A STUDY OF THE COPPER (II) AND NICKEL (II) COMPLEXES OF SOME 5-SUBSTITUTED TETRAZOLES

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Major professor

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ABSTRACT

A STUDY OF THE COPPER (II) AND NICKEL (II) COMPLEXES OF SOME 5-SUBSTITUTED TETRAZOLES

by Ned A. Daugherty

A study of the copper (II) and nickel (II) complexes of some 5-substituted tetrazoles was made. In all of the cases studied, the tetrazoles coordinated as tetrazolate anions. The maximum number of tetrazoles that can coordinate per metal ion appears to be two.

Three crystalline copper complexes of 5-phenyltetrazole having the formulae $Cu(C_7H_5N_4)_2 \cdot H_2O$, $Cu(C_7H_5N_4)OH$, and $Cu(C_7H_5N_4)Cl$ were prepared and characterized. Several other crystalline copper complexes of 5-aryltetrazoles were also prepared and characterized. In general, the copper complexes are hygroscopic, insoluble in a wide variety of solvents, and sensitive to heat.

The anion of the copper salt used was found to have an unusual effect on the formation of the solid complexes. The anion effect was investigated for the reactions of copper (II) ion with 5-aminotetrazole.

The reported acid-induced decomposition of the copper (II)-5-aminotetrazole complexes was studied. It was found that the extent of decomposition was very slight.

The nickel complexes of several tetrazoles were isolated as solids. The solid nickel complexes were poorly characterized, amorphous solids, containing 1.5-1.9 tetrazoles per nickel. The magnetic susceptibility of the nickel complex of 5-aminotetrazole was measured. The solid is paramagnetic.

A study of the nickel complexes in solution was carried out. There is strong evidence for the existence of ions corresponding to the formula $Ni_2T_3^+$ (T = a tetrazolate ion) in solution.

The visible spectra of the nickel complexes suggest that the complexes are cubic in solution.

A gravimetric method of analysis for tetrazoles was developed and applied to the analysis of the solid complexes.

A STUDY OF THE COPPER (II) AND NICKEL (II) COMPLEXES OF SOME 5-SUBSTITUTED TETRAZOLES

By

rthur
Ned A. Daugherty

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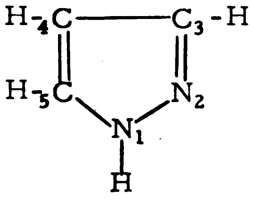
I. HISTORICAL

According to the theory of Sidgwick (1) and Lowry (2), a coordinate bond can be formed between any atom or ion which can act as an electron pair acceptor and any atom or ion which can act as an electron pair donor. Compounds which exhibit chemical bonding of this type are called coordination compounds.

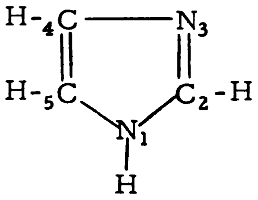
Nearly all of the work in coordination chemistry has been focused on compounds in which a metal ion acts as the electron pair acceptor and is surrounded by one or more ions or molecules, called ligands, which act as electron pair donors. Coordination compounds have been described for a number of metal ions and for a large number of ligands.

Most ligands have in their structure an atom having an unshared pair of electrons which is donated to the metal, forming a coordinate bond. However, there are coordination compounds in which the coordinate bond does not arise from the donation of an unshared electron pair of a specific ligand atom. The phenyl and napthyl complexes of the transition metals, metal-olefin complexes, and the metal-cyclopentadienyls are examples of this type of coordination compound. A molecular orbital treatment has been used to explain the bonding in these compounds.

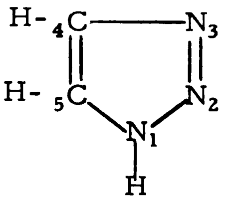
Azoles such as pyrazoles, imidazoles, triazoles and tetrazoles contain nitrogen atoms having unshared electron pairs. Azoles also have an electronic structure quite similar to that of cyclopentadiene. Therefore, one might expect azoles to form either "simple" coordination compounds or π complexes with metal ions. The structural formulas and numbering systems of these azoles are given below:



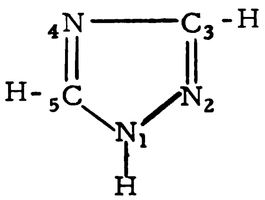
pyrazole



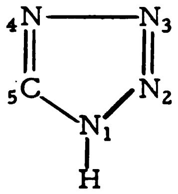
imidazole



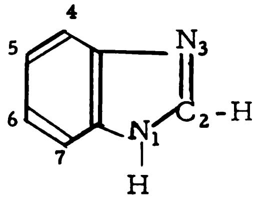
1, 2, 3 triazole



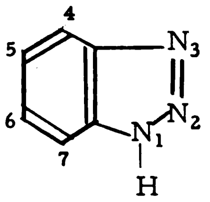
1, 2, 4 triazole



tetrazole



benzimidazole



benzotriazole

Pyrazole is reported to form silver and cobalt salts, but very little has been done to characterize or study these compounds.

On the other hand, much work has been done with the coordination compounds of imidazole and its derivatives. The silver salt was first described by Wyss (3) in 1877. More recently, the discovery that vitamin B_{12} contains cobalt coordinated to the imidazole portion of histidine, has prompted the investigation of various metal-imidazole complexes.

