive effects has a minimal effect on coordination behavior.

**Formation Constants of Cu(II) Ion with C(1,2)-Substituted  
1,2-ethylenediamines <sup>b</sup>**

I = .50M NO<sub>3</sub><sup>-</sup> , 25°C

Ligand	Log k <sub>1</sub>	Log k <sub>2</sub>	Log k <sub>T</sub>
1,2-ethylenediamine	10.76	9.37	20.13
rac-2,3-butylenediamine	11.39	9.82	21.21
Meso-2,3-butylenediamine	10.72	9.34	20.06
2-methyl-1,2-propylenediamine	10.53	9.05	19.58
2,3-dimethyl-2,3-butylene- diamine	11.63	10.24	21.87

b ref. 13

Thermodynamic studies<sup>(14)</sup> performed in perchlorate ion solutions using C (1)-substituted ethylenediamines indicate a slight decrease in stability with increasing substituent chain length, and number of methyl groups on the C (1) carbon. Table 4 lists the pertinent data. The data also indicated an upward trend in entropy and stability constant values with increasing ionic strength.

The effect of methylation on six-membered ring systems was studied by Hares<sup>(9)</sup> in a limited investigation. The data listed in Table 5 indicates an increasing stability for the methyl derivative. This fact led Hares to conclude that solvent interactions with methyl groups produced favorable entropy effects.

The effect of mono-substitution of the amine nitrogen was studied by Basolo and Murmann in 1952.<sup>(15)</sup> The data collected is listed in Table 6. Upon inspection, the data indicates a noticeable decrease in the stability of the complex ion as a function of substituent chain length, the exception being the N-n-butyl derivative. Basolo concluded, (as other researchers had<sup>(8,9,13,14)</sup>) that the decrease in stability and slight increase for N-n butyl derivative, were attributable to entropy effects. McIntyre<sup>(16)</sup> performed a similar study using 1,2-ethylenediamine and N-methyl ethylenediamine, and arrived at the same conclusion.

It was reported in 1953<sup>(17)</sup> that the N-di-substituted ethylenediamines exhibited the similar thermodynamic and complexation behavior as the N-monosubstituted molecules. Table 7 is a listing of the data. Hares reported<sup>(10)</sup> the instability of N-isopropyl and N,N-dimethyl-1,3-propylenediamine with copper (II) ion. Precipitation occurred with both molecules. Instability was attributed to unfavorable entropy effects,

**Formation Constants of Cu (II) Ion with C(1)-Substituted  
1,2-ethylenediamines<sup>c</sup>**

I = .20M ClO<sub>4</sub><sup>-</sup> , 25°C

Ligand	Log k <sub>1</sub>	Log k <sub>2</sub>	Log K <sub>T</sub>
1,2-ethylenediamine	10.76	9.37	20.13
1-methyl-1,2-ethylenediamine	10.56	9.02	19.58
1,1-dimethyl-1,2-ethylenediamine	10.18	8.92	19.10
1-ethyl-1,2-ethylenediamine	10.49	9.12	19.61

c ref. 14

Formation Constants of Cu (II) Ion with 1,3-propylenediamine and  
Methyl Derivative<sup>d</sup>

30°C, I = 1.0M NO<sub>3</sub><sup>-</sup>

Ligand	Log k <sub>1</sub>	Log k <sub>2</sub>	Log k <sub>T</sub>
1,3-propylenediamine	9.62	7.00	16.62
2,2-dimethyl-1,3-propylenediamine	9.94	7.45	17.39

d ref.9

Formation Constants of Cu (II) with N-Alkylethylenediamine<sup>a</sup>

I = .50M NO<sub>3</sub><sup>-</sup> , 25°C

Ligand	Log k <sub>1</sub>	Log k <sub>2</sub>	Log K <sub>T</sub>
1,2-ethylenediamine	10.76	9.37	20.13
N-methylethylenediamine	10.55	8.56	19.11
N-ethylethylenediamine	10.19	8.38	18.57
N-n-propylethylenediamine	9.98	8.16	18.14

<sup>a</sup> ref. 15

Formation Constants of Cu (II) with  
N,N' - Dialkylethylenediamine<sup>f</sup>

I = .50M NO<sub>3</sub><sup>-</sup> , 25°C

Ligand	Log k <sub>1</sub>	Log k <sub>2</sub>	Log K <sub>T</sub>
1,2-ethylenediamine	10.76	9.37	20.13
N,N'-dimethylethylenediamine	10.47	7.63	18.10
N,N'-diethylethylenediamine	9.30	6.32	15.62
N,N'-di-n-propylethylenediamine	8.79	5.55	14.34

<sup>f</sup> ref. 17

increased chelate ring size and methyl substitution on the amine nitrogen.

Reports of research performed with N-tri and tetra substituted ethylene and 1,3-propylenediamines are scarce in the literature, and those present in the literature are very incomplete. (18)



## Perchlorate Ion

The perchlorate ion is a very poor ligand. Perchlorate ion association in complex systems exists when the complex in question is weak itself. (19) Thus, perchlorate ion association is a possibility in the case of weak complex formation in perchlorate solutions.

In this investigation, the effect of chelation and subsequent entropy influences will possibly negate any perchlorate association. The presence of perchlorate ion should have some influence on stability in terms of the complex ion's chemical environment. (20)

## EXPERIMENTAL

### Reagents and Equipment

The chemicals used in this investigation were of analytical reagent grade. Deionized water was used in dilutions. All volumetric pipets and burets were calibrated before use. Glassware was of Class A grade.

### Reagents

Barium perchlorate, anhydrous, sodium perchlorate, hydrate, and copper perchlorate, hexahydrate were purchased from the G. Frederick Smith Chemical Company.

The 1,2-ethylenediamine, 98.5% was obtained from the Fisher Scientific Company. N,N,N',N'-tetramethylpropylenediamine, 99-%, N,N,N',N'-tetramethylethylenediamine, 99%, and 1,3-propylenediamine, 98% were obtained from the Aldrich Chemical Company. They were used as obtained.

Perchloric Acid, 70%, was obtained from the Mallinckrodt Chemical Company.

Buffer pH 4.00  $\pm$  .01 was obtained from the Curtis Matheson Scientific, Inc. Buffer pH 8.00  $\pm$  .02 was obtained from the Fisher Scientific Company.

Prepurified nitrogen gas was obtained from the Linde Div.--Union Carbide Corp.

### Equipment

For temperature control a Forma Temp. Jr., Model 2095-2, refrigerated and heated circulating water bath, and Magni Whirl constant temperature bath were used.

For potentiometric measurements an Horizon Ecology pH meter, Model 5998-10 equipped with a Fisher reference electrode and a Perkin Elmer Tri-purpose glass electrode were used.

Temperatures were monitored using a Sargent G thermometer, range 18-31°C, and a Fisher Scientific 15-00A, range 10-31°C.

#### Water Bath Temperature

Forma Temp. Jr. constant temperature bath was calibrated to within  $\pm .01^\circ\text{C}$  of desired temperature. A Sargent G thermometer was used for temperatures 20° and 30°C. Fisher Scientific 15-00A was used for 40°C determinations. Temperature equilibration required 1-1.5 hours. Magni Whirl water bath was calibrated to within  $\pm .10^\circ\text{C}$ .

#### Calibration of pH Meter

Horizon pH meter was calibrated using standard pH 4.00  $\pm .01$  and 8.00  $\pm .02$  buffers. Buffer solutions were allowed to sit in the constant temperature bath for one hour to ensure temperature equilibrium. Reference and pH electrodes were allowed to sit in a container of deionized water at temperature of investigation until use. This ensured temperature equilibrium throughout the system.

#### Preparation of Solutions

##### Acid-Electrolyte Solutions

Solutions were prepared from a stock solution containing .100M  $\text{Ba}(\text{ClO}_4)_2$  and .0983M  $\text{HClO}_4$ . Stock solution was analyzed for acid content using standard analytical methods. All subsequent solutions were prepared from this stock solution.

### Acid-Metal ion Solutions

Solutions were prepared from a stock solution containing .1402M  $\text{Cu}(\text{ClO}_4)_2$  and .1018M  $\text{HClO}_4$ . Stock solution was analyzed for copper content using atomic absorption. Stock solution was prepared for analysis by diluting volumetrically a 10 ml aliquot to approximately 7 ppm copper content. Standards were prepared by diluting volumetrically a standard stock solution of copper to 1,5,10, and 25 ppm. Standard stock copper solution was prepared by dissolving one gram copper wire in 5 ml concentrated nitric acid, and diluting solution to 1000 ml. Standards and diluted stock solution were run and absorption spectra obtained. Spectral points were graphed using Hewitt Packard computer and plotter, and a least squares plot program.

Acid content was analyzed using standard quantitative methods. All subsequent solutions were prepared from this stock solution.

### Base Solutions

All base solutions were prepared by diluting concentrated base solutions with deionized water. The molarity of concentrated bases was calculated using percent by weight and density values. Concentrations of diluted base solutions were analyzed using standard quantitative methods.

### Procedure

The procedure that was used for the Bjerrum potentiometric determination of formation constants is as follows:

Two solutions were prepared from a standard stock solution. The first contained .001M  $\text{Ba}(\text{ClO}_4)_2$  and .002M  $\text{HClO}_4$ . The second contained .001M  $\text{Cu}(\text{ClO}_4)_2$  and .002M  $\text{HClO}_4$ . Concentrated perchloric acid was added to adjust acid concentration to .002M  $\text{HClO}_4$ .