It has been shown that, in acidic solutions, imidazole molecules (as such) coordinate to metal ions. Ions of copper, cadmium, and zinc exhibit a coordination number of four in these complexes while nickel ion is hexa-coordinate. Formation constants for these complexes have been determined (4, 5, 6, 7), and suggest that the site of bonding is the "pyridine nitrogen." The zinc complex is unusually stable.

Solid metal-imidazole complexes have been prepared. The imidazole may be present as a cation, neutral molecule, or anion (8).

From acidic solutions compounds such as $Zn(C_3N_2H_5)_2Cl_4$ and $Zn(C_3N_2H_4)Cl_2$ have been isolated. Complexes of the formula $Zn(C_3N_2H_3)_2$ precipitate from weakly alkaline solutions. From $Zn(C_2H_3O_2)_2$ solutions, adjusted to pH 7, compounds of the type $Zn(C_3N_2H_3)C_2H_3O_2$ have been isolated. The infra-red spectra (9) and crystal structure (10) of some metal-imidazole complexes have been studied.

Several metal-benzimidazole complexes have been described in the literature. Although complexes are known in which benzimidazole occurs as the neutral molecule (11) the majority of the benzimidazole complexes are formed with loss of the hydrogen in the 1-position. The insoluble silver salt, $AgC_7H_5N_2$, first prepared by Bamberger (12) is of sufficiently definite composition that benzimidazole has been used as a quantitative precipitant for silver ion (13). With bivalent metal ions such as Cu^{++}, Ni^{++}, Co^{++}, Cd^{++}, Hg_2^{++}, and Zn^{++} benzimidazole forms compounds having the general formula $M(C_7H_5N_2)_2$ (14, 15).

That replacement of the hydrogen in the 1-position by alkyl or aryl groups decreases the coordinating ability of benzimidazole is shown by the fact that 1-phenylbenzimidazole, 1-benzylbenzimidazole, and 1, 6-dimethylbenzimidazole do not form complexes with Cu^{++}, Cd^{++}, Co^{++}, Zn^{++}, or Ag^{+}. However, 1-phenylbenzimidazole and 1-p-tolyldenzimidazole do complex with Hg_2Cl_2 (16, 17).

With transition metal ions of the fourth period 1, 2, 3 triazoles coordinate as anions (18, 19). However, Wilson and his co-workers have prepared 1, 2, 3 benzotriazole complexes of Pd, Rh, and Os in which the triazole coordinates as both the anion and the neutral molecule (20-23).

Under basic conditions, 1, 2, 4 triazole also coordinates as the anion (24, 25).

Under less basic conditions, 1, 2, 4 triazoles may coordinate as the neutral molecule with Ni^{++}, Co^{++}, or Cu^{++} forming complexes containing one or two triazoles per metal ion (26, 27). Silver, mercury and platinum complexes of 1, 2, 4 triazoles have also been reported (28-32).

Early workers (33, 34, 35) have reported the formation of metal salts of tetrazoles. The silver salts of 5-monosubstituted tetrazoles are well-known and can easily be prepared simply by mixing $AgNO_3$, dissolved in alcohol or water, with an aqueous or alcoholic solution of the tetrazole. The complexes formed precipitate at once and contain Ag^+ and tetrazolate ion in a 1:1 molar ratio (36). These complexes have been used to characterize 5-substituted tetrazoles (37). Other metal derivatives have been prepared (24, 38) and have found a variety of uses.

Silver salts of 5-thioltetrazole are used in photography. Heavy metal salts and salts of azotetrazoles find use as detonators. Finnegan (39) has used cupric salts of 5-substituted-tetrazoles as a means of isolating water soluble tetrazoles during their synthesis.

Earlier workers considered these metal-tetrazole compounds to be simple salts. However, Popov (40) and Brubaker (41) have recently shown that certain of these compounds are coordination compounds. Popov has investigated the silver complexes of metrazole and some of its alkyl derivatives. Solid complexes of the formula $Ag(metrazole)_2NO_3$ were obtained. In acetonitrile solutions the stability constants for these complexes were determined potentiometrically and found to be about 10^2. Polarographic studies in aqueous solutions indicated very slight interaction between metrazole and Cd^{++}, Tl^+ and Co^{++}.

Brubaker has studied the cupric complexes of 5-aminotetrazole and has isolated and characterized two crystalline forms of this complex. Coordination of 5-aminotetrazole occurs with the loss of a proton by the tetrazole. A stability constant for this complex has been calculated from spectrophotometric data and pH measurements and has a value of about 10^{12}. The infra-red spectra of these complexes suggests that the amino group is not coordinated. The anion of the copper salt used determines which of the two complexes is formed, but only trace amounts of the anion is found in the solid complexes. Both complexes are insoluble in a variety of solvents. Although 5-aminotetrazole is relatively stable in the presence of acids, the complexes are reported to decompose with rupture of the tetrazole ring in the presence of dilute acids. Such behavior suggests that metal-tetrazole complexes may have an unusual structure. The nature of the metal-tetrazole bond has not been determined.

The type of complexes formed with other tetrazoles and other metals has not been fully investigated. A study of the effect of varying the substituent on the tetrazole ring on the stability of the complex may be of value in elucidating the structure of the complex. Another area of interest would be the determination of the role played by the metal salt anion during complex formation. Therefore, further investigation of metal-tetrazole complexes would be of scientific interest.

II. EXPERIMENTAL

Materials Used

Reagent grade chemicals were used throughout this investigation with the exception of the chemicals listed below:

sodium azide -- Eastman-Kodak yellow-label
benzonitrile -- Eastman-Kodak white label aniline free
cyanoguanadine -- Eastman-Kodak white-label
anisonitrile -- Eastman-Kodak white-label
acetonitrile -- Matheson Coleman and Bell lot 302467

N, N-dimethylformamide was obtained from Matheson Coleman and Bell. A portion of this solvent was shaken successively with lime and potassium hydroxide. The solvent was decanted and distilled. The fraction boiling at 149-150° was collected. The index of refraction of the distillate was n_D^{28} 1.4259. The index of refraction of the solvent before purification was n_D^{28} 1.4258 (literature value, n_D^{25} 1.4269 (42). The remainder of the solvent was used without further purification.

Several of the tetrazoles used were obtained from Professor R. M. Herbst. The melting points and equivalent weights of the tetrazoles were determined as a check on their purity.

Preparation of Tetrazoles

5-Phenyltetrazole

This compound was prepared according to the method of Finnegan and Henry(39). In a 500 ml. 3-neck flask fitted with stirrer, reflux condenser, and alcohol thermometer, 28.6 g. of NaN_3(0.44 mole), 21.2 g. of NH_4Cl (0.40 mole), 17.0 g. of LiCl (0.40 mole), and 41.2 g. of benzonitrile (0.40 mole) were suspended in 300 ml. of dimethylformamide. The mixture was stirred and heated at 100-110°

for 17 hours. During this time the originally colorless mixture turned orange-brown.

The solvent was removed as completely as possible by distillation under reduced pressure. The residue in the flask was dissolved in 200 ml. of water. The solution was acidified to pH 2 with concentrated HCl resulting in the precipitation of the water insoluble tetrazole. The product was collected on a Büchner funnel and thoroughly washed with ice water. The crude 5-phenyltetrazole was recrystallized from hot water. The product was obtained as long, colorless needles melting at 215° (uncorr.) with decomposition. The melting point given in the literature (39) is 213-215° with decomposition. The yield was 52 g. (89% based on benzonitrite). The equivalent weight determined by titration with standard alkali was 147 (calcd. 146).

5-Cyclohexyltetrazole

The method of synthesis was essentially the same as described for 5-phenyltetrazole except that cyclohexylnitrile was used in place of benzonitrile and the reaction time was increased to 48 hours. After recrystallization from water the product melted at 134-135° (literature (37) value 134-135°). The yield was 85% of the theoretical yield (based on amount of nitrile used). Equivalent weight 151 (calcd. 152).

5-p-Methoxyphenyltetrazole

The procedure described for the preparation of 5-phenyltetrazole was followed using anisonitrile in place of benzonitrile. However, in this case, boiling absolute alcohol was used as the recrystallization solvent. The product separated as white needles melting at 229-230° (literature value (43) 238-239 corr.). Titration by standard alkali gave an equivalent weight of 177 (calcd. 176). The yield was 60% of the theoretical yield.

5-Methyltetrazole

Since 5-methyltetrazole is water soluble, the method of synthesis used for 5-phenyltetrazole was modified. In a 1000 ml. 3-neck flask fitted with stirrer, alcohol thermometer, and reflux condenser were placed 28.6 g. of NaN_3 (0.44 mole), 21.4 g. of NH_4Cl (0.40 mole), 16.4 g. of acetonitrile (0.40 mole) and 350 ml. of dimethylformamide.

The mixture was heated at 110° with stirring for 20 hours. The mixture slowly turned orange-brown. The solvent was removed as completely as possible by distillation under reduced pressure. The solid residue in the reaction flask was dissolved in 100 ml. of water and made alkaline to phenolphthalein with 50% NaOH solution. The solvent was again removed by distillation. The residue was redissolved in 100 ml. of water and acidified to pH 2 with concentrated HCl solution. The solution was transferred to a one liter beaker and evaporated to dryness under an air jet. The dry residue was extracted for 4 hours with absolute alcohol in a Soxhlet extractor. The alcohol solution was evaporated to dryness yielding 13 g. of crude 5-methyltetrazole. The solid remaining in the extractor thimble was extracted for 2 hours with 200 ml. of methanol. The methanol solution gave 2.1 g. of solid after evaporation of the solvent. The crude 5-methyltetrazole fractions were combined and recrystallized from ethylacetate yielding 9.0 g. (27%) of 5-methyltetrazole m.p. 143.5-145° (literature value (37) 148-148.5 corr.). Equivalent weight 84.5 (calcd. 84.1).

5-Aminotetrazole

The synthesis described by Herbst and Mihina (37) was employed. A suspension of 84 g. (1 mole) of dicyandiamide and 117 g. of NaN_3 (1.8 moles) in 200 ml. of water was placed in a 3-neck 100 ml. flask fitted with reflux condenser and dropping funnel. The flask was heated to 65° in a water bath and 150 ml. (1.8 moles) of concentrated HCl was added over a period of 4 hours. The temperature was maintained at 60-65° and the flask was shaken frequently. Before addition of the acid was completed, the mixture turned orange-brown and crystals of the product began to form. The mixture was heated at 65-70° for 6 hours after the last addition of acid. The semi-solid mass was allowed to stand overnight. The flask and contents were thoroughly cooled in an ice bath and the product was collected on a Büchner funnel. After it was washed several times with cold water, the product was recrystallized from water giving 139.4 g. of the monohydrate (74%). The melting point of the monohydrate was 198°. Anhydrous 5-aminotetrazole was obtained by heating the monohydrate for 2 hours at 110°.