Two additional solutions were prepared by dilution of 50 ml aliquots from each of the previously prepared solutions. The first solution contained .0001M  $\text{Ba}(\text{ClO}_4)_2$  and .0002M  $\text{HClO}_4$ . The second solution contained

.0001M  $\text{Cu}(\text{ClO}_4)_2$  and .0002M  $\text{HClO}_4$ . Sodium perchlorate was added to all solutions to adjust ionic strength.

Between 200 and 225 ml of each previously prepared solution were placed into 250 erlenmeyer flasks and placed in constant temperature bath. A minimum of two hours was allowed for thermal equilibration. Nitrogen gas was bubbled into the each flask for approximately twenty minutes, to expel  $\text{CO}_2$  and  $\text{O}_2$ . Each flask was then stoppered until used for the titration.

Fifty ml of solution was pipetted from flask into a 150 ml beaker which was partially submerged in the constant temperature bath. Several minutes were allowed for thermal equilibrium.

Barium perchlorate solutions were used to determine acid dissociation constants of the diamines, and the  $\text{Cu}(\text{ClO}_4)_2$  solutions were used to determine formation constants. Both of these solutions were titrated with aqueous amine solutions. After each amine volume addition one minute was allowed for thermal equilibrium. The pH of the solution was recorded after thermal equilibrium was attained. In the case of  $\text{N,N,N',N'}$ -tetramethylpropylenediamine up to five minutes was allowed for the reaction to reach equilibrium before a pH reading was taken. Nitrogen gas was bubbled slowly into solution during titration.

The amine solutions were added with a calibrated 10 ml Class A buret with .05 ml graduations, and Eppendorf pipets adjusted to deliver .005 and .01 ml of solution. The pH meter was recalibrated after each titration. Ionic strengths used were 1.0, .50, .30 and .10 M. Temperatures used were 20°, 30° and 40°C.

### Determination of Acid Dissociation Constant

The base strength of a base is inversely related to its acid dissociation constant. The two are related by the expression

$$K_w = K_b \cdot K_a \quad (1)$$

Solving equation (1) for  $K_a$ , the following expression is obtained.

$$K_a = \frac{K_w}{K_b} \quad (2)$$

where  $K_w$  is the ionization constant of water,  $K_b$  the base constant and  $K_a$  the acid dissociation constant.

The acid dissociation constant is for the following equation



where  $AH^+$  is the base cation,  $A$  the unprotonated base and  $H^+$  the acid.

The following expression can be derived

$$K = \frac{[A][H^+]}{[A H^+]} = K_a \quad (\text{for base}) \quad (4)$$

where  $K_a$  is the acid dissociation constant.

Equation (4) is valid for a mono-basic molecule. When the molecule is di-basic, such as diamines, the following equations hold true



where  $AH_2^{2+}$  is the second base moiety.

The following expressions can be derived from equations (5) and (6)

$$K_1 = \frac{[A][H^+]}{[A H^+]} \quad (7)$$

$$K_2 = \frac{[H^+][A H^+]}{[A H_2^{2+}]} \quad (8)$$

where  $K_1$  is the first acid dissociation constant and  $K_2$  is the second

acid dissociation constant.

It is a matter of convenience to express  $K_1$  and  $K_2$  in terms of log values. The following expressions can be derived by taking the log of K expressions

$$\log K_1 = \log [H^+] + \log \frac{[A]}{[AH^+]} \quad (9)$$

Multiplying both sides of equation (9) by negative one, we obtain

$$-\log K_1 = -\log [H^+] - \log \frac{[A]}{[AH^+]} \quad (10)$$

which gives

$$pK_1 = pH - \log \frac{[A]}{[AH^+]} \quad (11)$$

Equation (11) is a variation of the Henderson - Haselbach equation. If

$K_2$  is given the same treatment, we obtain

$$pK_2 = pH - \log \frac{[AH^+]}{[AH_2^{2+}]} \quad (12)$$

Equations (11) and (12) were used to calculate the acid dissociation constants for each diamine. Computer programs were written to help facilitate the calculation of each pK value.

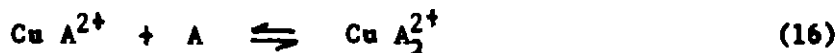
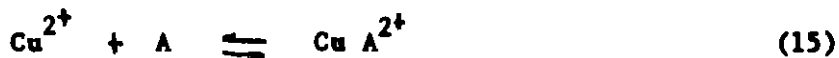
#### Determination of Formation Constant

The following mass action expressions are valid<sup>(1)</sup>

$$k_1 = \frac{[Cu A^{2+}]}{[Cu^{2+}] [A]} \quad (13)$$

$$k_2 = \frac{[Cu A_2^{2+}]}{[Cu A^{2+}] [A]} \quad (14)$$

where  $[A]$  is the diamine concentration. Equation (13) and (14) are derived from the following complexation equilibrium



Constants  $k_1$  and  $k_2$  are called concentration constants, and are not true thermodynamic constants. To be true thermodynamic constants, the activity of each species need be factored into each equation. However, the activity coefficient of each species can be assumed to be constant when a high constant ionic strength medium is employed.

According to Bjerrum,<sup>(2)</sup> the concentration constants are formation constants. The same terminology will be used here. The maximum number of ligands complexed to copper (II) ion is two; only these equations will be developed and used. To determine the formation constants, the term  $n$  must be known. The term  $\bar{n}$  is defined as

$$\bar{n} = \frac{[MA] + 2[MA_2] + \cdots N[MA_N]}{[M] + [MA] + [MA_2] + \cdots [MA_N]} \quad (17)$$

where  $N$  is the maximum number of ligands. For copper (II) - diamine complexes of  $N = 2$ , and the term  $\bar{n}$  becomes

$$\bar{n} = \frac{[\text{CuA}^{2+}] + 2[\text{CuA}_2^{2+}]}{[\text{Cu}^{2+}] + [\text{CuA}^{2+}] + [\text{CuA}_2^{2+}]} \quad (18)$$

The term  $\bar{n}$  is defined as the average number of ligands attached to the copper (II) ion and expresses an unambiguous relationship between  $\bar{n}$  and the free amine concentration.<sup>(2)</sup> Substituting equations (13) and (14) into (18) and eliminating  $[\text{Cu}^{2+}]$  gives

$$\bar{n} = \frac{k_1 [A] + 2 k_1 k_2 [A]^2}{1 + k_1 [A] + k_1 k_2 [A]^2} \quad (19)$$



where  $k_1$  and  $k_2$  are considered unknown quantities. Rearrangement of equation (19)<sup>(22)</sup> and combining terms gives

$$\bar{n} + (\bar{n} - 1) k_1 [A] + (\bar{n} - 2) k_1 k_2 [A]^2 = 0 \quad (20)$$

and solving equation (20) for each individual formation constant gives

$$k_1 = \frac{1}{[A]} \cdot \frac{\bar{n}}{(1-\bar{n}) - (2-\bar{n}) [A] k_2} \quad (21)$$

$$k_2 = \frac{1}{[A]} \cdot \frac{\bar{n}}{k_1 [A]} + (\bar{n} - 1) \quad (22)$$

Before actual constants can be calculated a set of approximate constants  $k_1$  and  $k_2$  must be determined.<sup>(21)</sup>

The inverse of  $[A]$  at half  $\bar{n}$  values was used as an approximation of the formation constant.<sup>(21)</sup> Doing so results in

$$k_1 = \frac{1}{[A]_{\bar{n} = .5}} \quad (23)$$

$$k_2 = \frac{1}{[A]_{\bar{n} = 1.5}} \quad (24)$$

There exists equal amounts of  $\text{Cu}^{2+}$  and  $\text{CuA}^{2+}$  for  $k_1$  at  $\bar{n} = .5$ , and of  $\text{CuA}^{2+}$  and  $\text{CuA}_2^{2+}$  for  $k_2$  at  $\bar{n} = 1.5$ . Substitution of equation (23) into (21) and equation (24) into (22) gives

$$k_1 = \frac{1}{[A]_{\bar{n} = .5}} \cdot \frac{1}{1 - 3 k_2 [A]_{\bar{n} = .5}} \quad (25)$$

$$k_2 = \frac{1}{[A]_{\bar{n} = 1.5}} \cdot 1 - \frac{3}{k_1 [A]_{\bar{n} = 1.5}} \quad (26)$$

Equations (25) and (26) are the actual formation constant equations.

## Results

Table 8 contains the acid dissociation and formation constants of 1,3-propanediamine with copper (II) ion at 30°C.

Tables 9 and 10 contain the formation constants for N,N,N',N'-tetramethylethylenediamine and N,N,N',N'-tetramethylpropylenediamine, respectively with copper (II) ion. Tables 11 and 12 are listings of the acid dissociation constants for N,N,N',N'-tetramethylethylenediamine and N,N,N',N'-tetramethylpropylenediamine, respectively. All data were calculated with a computer programmed using the Bjerrum potentiometric method. Computer programs are listed in Appendices A-D. The formation constant data for N,N,N',N'-tetramethylpropylenediamine was determined in .0001M  $\text{Cu}^{2+}$  solutions. Precipitation of complex occurred in .001M  $\text{Cu}^{2+}$  solutions. No precipitation occurred when 1,3-propylenediamine and N,N,N',N'-tetramethylethylenediamine were used with the .001M  $\text{Cu}^{2+}$  solutions.

Acid dissociation constants for 1,3-propylenediamine and N,N,N',N'-tetramethylethylenediamine were determined in .001M  $\text{Ba}^{2+}$  solutions, and those for N,N,N',N'-tetramethylpropylenediamine were determined in .0001M  $\text{Ba}^{2+}$  solutions.

Tables 13 and 14 contain thermodynamic parameters for N,N,N',N'-tetramethylethylenediamine and N,N,N',N'-tetramethylpropylenediamine complexes with copper (II) ion. A plot of  $\ln K$  vs  $I$  or  $\ln K$  vs  $I^{1/2}$  and extrapolating to zero ionic strength gives the thermodynamic formation constant,  $K$ . The slope of a plot of  $\ln K$  vs  $1/T$  is related to  $\Delta H^\circ$  by:

$$\text{slope} = -\Delta H^\circ/R \quad (1)$$

where  $\Delta H^\circ$  is the thermodynamic enthalpy term and  $R$  is the gas constant. The above equation is obtained from the van't Hoff equation.

DATA FOR 1,3-PROPYLENEDIAMINE

At 30° C

Acid Dissociation Constants

Formation Constants Using Copper (II) Ion

MOLAR NaClO <sub>4</sub>	K <sub>1</sub>	-log K <sub>1</sub>	K <sub>2</sub>	-log K <sub>2</sub>	k <sub>1</sub>	-log k <sub>1</sub>	k <sub>2</sub>	log k <sub>2</sub>
1.0	4.98x10 <sup>-11</sup>	10.30(.03)	1.92 x 10 <sup>-9</sup>	8.72(.02)	3.95 x 10 <sup>9</sup>	9.60(.01)	1.05x10 <sup>7</sup>	7.02(.0
.50	5.25x10 <sup>-11</sup>	10.28(.01)	1.82x10 <sup>-9</sup>	8.74(.01)	5.19x10 <sup>9</sup>	9.71(.03)	1.77x10 <sup>7</sup>	7.25(.0
.30	4.42x10 <sup>-11</sup>	10.35(.03)	1.69x10 <sup>-9</sup>	8.77(.01)	2.31x10	9.36(.02)	7.15x10 <sup>5</sup>	5.87(.1
.10	4.10x10 <sup>-11</sup>	10.39(.02)	2.46x10 <sup>-9</sup>	8.61(.04)	2.69x10	9.43(.01)	6.34x10 <sup>6</sup>	6.80(.0

Standard deviations in parentheses

TABLE 9

FORMATION CONSTANTS OF COPPER (II) ION  
WITH N,N,N',N'-tetramethylethylenediamine

Temp (°C)	MOLAR NaClO <sub>4</sub>	k <sub>1</sub>	log k <sub>1</sub>	k <sub>2</sub>	log k <sub>2</sub>
20	1.0	8.65x10 <sup>7</sup>	7.94(.01)	8.08x10 <sup>4</sup>	4.90(.07)
	.50	3.72x10 <sup>7</sup>	7.57(.02)	7.83x10 <sup>4</sup>	4.89(.02)
	.30	1.44x10 <sup>7</sup>	7.16(.00)	5.54x10 <sup>4</sup>	3.74(.00)
	.10	2.22x10 <sup>7</sup>	7.35(.02)	2.45x10 <sup>4</sup>	4.39(.01)
30	1.0	5.03x10 <sup>7</sup>	7.70(.00)	3.60x10 <sup>4</sup>	4.56(.02)
	.50	4.78x10 <sup>7</sup>	7.68(.02)	5.55x10 <sup>4</sup>	4.74(.01)
	.30	8.96x10 <sup>6</sup>	6.95(.00)	1.72x10 <sup>3</sup>	3.24(.00)
	.10	1.05x10 <sup>7</sup>	7.02(.05)	1.15x10 <sup>4</sup>	4.06(.03)
40	1.0	3.144x10 <sup>7</sup>	7.50(.00)	5.92x10 <sup>4</sup>	4.77(.01)
	.50	1.91x10 <sup>7</sup>	7.28(.00)	6.77x10 <sup>4</sup>	4.83(.00)
	.30	1.22x10 <sup>7</sup>	7.09(.00)	8.25x10 <sup>3</sup>	3.92(.03)
	.10	2.11x10 <sup>7</sup>	7.33(.03)	2.95x10 <sup>4</sup>	4.47(.01)

Standard deviations in parentheses

TABLE 10  
FORMATION CONSTANTS OF COPPER (II) ION  
WITH N,N,N',N'-tetramethylpropylenediamine

Temp (°C)	MOLAR NaClO <sub>4</sub>	k <sub>1</sub>	log k <sub>1</sub>	k <sub>2</sub>	log k <sub>2</sub>
20	1.0	1.59x10 <sup>8</sup>	8.20(.02)	6.94x10 <sup>4</sup>	4.83(.13)
	.50	6.81x10 <sup>6</sup>	6.83(.00)	4.912x10 <sup>4</sup>	4.69(.10)
	.30	1.53x10 <sup>6</sup>	6.19(.00)	4.56x10 <sup>4</sup>	4.66(.05)
	.10	2.10x10 <sup>6</sup>	6.32(.02)	3.11x10 <sup>5</sup>	5.49(.01)
30	1.0	3.03x10 <sup>7</sup>	7.48(.05)	5.17x10 <sup>4</sup>	4.71(.05)
	.50	1.06x10 <sup>7</sup>	7.03(.02)	7.25x10 <sup>4</sup>	4.86(.00)
	.30	1.08x10 <sup>7</sup>	7.03(.10)	5.36x10 <sup>4</sup>	4.72(.07)
	.10	1.47x10 <sup>7</sup>	7.16(.11)	2.70x10 <sup>5</sup>	5.43(.06)
40	1.0	3.04x10 <sup>7</sup>	7.48(.07)	6.22x10 <sup>4</sup>	4.79(.07)
	.50	1.33x10 <sup>7</sup>	7.12(.00)	1.317x10 <sup>5</sup>	5.13(.01)
	.30	4.38x10 <sup>6</sup>	6.64(.04)	8.17x10 <sup>4</sup>	4.90(.15)
	.10	3.70x10 <sup>7</sup>	7.56(.11)	2.79x10 <sup>6</sup>	6.421(.18)

Standard deviations in parentheses

## ACID DISSOCIATION CONSTANTS OF N,N,N',N'-tetramethylethylenediamine

Temp (°C)	MOLAR NaClO <sub>4</sub>	K <sub>1</sub>	-log K <sub>1</sub>	K <sub>2</sub>	-log K <sub>2</sub>
20	1.0	2.36x10 <sup>-10</sup>	9.63(.02)	2.76x10 <sup>-7</sup>	6.56(.00)
	.50	3.55x10 <sup>-10</sup>	9.45(.03)	5.16x10 <sup>-7</sup>	6.29(.01)
	.30	3.318x10 <sup>-10</sup>	9.48(.03)	4.96x10 <sup>-7</sup>	6.31(.01)
	.10	4.32x10 <sup>-10</sup>	9.36(.02)	7.15x10 <sup>-7</sup>	6.13(.02)
30	1.0	3.80x10 <sup>-10</sup>	9.42(.01)	4.33x10 <sup>-7</sup>	6.36(.01)
	.50	4.93x10 <sup>-10</sup>	9.31(.02)	6.12x10 <sup>-7</sup>	6.21(.01)
	.30	6.26x10 <sup>-10</sup>	9.20(.01)	7.91x10 <sup>-7</sup>	6.10(.01)
	.10	7.37x10 <sup>-10</sup>	9.13(.01)	1.14x10 <sup>-6</sup>	5.95(.02)
40	1.0	6.97x10 <sup>-10</sup>	9.16(.01)	9.30x10 <sup>-7</sup>	6.03(.01)
	.50	9.04x10 <sup>-10</sup>	9.04(.01)	1.429x10 <sup>-6</sup>	5.85(.01)
	.30	8.19x10 <sup>-10</sup>	9.09(.01)	9.81x10 <sup>-7</sup>	6.01(.01)
	.10	1.01x10 <sup>-9</sup>	8.99(.02)	1.21x10 <sup>-6</sup>	5.92(.01)