Tetrazole

Tetrazole was prepared by the deamination of 5-aminotetrazole according to the procedure of Finnegan and Henry (44). To a slurry of 25.7 g. of 5-aminotetrazole monohydrate (.25 mole) and 36.3 g. of 50% H_3PO_2 (.275 mole) in 125 ml. of water, 17.3 g. of $NaNO_2$ (.25 mole) in 50 ml. of water was added dropwise with vigorous mechanical stirring. The reaction was carried out in a 600 ml. beaker. When the temperature of the reaction mixture reached 35°, the beaker was cooled by an external water bath and the temperature was maintained at 30-35°. After addition of the $NaNO_2$ solution, the reaction mixture was stirred another half hour.

This procedure was repeated with three other 0.25 mole portions of 5-aminotetrazole. The pale yellow reaction mixtures were combined and the pH was adjusted to 3.5 with 50% NaOH. The solvent was removed by distillation under reduced pressure until crystallization began. The mixture was allowed to cool. The resulting solid mass was refluxed 10-15 minutes with 500 ml. of a 50-50 acetone-alcohol mixture. The solvent was decanted and the reflux-decanting procedure was repeated with one 250 ml. portion of solvent, and four 100 ml. portions. The extracts were combined and evaporated to dryness.

The solid was extracted with one 200 ml. portion, one 150 ml. portion, one 100 ml. portion, and two 50 ml. portions of boiling ethylacetate. Any insoluble gum was discarded. The ethylacetate extracts were combined and evaporated to dryness. The residue was dissolved in 50 ml. of hot acetic acid. Cooling to 15° caused crystallization of the product. The crystals were separated by filtration and washed first with cold acetic acid and then with ether. The product was contaminated with acetic acid and was recrystallized twice from absolute alcohol to give 23.4 g. of product which melted at 155-156° (literature value 156-158°). Evaporation of the mother liquor gave 9.2 g. of crude (m.p. 147-153°) tetrazole. The over-all yield was 32.6 g. (47% of the theoretical). Equivalent weight found 70.7 (calc'd. 70.7).

Sodium Salts of Tetrazoles

The sodium salts of the tetrazoles used in this study were prepared by potentiometric titration of aqueous solutions (or suspensions) of the tetrazoles with 0.10 M NaOH. The water insoluble tetrazoles were suspended in water and titrated very slowly. In every case, the tetrazole dissolved before the equivalence point was reached. The aqueous solutions of the sodium salts were evaporated nearly to dryness on the steam bath. The solutions were cooled and the crystallized salt removed by filtration. The salts were then recrystallized twice from either ethanol or isopropyl alcohol and dried at 110° before use.

Analytical Methods

During the course of this investigation several solid metal-tetrazole complexes were prepared and analyzed. Since the solids usually were quite hygroscopic, it was necessary to dry the samples prior to analysis. Although some samples could be oven dried at 110°, other samples decomposed under such treatment. Therefore, the samples were dried over $Mg(ClO_4)_2$ in a vacuum desiccator. Several days were usually needed before constant weight was attained. The dried samples were analyzed for copper, nickel, tetrazole and sulfate according to the following procedures.

Copper

Samples for analysis were weighed by difference from stoppered weighing bottles. The weight of sample used was varied according to the expected copper content, but 20 to 40 mg. usually were sufficient for analysis.

The complexes were decomposed by heating the solids with five ml. of concentrated nitric acid until the samples dissolved and the color of the solutions turned pale blue. Most of the nitric acid was fumed away by additional heating. The solutions were cooled and diluted with a small amount of water. The sample solutions were then quantitatively transferred to 25 ml. volumetric flasks and 10 ml. of a buffer which was 5.0 M with respect to both NH_3 and NH_4Cl was added to each (41). The dark blue color of the copper ammine complex formed at once. The samples were diluted to volume with distilled water and their absorbancies measured at 620 mμ using a Beckman model DU spectrophotometer.

Each time that a copper analysis was made, two or more knowns were also run by taking aliquots of a standard $Cu(NO_3)_2$ solution, prepared by dissolving a weighed amount of copper oxide in a minimum of nitric acid, and treating them in the same manner as the unknowns.

The copper content of the unknowns was determined either by preparing a calibration plot of absorbancy *versus* concentration from the known samples and picking concentrations of the unknowns from this plot or, more frequently, by calculating copper content using the absorbancies of the knowns and assuming the Beer-Lambert law to be valid over the concentration range. A plot of absorbancy *versus* concentration for a series of knowns was linear over a concentration range of 1×10^{-4} g. of Cu/ml. to 10×10^{-4} g. of Cu/ml. The concentration range for unknowns usually fell in the interval of 1×10^{-4} g. of Cu/ml. to 3×10^{-4} g. of Cu/ml.

Certain of the copper complexes, particularly complexes of substituted 5-phenyl tetrazoles, did not dissolve in nitric acid to give blue solutions, but instead gave greenish-yellow solutions. When these greenish-yellow solutions were poured into the NH_3-NH_4Cl buffer, the usual blue color did not develop. These complexes were analyzed for copper by weighing samples directly into 25 ml. volumetric flasks, adding 10 ml. of buffer, and allowing the stoppered flasks to stand overnight. The samples dissolved to give the deep blue color of the copper ammine complex. The samples were then diluted to volume and the amount of copper determined in the usual manner. Samples that could be decomposed with nitric acid were also analyzed by this method giving results in good agreement with those obtained by decomposing the samples in nitric acid.