Standard deviations in parentheses

TABLE 12

## ACID DISSOCIATION CONSTANTS OF N,N,N',N'-tetramethylpropylenediamine

Temp (°C)	MOLAR NaClO <sub>4</sub>	K <sub>1</sub>	-log K <sub>1</sub>	K <sub>2</sub>	-log K <sub>2</sub>
20	1.0	$2.64 \times 10^{-10}$	9.58(.04)	$8.13 \times 10^{-9}$	8.09(.07)
	.50	$3.66 \times 10^{-10}$	9.44(.04)	$1.52 \times 10^{-8}$	7.82(.09)
	.30	$5.60 \times 10^{-10}$	9.25(.02)	$1.81 \times 10^{-8}$	7.74(.01)
	.10	$5.89 \times 10^{-10}$	9.23(.05)	$1.93 \times 10^{-8}$	7.72(.02)
30	1.0	$5.47 \times 10^{-10}$	9.26(.02)	$1.53 \times 10^{-8}$	7.81(.02)
	.50	$5.31 \times 10^{-10}$	9.28(.03)	$2.22 \times 10^{-8}$	7.65(.03)
	.30	$4.53 \times 10^{-10}$	9.35(.04)	$1.96 \times 10^{-8}$	7.71(.02)
	.10	$2.73 \times 10^{-10}$	9.57(.02)	$1.66 \times 10^{-8}$	7.78(.01)
40	1.0	$8.90 \times 10^{-10}$	9.05(.02)	$3.63 \times 10^{-8}$	7.44(.02)
	.50	$4.06 \times 10^{-10}$	9.39(.02)	$3.13 \times 10^{-8}$	7.51(.01)
	.30	$8.07 \times 10^{-10}$	9.09(.01)	$2.55 \times 10^{-8}$	7.59(.01)
	.10	$4.24 \times 10^{-10}$	9.37(.01)	$1.35 \times 10^{-8}$	7.87(.05)

Standard deviations in parentheses



TABLE 13

Thermodynamic Data of Copper (II) Ion  
with N-tetramethylated Diamines  
for First Formation Constant

	N,N,N',N'-tetramethyl- ethylenediamine	N,N,N',N'-tetramethyl- propylenediamine
20°C		
log $k_1^{\circ}$	6.31	5.36
$\Delta G_1^{\circ}$ (kcal)	-8.46	-7.19
$\Delta H_1^{\circ}$ (kcal)	7.25	24.34
$\Delta S_1^{\circ}$ (cal/deg)	53.59	107.56
30°C		
log $k_1^{\circ}$	6.58	6.77
$\Delta G_1^{\circ}$ (kcal)	-9.13	-8.00
$\Delta H_1^{\circ}$ (kcal)	7.25	24.34
$\Delta S_1^{\circ}$ (cal/deg)	54.03	106.68
40°C		
log $k_1^{\circ}$	6.62	6.42
$\Delta G_1^{\circ}$ (kcal)	-9.49	-7.63
$\Delta H_1^{\circ}$ (kcal)	7.25	24.34
$\Delta S_1^{\circ}$ (cal/deg)	53.46	102.09

## Thermodynamic Parameters for Protonation of Bases

	°C	$\Delta H_1^\circ$	$\Delta H_2^\circ$	$\Delta H_{1,2}^\circ$	$\Delta G_1^\circ$	$\Delta G_2^\circ$	$\Delta G_{1,2}^\circ$	$\Delta S_1^\circ$	$\Delta S_2^\circ$	$\Delta S_{1,2}^\circ$	$-\log K_1$	$-\log K_2$
N,N,N',N'-tetramethyl ethylenediamine	20	8.25	4.87	13.12	-12.55	-8.21	-20.76	70.93	44.60	115.53	9.35	6.12
	30	8.25	4.87	13.12	-12.64	-8.24	-20.88	68.91	43.24	112.15	9.12	5.94
	40	8.25	4.87	13.12	-12.89	-8.46	-21.35	67.48	42.57	110.05	8.99	5.91
N,N,N',N'-tetramethyl Propylenediamine	20	-4.07	-3.78	-7.85	-12.31	-10.24	-22.55	28.09	22.05	50.14	9.18	7.64
	30	-4.07	-3.78	-7.85	-13.17	-10.73	-23.90	30.00	22.94	52.94	9.49	7.74
	40	-4.07	-3.78	-7.85	-13.40	-11.18	-24.58	29.79	23.63	53.42	9.35	7.80

$\Delta H^\circ$  and  $\Delta G^\circ$  are in kcal;  $\Delta S^\circ$  in cal/deg.

Figure 1. Thermodynamic Plot Of Conper (II) Ion With  
N,N,N',N'-tetramethylpropylenediamine

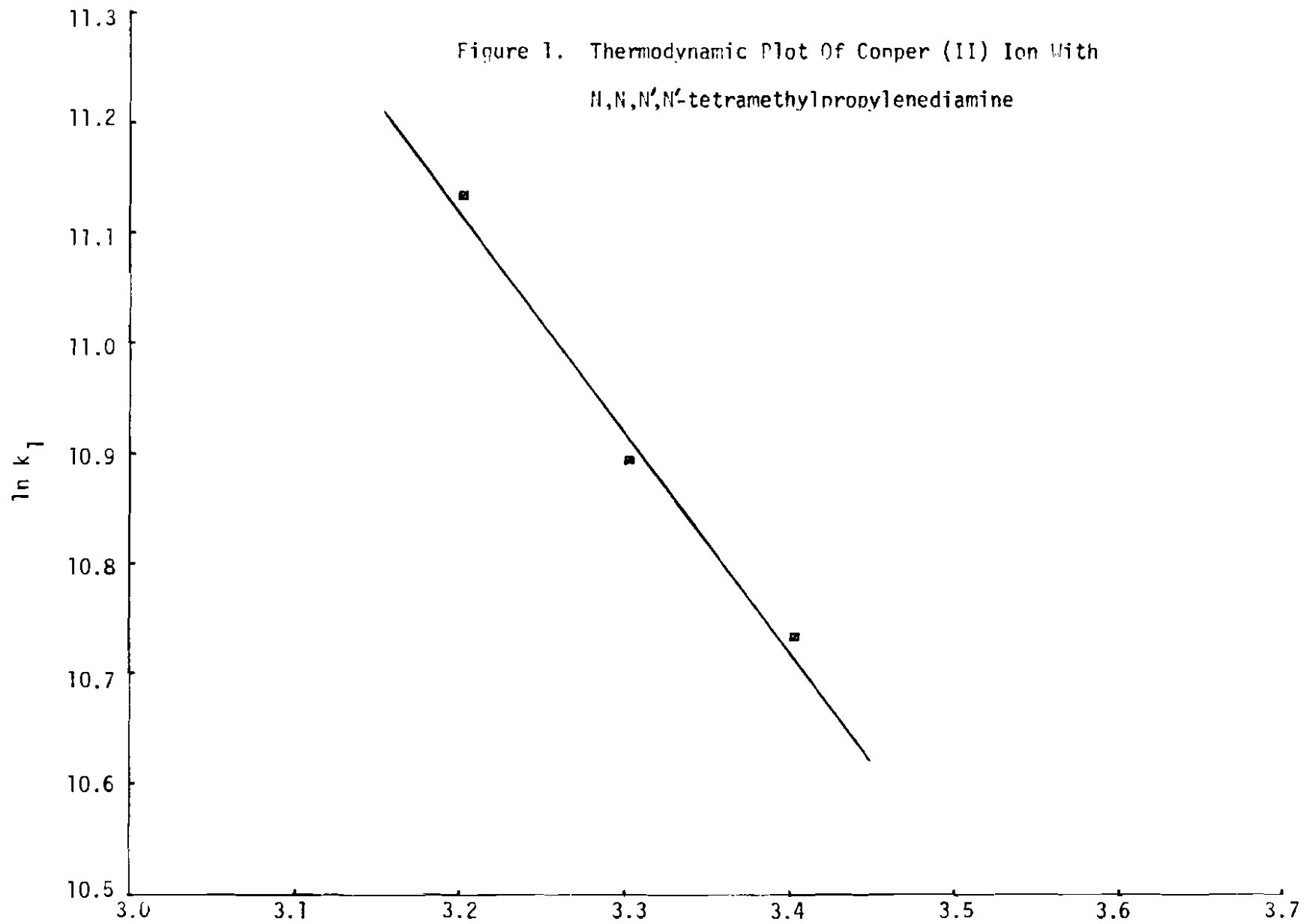
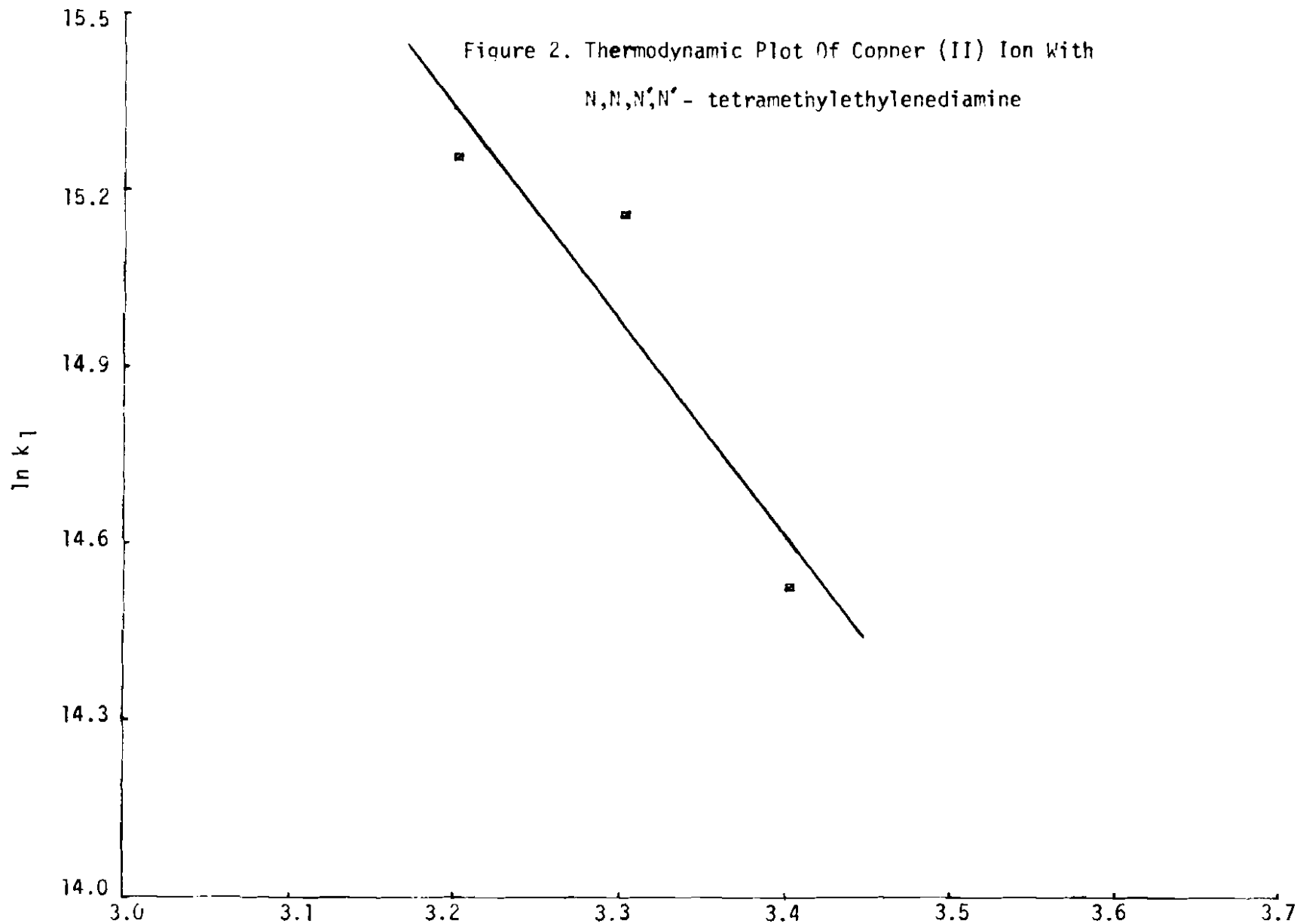