The accuracy of the method, estimated from the results of duplicate analyses, was about 3%.

Nickel

A spectrophotometric method for nickel, similar to the method for copper, was developed. The method used slightly larger samples

(40-100 mg.) and the measurements were made at 575 mμ. The method was used with some success for nickel complexes of 5-aminotetrazole. However, with all other nickel-tetrazole complexes, treatment of the solids with concentrated nitric acid, concentrated nitric-sulfuric acid mixture, and aqua reqia resulted in yellow solutions that were not affected by the addition of NH_3-NH_4Cl buffer. Moreover, the nickel complexes were insoluble in both the NH_3-NH_4Cl buffer and concentrated aqueous ammonia.

A successful method for the determination of nickel in solid nickel complexes involved dissolution of the solid in ammoniacal cyanide solutions and titration of the excess cyanide with standard silver nitrate solution. The details of the procedure are as follows:

Samples for analysis (20-70 mg.) were weighed by difference from stoppered weighing bottles into glass stoppered 125 ml. Erlenmeyer flasks. To each sample flask was added 20 ml. of freshly prepared 0.1 M KCN solution, 5 ml. of concentrated aqueous ammonia, and 1 ml. of a KI solution containing 0.1 g. of KI/ml. The walls of the flasks were rinsed down with distilled water and the flasks were stoppered and allowed to stand overnight. Two or more blanks containing 20 ml. of cyanide solution, 5 ml. of ammonia, and 1 ml. of KI solution were also prepared.

After standing overnight, the complexes had dissolved to give pale yellow solutions. The cyanide solution was standardized by titrating the blanks with 0.100 M Ag NO_3 solution until the appearance of a permanent yellow opalescence. The silver nitrate solution was freshly prepared by weighing dried $AgNO_3$, dissolving the $AgNO_3$ in distilled water, and diluting to a known volume. The excess cyanide in the sample solutions was titrated with $AgNO_3$ solution delivered from a 10 ml. buret.

The amount of nickel in the sample was calculated from the difference in the volume of silver solution needed for the cyanide blanks and the amount needed for the sample solution.

Titrations of known nickel samples in the presence of tetrazoles resulted in an error of less than 2 parts per 100.

Sulfate

Some of the copper complexes of water insoluble tetrazoles contained more than trace amounts of sulfate ion. The sulfate present was determined gravimetrically by precipitation and weighing of the sulfate as $BaSO_4$.

Analytical samples were weighed out in the usual manner by use of a Mettler semi-micro balance. Samples weighing 50 to 100 mg. were used. The samples were rinsed from the spatula into 50 ml. beakers with a stream of 95% ethanol. About 5 ml. of ethanol were used. Then 5 ml. of 1.0 $\underline{M}$ NaOH was added to each sample, the beaker was covered with a watch glass, and was placed on the steam bath. After 15 or 20 minutes, the sample had decomposed leaving a solution containing the sulfate and a black solid, copper oxide.

The samples were filtered through Whatman #42 paper and the residue was thoroughly washed several times with distilled water. The filtrate and washings were made strongly acidic with concentrated HCl, causing the water insoluble tetrazole to precipitate. The samples were again filtered and the residue thoroughly washed. The pH of the filtrate was adjusted to about 3 with 1.0 $\underline{M}$ NaOH solution.

The amount of 0.10 $\underline{M}$ $BaCl_2$ needed to precipitate the sulfate in the sample was calculated and this amount plus a 20% excess of 0.10 $\underline{M}$ $BaCl_2$ was added. The precipitate was digested overnight on the steam bath. The samples were cooled and tested for completeness of precipitation by the addition of a few drops of the $BaCl_2$ solution.

The samples were filtered through Whatman #42 paper and the precipitate was washed until the washings were chloride free. The filter paper was carefully burned away and the precipitate ignited to constant weight in platinum crucibles. The per cent sulfate in the sample was calculated from the weight of $BaSO_4$ thus obtained.

Tetrazole

Although the silver salts of tetrazoles are of sufficiently definite composition to be of use in characterizing 5-substituted tetrazoles, silver ion has not been previously reported as a quantitative precipitant for tetrazolate ion. However, experiments using weighed amounts of a variety of 5-substituted tetrazoles showed that at pH 6-6.5 silver ion quantitatively precipitates tetrazolate ion. Comparison of the weight of tetrazole used and the weight of tetrazole calculated from the silver salt obtained showed that the maximum error for the method was about 1%. From solutions more acidic than pH 6 the precipitation was not quantitative. A large excess of silver nitrate must be avoided or some occlusion may occur. The silver salts of tetrazoles are about as light sensitive as AgCl.

Analytical samples (10-50 mg.) were weighed out in the usual manner using a Mettler semi-micro balance. The samples were rinsed from the spatula into 50 ml. beakers using about 5 ml. of 95% ethanol. Alcohol wets the solids better than water and hastens decomposition of the complex. The complexes were decomposed by adding 5 ml. of 1.0 M NaOH and heating the samples on the steam-bath 10-15 minutes. This treatment resulted in separation of the metal as the oxide or hydroxide leaving the tetrazolate ion in solution. The samples were filtered through Whatman #42 paper and the residues were repeatedly washed with small portions of distilled water. The filtrate and washings were acidified to pH 6-6.5 with dilute nitric acid. The amount of 0.02 M $AgNO_3$ necessary to precipitate the maximum amount of tetrazole in the samples was calculated and this amount plus a 10% excess of 0.02 M $AgNO_3$ was slowly added to the sample solutions. The water insoluble silver salts formed at once.