Figure 2. Thermodynamic Plot Of Copper (II) Ion With  
N,N,N',N' - tetramethylethylenediamine



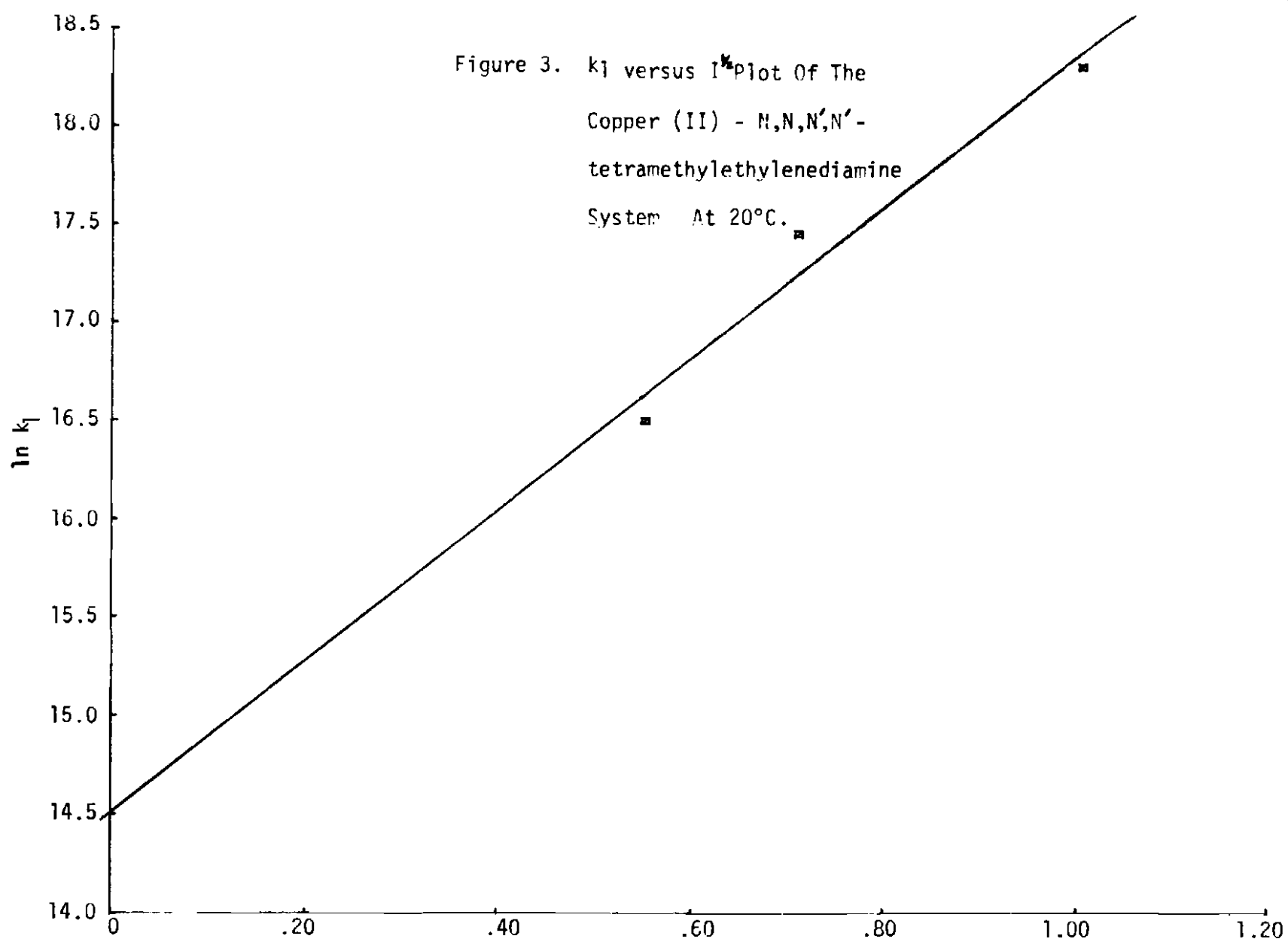


Figure 4.  $k_2$  versus  $I^{1/2}$  Plot Of The Conper (II)-  
N,N,N',N'- tetramethylethylenediamine  
System. At 20°C.

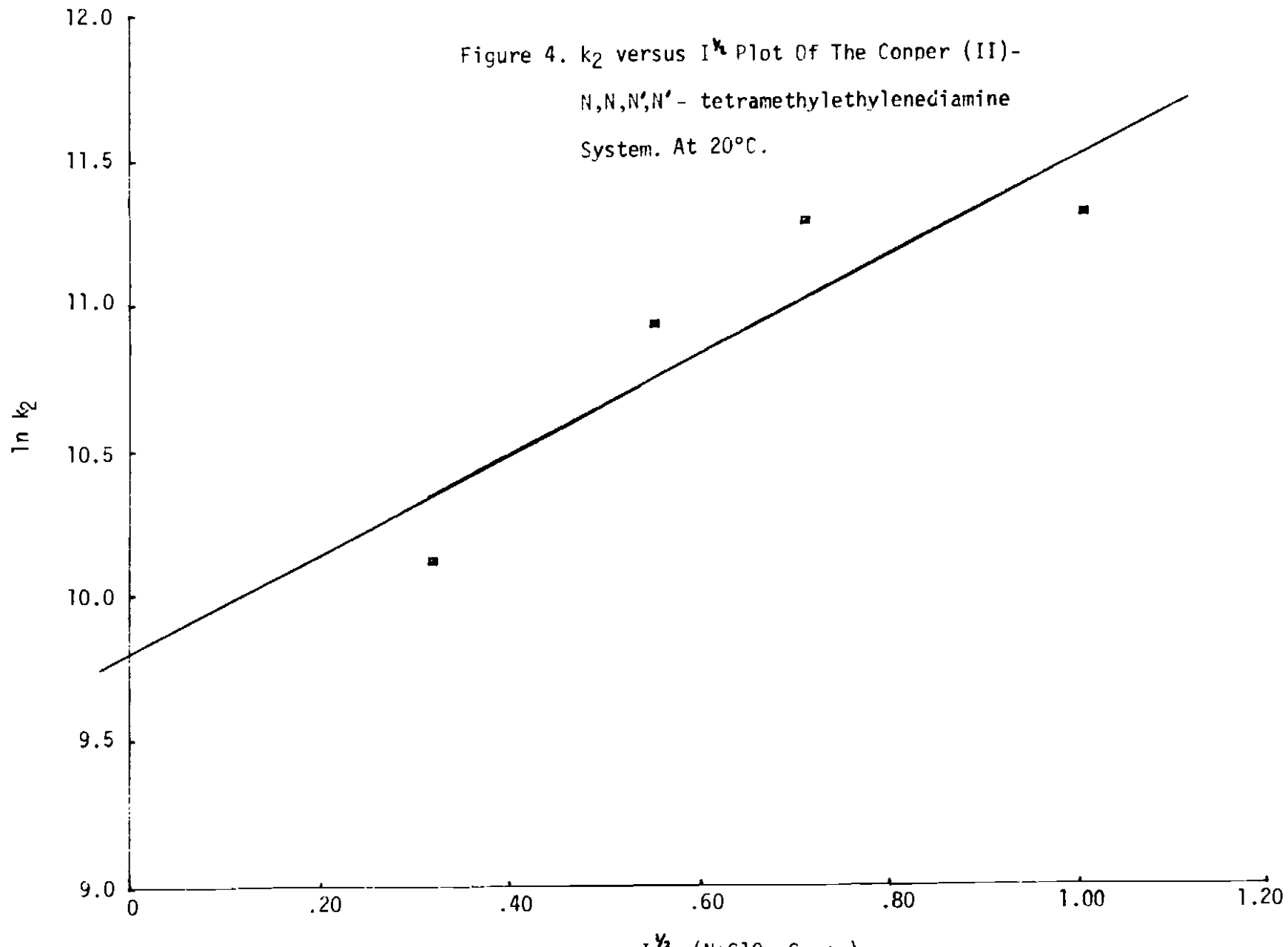


Figure 5.  $k_1$  versus I Plot Of The Copper (II) -  
N,N,N',N' - tetramethylpropylenediamine  
System At 20°C.

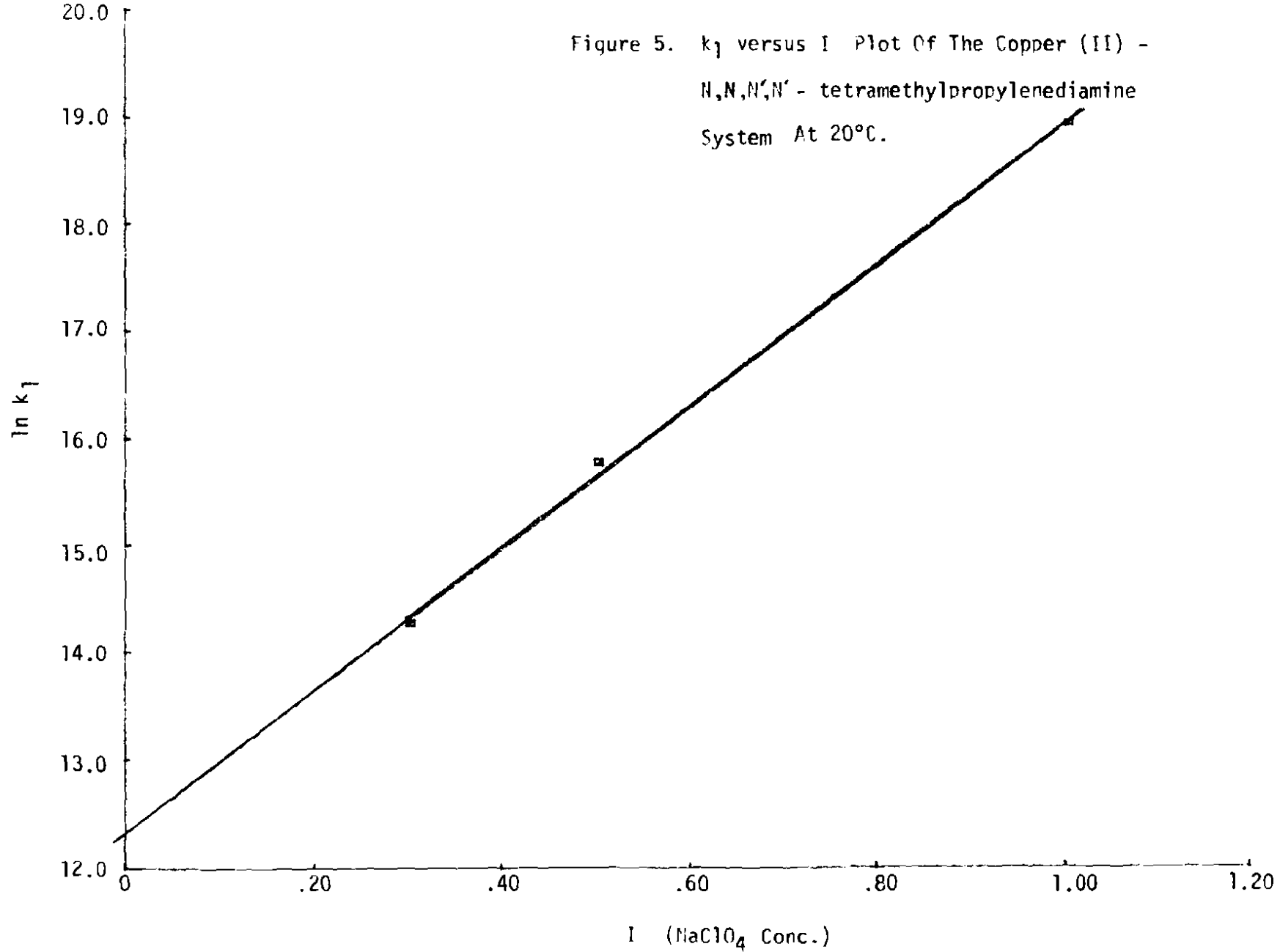
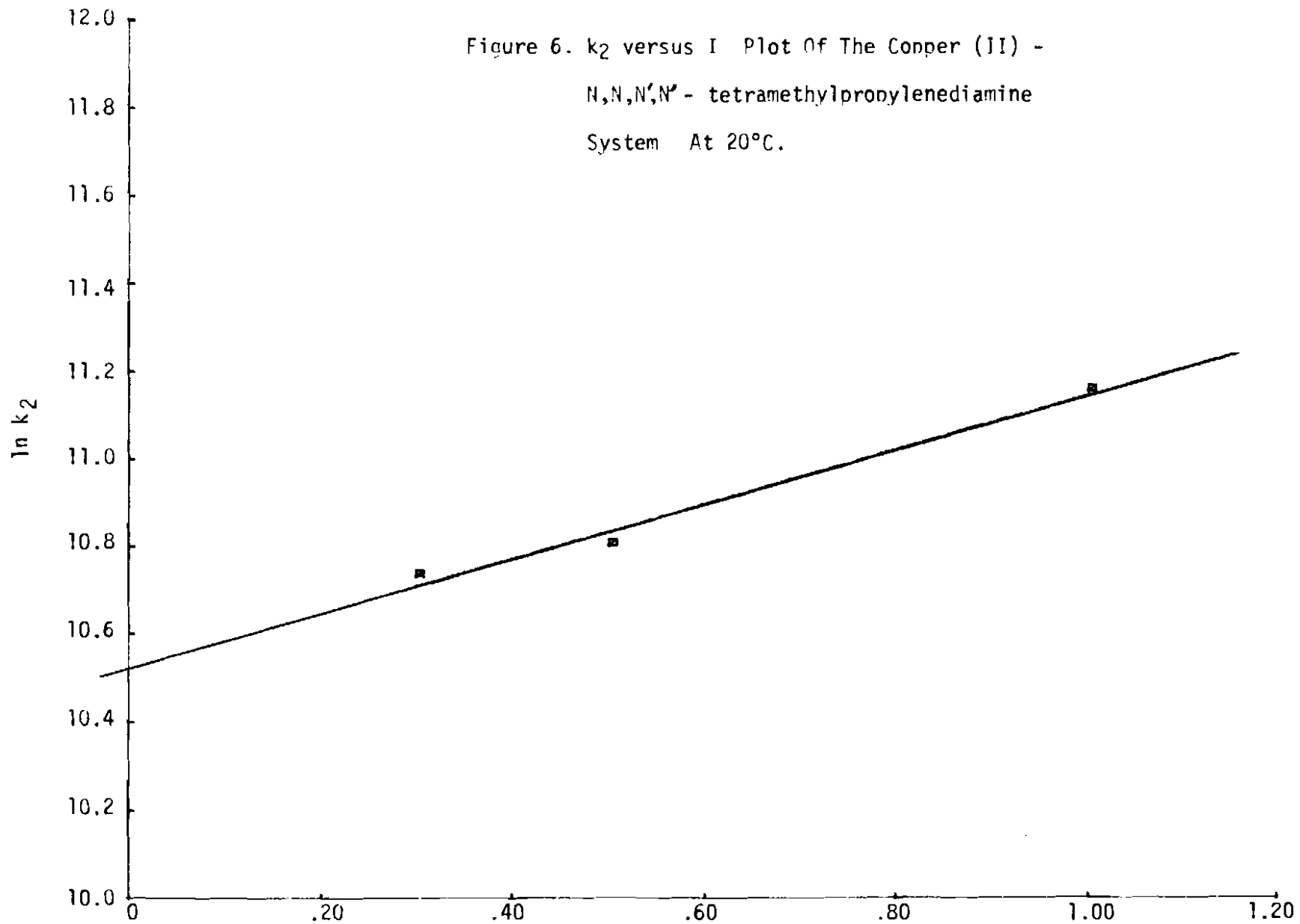


Figure 6.  $k_2$  versus I Plot Of The Copper (II) -  
N,N,N',N' - tetramethylpropylenediamine  
System At 20°C.