The samples were digested one hour on the steam bath, cooled in an ice bath, tested for completeness of precipitation, and filtered through tared, sintered-glass crucibles. The precipitates were dried to constant weight at 90°. The amount of tetrazolate in the samples was calculated from the weights of the silver salts.

The method appeared to work well for copper complexes, but the results for nickel complexes were less satisfactory. This may have been due to increased difficulty in washing $Ni(OH)_2$ free of tetrazolate as compared to CuO.

Carbon, Hydrogen, Nitrogen

Carbon, hydrogen, and nitrogen microanalyses were performed by commercial analytical houses. Most of the samples exploded on analysis and with few exceptions, the results were unsatisfactory.

Magnetic Susceptibility Measurements

The magnetic susceptibilities of the copper and nickel complexes of 5-aminotetrazole were determined by the Gouy method. The Gouy technique involves measuring the apparent gain or loss in the weight of a sample when it is placed in a magnetic field. The sample is contained in a Pyrex susceptibility tube and is suspended, by means of a gold chain attached to the beam of an analytical balance, between the pole faces of an electromagnet. The apparent change in weight of the sample is observed for several values of a magnetic field produced by passing current through an electromagnet. The apparatus is calibrated by using samples of known magnetic susceptibility. The volume susceptibility, denoted by K, of the sample can then be calculated from the expression

$$K - K_{air} = \frac{\Delta\omega}{\Delta\omega_s} \; (K_s - K_{air})$$

$\Delta\omega$ = change in weight of unknown sample

$\Delta\omega_s$ = volume susceptibility of known sample

Gram susceptibility, X, can be obtained from the equation

$$X = K/d$$

where d is the density of the sample.

The molar susceptibility, X_M, can be calculated by multiplying the molecular weight, M, of the sample by X.

$$X_M = MX$$

The apparatus and the techniques for its operation have been described in detail elsewhere (45).

The susceptibility tube used in this study was constructed from 3.0 mm. (O.D.) Pyrex tubing. The tube was of the double or compensated type of tube described by Vander Vennen (45). The distance from the reference mark to the septum of this tube was 6.7 cm. The volume of the tube was determined by measuring the weight of powdered ferrous ammonium sulfate hexahydrate needed to fill the tube to the reference mark. Five determinations were made. The weight of salt needed to fill the tube in any single determination did not deviate more than 2% from the average weight of salt required. The volume of the tube was calculated by dividing the weight of salt needed by the density of the salt. The volume of the tube was 0.0849 ml.

The change in weight of the empty susceptibility tube due to the presence of the magnetic field must be measured and, if not negligible, it must be applied as a correction to the $\Delta\omega$ values for the samples. When the empty susceptibility tube was calibrated, the presence of the magnetic field caused an apparent gain in weight which was much larger than expected. Repeated and careful cleansing of the tube did not alter the experimental values obtained. It was concluded that some impurity in the glass itself was responsible for this anomalous behavior.

Powdered ferrous ammonium sulfate hexahydrate was employed as a calibration standard. Care was taken to obtain a uniform packing of the tube.

Dried, powdered samples of the complexes were also carefully packed into the tube and the apparent change in weight was observed for different amperages of current flowing through the electromagnet.

Calibration data as well as susceptibility data for the complexes are presented in Table 1.

Table 1. Magnetic Susceptibility Data. All Measurements at 25°C.

Sample	Empty Tube	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	$Cu-CN_5H_3$ Complex	$Ni-CN_5H_3$ Complex
amperage	$\Delta\omega$(mg.) (a)	$\Delta\omega$(mg.) (b)	$\Delta\omega$(mg.) (a)	$\Delta\omega$(mg.) (a)
12	1.9	49.2	10.1	26.6
10	1.4	36.8	8.4	20.2
8	1.0	24.3	5.6	13.7
6	0.6	13.6	3.3	7.7
4	0.3	-	-	-

(a) Average values from 3 runs.
(b) Average values from 5 runs.

Calculation of the Magnetic Susceptibility of the Copper Complex of 5-Aminotetrazole

The data in Table 1 were used to calculate the magnetic susceptibility for the copper complex, $Cu(CN_5H_2)_2 \frac{1}{2} H_2O$.

The value of the magnetic susceptibility used for the calibration standard was obtained from Selwood (46).

The volume susceptibility for the copper complex was calculated for each field strength. The average value obtained was 6.17×10^{-6}. The weight of copper complex needed to fill the tube was 0.17406 g.

The density of the copper complex was calculated to be 2.05 g./cm^3 by dividing the sample weight by .0849, the volume of the tube.

The gram susceptibility, X, and the molar susceptibility X_M were calculated and were 3.01×10^{-6} and 7.24×10^{-4} respectively.

If one neglects any correction for diamagnetism, the magnetic moment expressed in Bohr magnetons may be calculated from the relationship (46):

$$X_M = \frac{N \beta^2 \mu_\beta^2}{3kT}$$

N = Avogadro's number

β = $.917 \times 10^{-20}$ erg-oersted^{-1}

μ_β = magnetic moment in Bohr magnetons

k = Boltzmann's constant

T = absolute temperature

The value of μ_β for the dark green, copper complex of 5-aminotetrazole is 2.02. The magnetic moment of this complex indicates the presence of one unpaired electron per copper atom.

Calculation of the Magnetic Susceptibility of the Nickel Complex of 5-Aminotetrazole

The susceptibility for the nickel complex was calculated in the same manner as described for the copper complex. The values obtained were:

K = 17.0×10^{-6}

X = 11.9×10^{-6}

X_M = 26.9×10^{-4} assuming the complex to be $Ni(CN_5H_2)_2$

μ_β = 3.9

The values obtained for the nickel complex are not very reliable for two reasons: (1) the sample packs rather poorly and its calculated density, 1.42 g./cm^3, may be too low, (2) the exact composition of the solid is not known and therefore the molecular weight is also unknown. However, there seems to be little doubt that the complex is paramagnetic.

Copper (II) - 5-Aminotetrazole Complexes

Preparation of Solid Complexes

The light green complex described by Brubaker (41) was prepared by pouring a solution of 10.3 g. (0.10 mole) of 5-aminotetrazole monohydrate, $CN_5H_3 \cdot H_2O$, dissolved in 400 ml. of water into a solution of 12.5 g. of copper sulfate pentahydrate dissolved in 200 ml. of water. The light green solid formed at once. After it had been standing three hours, the solid was separated by centrifugation and the gelatinous solid was washed six times with small portions of distilled water. Although the washings gave a positive test for sulfate, additional washings were not carried out because excessive washing has been reported to convert the light green complex to a different crystalline form (41).

The solid was dried over magnesium perchlorate in an evacuated desiccator. On the basis of copper, nitrogen, and sulfate analyses, the solid was assumed to be a mixture of bis(5-aminotetrazolato)copper (II) hemi-hydrate, $Cu(CN_5H_2)_2\frac{1}{2} H_2O$, and copper sulfate. Calculated for $Cu(CN_5H_2)\frac{1}{2} H_2O$ plus 21% $CuSO_4$: Cu, 29.3%; N, 46.0%; $SO_4^=$, 12.6%. Found: Cu, 28.8%; N, 46.0%; $SO_4^=$, 12.6%.

The dark green crystalline form of the complex was prepared from solutions of copper perchlorate and $CN_5H_3 \cdot H_2O$. Copper perchlorate solution was prepared by dissolving 3.97 g. (0.05 mole) of copper oxide in the minimum amount of perchloric acid and dilution of the solution to 500 ml. A solution of 10.3 g. (0.10 mole) of $CN_5H_3 \cdot H_2O$ dissolved in one liter of water was poured into the copper perchlorate solution resulting in a clear, deep green solution. The flask containing the solution was stoppered and allowed to stand.

After three days dark blue crystals began to precipitate from the green solution. After two weeks, the supernatant solution was pale blue. The blue crystals were then collected by filtration and washed thoroughly with distilled water. After having been dried over magnesium perchlorate, the crystals were dark green and gave an X-ray powder pattern identical with an authentic sample of dark green $Cu(CN_5H_2)_2 \cdot \frac{1}{2} H_2O$ (47). Calculated for $Cu(CN_5H_2) \cdot \frac{1}{2} H_2O$: Cu, 26.4%. Found: Cu, 26.3%.

Reaction of the Solids with Dilute Acids

When the light green solid is treated with dilute (3.0 M) sulfuric acid, the sample dissolves and the odor of hydrogen cyanide is easily detected. The dark green complex also dissolves in dilute sulfuric acid, but without evolution of hydrogen cyanide. It has been reported (41) that neutralization of the acid solution by alkali does not reprecipitate the complex. Hydrogen cyanide was the only decomposition product identified.

Qualitative tests for carbon dioxide, hydrazoic acid, hydrogen cyanide, and ammonia in the decomposition products were carried out as follows: Samples of both complexes weighing 50-80 mg. were placed in 60 ml. serum bottles and the bottles were tightly stoppered with serum caps. Three ml. of 3.0 M sulfuric acid was introduced into each bottle by means of a hypodermic syringe. The samples were allowed to stand 90 minutes. The samples completely dissolved during this time.

Samples were tested for the presence of hydrazoic acid by inserting the needle of a syringe filled with 0.10 M ferric chloride and depressing the plunger until a drop of ferric chloride solution formed on the needle tip. In the presence of hydrazoic acid the drop of ferric chloride turns deep red in color. In a similar manner, other samples were tested for carbon dioxide and hydrogen cyanide using saturated barium chloride and 0.10 M silver nitrate respectively as test reagents. Known samples were prepared using 10 mg. each of sodium carbonate, sodium azide and sodium cyanide. With the exception of the test for cyanide from the light green complex, all of the tests described for the complexes were negative. All tests with the "knowns" were positive.

The decomposition products were tested for ammonia by treating 50-70 mg. of each complex with 3 ml. of 3.0 M sulfuric acid in a stoppered test tube. After the samples had dissolved ($\sim$1 hr), 7.5 ml. of 6 M sodium hydroxide were added to each sample and the tubes were lightly stoppered. After standing overnight, the stoppers were removed and the tubes warmed in a water bath. No odor of ammonia could be detected from either sample.

Very small amounts of $Cu(NH_3)_4SO_4$ when treated with 6 M sodium hydroxide evolve ammonia in easily detectable quantities.

The amount of elemental nitrogen in the acid decomposition products of the light and dark green complexes was determined by running the reaction in a carbon dioxide atmosphere and sweeping any gaseous products through 50% potassium hydroxide solution into a semi-micro nitrometer. The apparatus used is pictured in Figure 1.