The thermodynamic entropy value,  $\Delta S^\circ$ , was calculated by solving equation (2) for  $\Delta S^\circ$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (2)$$

where  $\Delta G^\circ$  is the thermodynamic free energy term and T is the temperature in degrees Kelvin. The thermodynamic free energy term was calculated using equation (3)

$$\Delta G^\circ = -RT \ln K^\circ \quad (3)$$

Many of the graphs of  $\ln K$  vs I were non-linear. This non-linear behavior occurred principally in the  $30^\circ - 40^\circ$  C range and for the complexation of the second ligand to the copper (II) ion. As a result, plots of  $\ln K$  vs I were unusable for  $k_2$  at  $20^\circ$  C, and  $k_1$  and  $k_2$  at  $30^\circ - 40^\circ$  C. Figures 1-6 are plots of some of the usable data.

In the course of this investigation, it was necessary to determine the acid dissociation constant for each diamine. Acid dissociation constants for N,N,N',N'-tetramethylethylenediamine and N,N,N',N'-tetramethylpropylenediamine are less basic than the unsubstituted ligand. The thermodynamic parameters for 1,2-ethylenediamine<sup>(10)</sup> at  $20^\circ$  C are:  $\Delta H_1^\circ = -11.5$  kcal,  $\Delta H_2^\circ = -10.3$  kcal,  $\Delta G_1^\circ = -13.5$  kcal,  $\Delta G_2^\circ = -9.4$  kcal,  $\Delta S_1^\circ = +7$  cal/deg and  $\Delta S_2^\circ = -3$  cal/deg and those for 1,3 propylenediamine<sup>(10)</sup> at  $20^\circ$  C are:

$$\begin{aligned} \Delta H_1^\circ &= -13.3 \text{ kcal, } \Delta H_2^\circ = -13.9 \text{ kcal, } \Delta G_1^\circ = -14.3 \text{ kcal,} \\ \Delta G_2^\circ &= -11.6 \text{ kcal, } \Delta S_1^\circ = +3 \text{ cal/deg, and } \Delta S^\circ = -8 \text{ cal/deg} \end{aligned}$$

Comparison of the data with Table 14 reveals the increased acidic nature of the methylated derivatives.

## Discussion

In general, five-membered metal chelate ligand rings are more stable than six-membered rings. The effects of steric strain on each ring system accounts for the increased stability of five-membered rings over six-membered rings. Also, it has been reported<sup>(15, 16, 17)</sup> that methyl-substitution on the amine nitrogen has some effect on complex ion stability.

Inspection of the formation constants in Tables 8-10 indicate that methyl-substitution on the amine nitrogens causes marked decreases in complex ion stability. The data listed in Tables 8 and 10 indicate a significant decrease in both  $k_1$  and  $k_2$  values for the substituted ligand.

A comparison of data for 1,3-propylenediamine and N,N,N',N'-tetramethylpropylenediamine at 30° C (see Tables 8 and 10) indicate greater basicity for the 1,3-propylenediamine ligand. According to other investigators,<sup>(6)</sup> as the proton affinity of the ligand increases the tendency of the ligand to function as a chelate ligand decreases. However, the data in Tables 8 and 10 indicate otherwise. The more basic 1,3-propylenediamine was found to be more stable than its N-tetramethylated derivative.

It has been reported<sup>(13)</sup> that complex stability is greatly influenced by steric hindrance, that is, thermodynamically, the complex ion is destabilized by unfavorable entropy effects. A comparison of data by Hares<sup>(9)</sup> for 1,3-propylenediamine in Table 15, and the thermodynamic data listed in Table 13 give an indication of the origin of the N,N,N',N'-tetramethylpropylenediamine ligand's instability. According to the literature<sup>(9)</sup> free energy and enthalpy values are usually lower for ligands of lower basicity. The enthalpy values for the two ligands differ greatly, an indication that methylation destabilizes the

## COMPARISON OF THERMODYNAMIC DATA

Ligand	k value	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$	ref.
1,3-propylenediamine <sup>a</sup>	1	-13.3	-14.0	-3	9
	2	-9.7	-13.0	-12	
	1,2	-23.0	27.0	-15	
1,2-ethylenediamine <sup>b</sup>	1	-14.16	-8.6	21	15
	2	-12.43	-8.6	14	
	1,2	-26.59	-14.2	35	
N-methylethylenediamine <sup>b</sup>	1	-13.89	-8.5	20	15
	2	-11.28	-7.0	16	
	1,2	-25.17	-15.5	36	
N,N'-dimethylethylene- <sup>b</sup> diamine	1,2	-23.3	-17.5	21	17

$\Delta G^\circ$  and  $\Delta H^\circ$  are in kcal;  $\Delta S^\circ$  in cal/deg.

<sup>a</sup><sub>t</sub> = 30°C

<sup>b</sup><sub>t</sub> = 0°C

in terms of entropy values, be more stable.

The logic used by Cotton<sup>(6)</sup> to explain the instability of 1,3-propylenediamine ligand can be applied to its N-tetramethylated derivative. Ring closure on the N,N,N',N'-tetramethylpropylenediamine-copper (II) complex ion is hindered sterically by the methyl groups. The longer chain length of the ligand results in the requirement that the ligand need transverse a longer distance to complete ring formation. The longer distance requirement decreases the probability of ring formation. In lieu of this, when the required distance is transversed, the methyl groups will hinder chelation by physically not allowing the nitrogen electrons to approach close enough for bonding. In conjunction with this, the interaction of the methyl substituted amine nitrogens with the solvent will interfere with ring closure. For this reason, large positive entropy values were obtained for the N,N,N',N'-tetramethylpropylenediamine-copper (II) complex ion.

The N,N,N',N'-tetramethylethylenediamine ligand upon chelation has a shorter distance to transverse for ring closure. As reported by Basolo<sup>(15, 17)</sup>, methyl-substitution interferes with the chelating ability of the ligand (See Table 15). The aforementioned reasons for instability are applicable here. Also, Basolo found that increased methyl-substitution on the amine nitrogen causes a lessening of stability in terms of enthalpy and free energy values, and an enhancement of entropy values. The enhanced entropy values are attributable to the more hydrophobic character of the copper (II)-diamine complexes formed, that is, enhancement is due to solvent interactions with the ligand.

Comparison of Tables 13 and 15 indicate favorable free energy and enthalpy effects for the unsubstituted ligand, and enhanced entropic effects for the substituted ligand. The enhanced entropic effects reflect favorable interactions of the substituted ligand with the solvent.

N,N,N',N'-tetramethylpropylenediamine-copper (II) complex ion. Destabilization is of such a magnitude that the ensuing reaction becomes endothermic (positive enthalpy). Figure 1 illustrates the endothermic nature of complexation. A comparison of free energy values in Tables 13 and 15 indicate lower stability for the substituted propylenediamine ligand.

Increased randomness is evident when entropy values are compared. The 1,3-propylenediamine ligand is a well ordered system (negative entropy), and the N,N,N',N'-tetramethylpropylenediamine ligand is a wholly disordered system (positive entropy). The discrepancy in entropy values can be attributed to ligand interaction with the solvent, because, in terms of particle addition to the system, each ligand's contribution would be equivalent.

On the whole, the data indicated that for the copper (II)-N,N,N',N'-tetramethylpropylenediamine complex ion, entropy and enthalpy effects are working in opposite directions. This discrepancy in thermodynamic parameters is an indication of the system's instability.

The N,N,N',N'-tetramethylethylenediamine ligand is more stable than the N,N,N',N'-tetramethylpropylenediamine ligand with copper (II) ion. (See Tables 9 and 10) The stability increase involving the N,N,N',N'-tetramethylethylene diamine can be attributed to the chelate ring size. The chelate effect is a thermodynamic phenomenon. The thermodynamic data in Table 13 indicates that over all the N,N,N',N'-tetramethylethylenediamine is more stable thermodynamically, that is, the enthalpy values of the ligand indicate that the ligand and copper (II) ion form stronger bonds, and that complexation is endothermic. (See Figure 2). Also, the free energy values indicate that the substituted ethylenediamine is more stable. On the other hand, the entropy values indicate that the substituted propylenediamine should,

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**APPENDIX A**

C FRANKLIN N. RUSSELL  
C PROGRAM WAS WRITTEN JANUARY, 1981.  
C  
C THIS PROGRAM USES THE HJEPROM POTENTIOMETRIC METHOD OF FORMATION  
C AND STABILITY CONSTANT DETERMINATION.  
C THIS PROGRAM WILL BE USED TO ASSIST IN DETERMINING DIAMINE STABI-  
C LITY WITH COPPER (II) ION.  
C THIS PROGRAM WILL DO SO IN THREE STAGES.  
C THIS PROGRAM WILL BEGIN BY ESTABLISHING INITIAL ACID AND COPPER  
C CONCENTRATIONS BEFORE TITRATION (AMINE ADDITION)  
C SECONDLY, THIS PROGRAM WILL CALCULATE THE VARIOUS SUBSTANCE CONCEN-  
C TRATIONS OCCURRING DURING THE TITRATION PROCESS.  
C THIRDLY, QUANTITIES SUCH AS THE FRACTION OF AMINE NOT COMPLEX  
C BOUND WHICH EXIST AS FREE AMINE, THE NUMBER OF HYDROGEN IONS  
C NOT BOUND TO COMPLEX-BOUND AMINE, THE CONCENTRATION OF FREE AMINE,  
C AND THE FORMATION FUNCTION OF THE SYSTEM.  
C POINTS TWO AND THREE WILL BE CALCULATED IN A DO LOOP  
C ALL THE ABOVE QUANTITIES WILL BE PRINTED OUT BY WRITE STATEMENTS  
C AT THE END OF THE CALCULATION SEQUENCE.  
C



```

C
C THIS SECTION READS IN THE PK VALUES FOR THE DIAMINE, THE VOLUME
C OF SOLUTION TO BE TITRATED, THE GRAMS OF COPPER COMPOUND, THE MOL.
C WT. OF THE COPPER COMPOUND, THE MOLARITY OF THE CONC. ACID, AND
C THE AMINE, RESPECTIVELY.
      READ(5,30) PKAHT,PKAH,VOLSOL,GRCP,XMUCUP,VOLAC,XMOAC,TOTVOL,XMOAM
30      FORMAT(PF7.0)
C THIS SECTION WILL CALCULATE THE MOLARITY OF COPPER AND ACID BEING
C USED IN THIS DETERMINATION, AND IT WILL CONVERT THE PKAH VALUES
C TO KAH VALUES.
      RMCAC=(VOLAC*XMOAC)/TOTVOL
      RMCUP=GRCP/XMUCUP
      XKAHT=(1/(10**PKAHT))
      XKAH=(1/(10**PKAH))
      WRITE(6,4) PKAHT,PKAH,RMCAC,RMCUP,XKAHT,XKAH
4      FORMAT(1X,2(3X,F6.3),2(3X,F6.5),2(3X,1PE16.6))
      N=1
C IN THE FOLLOWING DO LOOP QUANTITIES DEALING WITH THE FORMATION OF
C THE COPPER-AMINE COMPLEX WILL BE CALCULATED AT EACH VOLUME OF
C AMINE ADDED.
      DO 7 J=1,N
C THIS SECTION WILL READ IN THE VOLUME OF AMINE AND THE PH.
      READ(5,77) VOLAM,PH
77      FORMAT(2F10.0)
C THIS SECTION WILL CALCULATE THE CONCENTRATION OF HYDROGEN IONS,
C ACID, TOTAL COPPER, AND TOTAL AMINE, RESPECTIVELY.
      CHYDR1=(1/(10**PH))
      CONAC=(RMCAC*VOLSOL)/(VOLSOL+VOLAM)
      CONCL=(RMCUP*VOLSOL)/(VOLSOL+VOLAM)
      CONAM=(VOLAM*XMOAM)/(VOLSOL+VOLAM)
C THIS SECTION WILL CALCULATE THE FRACTION OF AMINE NOT COMPLEX-
C BOUND, WHICH EXIST AS FREE AMINE: THE TERM CALPHA.
      BALPHA=((XKAHT*XKAHT)+(XKAHT*CHYDR1)+(CHYDR1**2))
      CALPHA=((XKAHT*XKAH)/BALPHA)*100000.0
      DALPHA=CALPHA*C-CPUR

```



**APPENDIX B**

```

C THIS SECTION READS IN THE ACID AND AMINE MOLARITIES
  XIVAC=50.0
  READ(5,12) ACMO,AMMO,N
12  FORMAT(2F10.0,I4)
C THIS SECTION WILL CALCULATE THE PKAH FOR THE DIAMINE
  DO 2 J=1,N
C THIS SECTION WILL READ THE VOLUME OF AMINE AND ACID, AND THE PH
  READ(5,20) AMV,PH
20  FORMAT(2F10.0)
C THIS SECTION WILL DO THE CALCULATIONS LEADING TO THE PKAH
  HAMINE=(AMV*AMMO)/(XIVAC+AMV)
  HACID=(XIVAC*ACMO)/(XIVAC+AMV)
  CRO=HAMINE-HACID
  CR=HAMINE-CRO
C THIS SECTION WILL CALC THE PKAH USING HENDERSON-HASSELBACH EQUA
C AND WRITE OUT THE VALUE WITH OTHER IMPORTANT INFO
  PKAH=PH-ALOG10(CRO/CR)
  WRITE(6,16) AMV,PH,HAMINE,HACID,CRO,CR,PKAH
16  FORMAT ( SX,F4.2,3X,F5.2,2(3X,F6.5),2(3X,F7.6), SX,F5.2)
  B CONTINUE
C THIS ENDS THE PROGRAM
  STOP
  END
*END PRINT          *** 23 RECORDS

```

**APPENDIX C**

```

C THIS SECTION READS IN THE ACID AND AMINE MOLARITIES
  XIVAC=50.0
  READ(5,12) ACMO,AMMO,N
12  FORMAT(2F10.0,I4)
C THIS SECTION WILL CALC THE PKAHT FOR THE MONO-AND DIAMINE
  DO 2 J=1,N
C THIS SECTION READS THE VOLUME OF AMINE AND ACID,AND THE PH
  READ(5,20) AMV,PH
20  FORMAT(2F10.0)
C THIS SECTION DOES THE CALCULATIONS LEADING TO PKAHT
  AMINE=(AMV*AMMO)/(XIVAC+AMV)
  ACID=(XIVAC*ACMO)/(XIVAC+AMV)
  CRTWO=ACID-AMINE
  CROAE=AMINE-CRTWO
C THIS SECTION CALC THE PKAHT USING THE HENDERSON-HASSELBACH EQ
C AND IT WILL WRITE OUT THE VALUE WITH OTHER IMPORTANT INFO
  PKAHT=PH-ALOG10(CROAE/CRTWO)
  WRITE(6,16) AMV,PH,AMINE,ACID,CRTWO,CROAE,PKAHT
16  FORMAT(5X,F5.3,3X,F5.2,2(3X,F7.6),2(3X,F7.6),5X,F4.2)
  B CONTINUE
C THIS ENDS THE PROGRAM
  STOP
  END
*END PRINT          *3 RECORDS

```

**APPENDIX D**

```

C   THIS PROGRAM WAS WRITTEN APRIL, 1981, BY FRANKLIN N. RUSSELL.
C
C
C   THE PURPOSE OF THIS PROGRAM IS TO CALCULATE THE SUCCESSIVE
C   FORMATION CONSTANTS FOR COPPER (II)-DIAMINE COMPLEXES
C   THIS PROGRAM IS DESIGNED FOR MAXIMUM N VALUE TWO (2).
C
C
C   THIS SECTION DOES THE PRELIMINARY CALCULATIONS FOR THE BLOCK-
C   MCINTYRE METHOD.
      N=1
      RNONE=1.0
      RNTWO=2.0
      DO 55 J=1,N
        READ(5,30) BARNO,BARNT,BRACA0,BRACAT
30      FORMAT (2F6.0,2E13.6)
        XJO=(RNONE-BARNO)*(BRACA0)
        XJOPR=(RNONE-BARNT)*(BRACAT)
        XJT=(RNTWO-BARNO)*(BRACA0**2)
        XJTPR=(RNTWO-BARNT)*(BRACAT**2)
        WRITE(6,70)
70      FORMAT (20X, '*****')
        WRITE(6,5) BARNO,XJO,XJT
5        FORMAT (5X,F5.3,2(5X,1PE12.4))
        WRITE(6,10) BARNT,XJOPR,XJTPR
10       FORMAT (5X,F5.3,2(5X,1PE12.4))
        WRITE(6,12)
12      FORMAT (20X, '*****')
C   THIS SECTION WILL USE THE BJERRUM POTENTIOMETRIC METHOD OF FORM-
C   ATION CONSTANT DETERMINATION.

```



```

C
C THIS SECTION WILL DETERMINE THE TEMPORARY FORMATION CONSTANTS
C FOR THE SYSTEM.
C   R=1.0/BRACAO
C   S=1.0/BRACAT
C THIS SECTION WILL CALCULATE THE FIRST FORMATION CONSTANT;
C THE TERM YKONE.
C   BR=1.0+(3.0*S*BRACAO)
C   YKONE=(R*(1.0/BR))
C THIS SECTION WILL CALCULATE THE SECOND FORMATION CONSTANT;
C THE TERM YKTWO.
C   SR=(R*BRACAT)
C   YKTWO= S*((3.0/SR)+1.0)
C THIS SECTION WILL CALCULATE THE STABILITY CONSTANT FOR THE SYSTEM.
C   YKTOT=YKONE*YKTWO
C THIS SECTION WILL CALCULATE THE LOG OF EACH OF THE ABOVEED CONSTANTS.
C SEE REFS. 2, 7 AND 20 FOR SUPPORTIVE INFORMATION.
C   BKONE=ALOG10 (YKONE)
C   BKTWO=ALOG10 (YKTWO)
C   BKTOT=ALOG10 (YKTOT)
C THIS PORTION OF THE PROGRAM USES THE BLOCK-MCINTYRE METHOD OF
C FORMATION CONSTANT DETERMINATION.
C SEE J. AMER. CHEM. SOC., 75, 5667 (1953) FOR MORE DETAILS.
C THE DATA OBTAINED FROM THIS SECTION WAS NOT USED IN THIS INVEST-
C IGATION.
C   XKONE=((BARN0*XJTPI)-(BARNT*XJT))/((XJO*XJTPI)-(XJOPR*XJT))

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