A typical run is described. The sample (30-70 mg.) was weighed into the bottom section of the reaction vessel. The apparatus was assembled and with the 3-way stopcock C open to the atmosphere was swept overnight with carbon dioxide from the generator. After sweeping was complete, the stopcock at the top of the nitrometer was opened and the potassium hydroxide leveling bulb placed in the upper ring at a convenient height. After five minutes, the stopcock was closed and the level of the potassium hydroxide solution was recorded. The leveling bulb was then placed in the lower ring stand. Stopcock C was

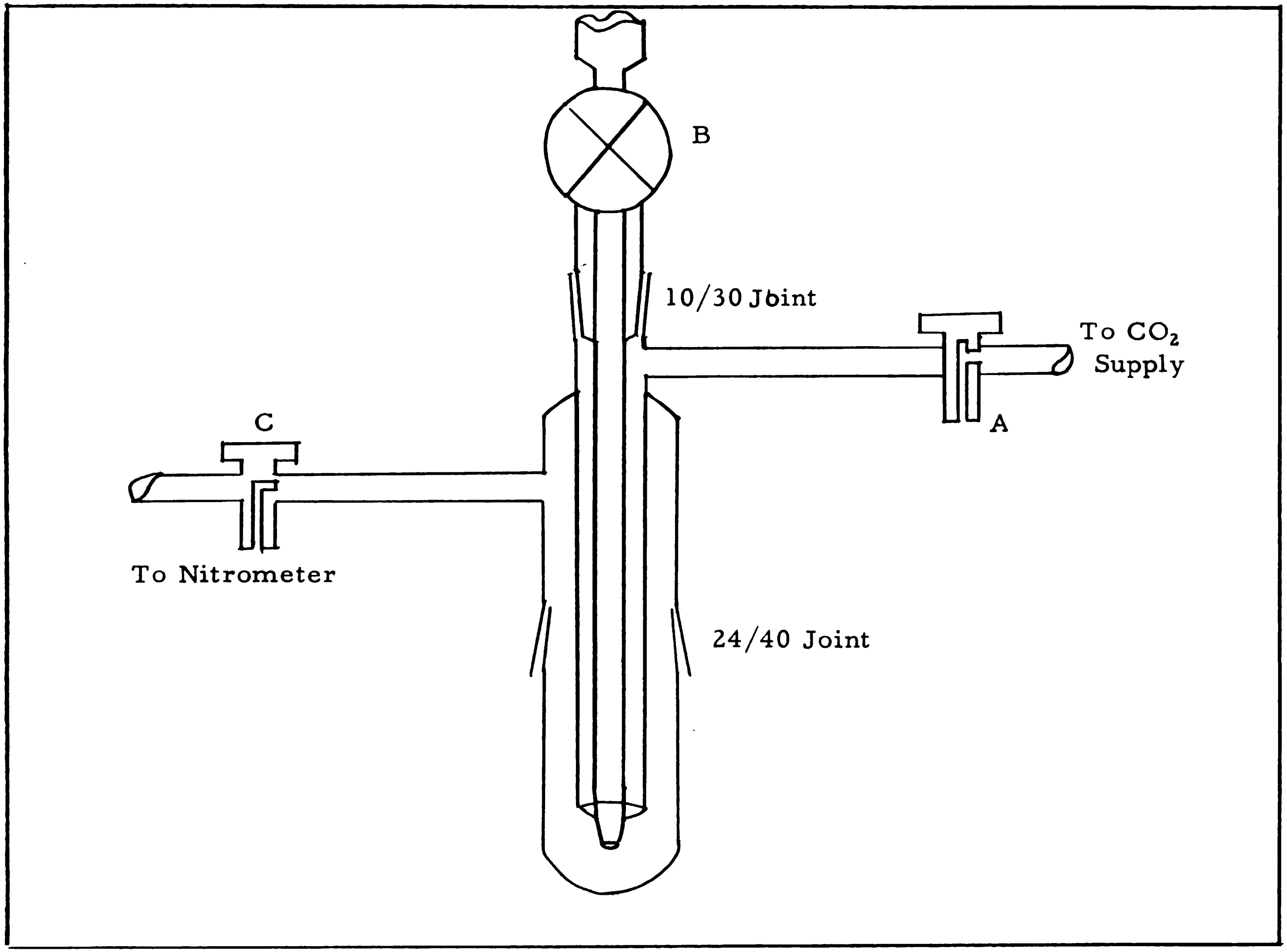


Figure 1. Reaction Vessel for Nitrogen Determinations. Not Drawn to Scale.

then opened to the nitrometer until a bubble rate of two bubbles per second was obtained. Three-way stopcock A was then opened to the atmosphere and two ml. of 3 M sulfuric acid was admitted through stopcock B by applying a slight pressure on the surface of the acid by means of a piece of rubber rubing attached to a gas jet. Upon addition of the acid the complex began to dissolve.

When the complex had completely dissolved, stopcock A was opened to the reaction vessel and the system swept with carbon dioxide for 90 minutes (always sufficient time to produce micro-bubbles) at a rate of two bubbles per second. Then stopcock C was opened to the atmosphere and the leveling bulb raised so that the liquid levels in the nitrometer and bulb were equal. The volume of gas evolved and the temperature and barometric pressure were recorded. The weight of nitrogen evolved was calculated. The results of the runs are given in Table 2.

Samples (150 mg.) of both complexes were weighed out and treated with 5 ml. of 3.0 M sulfuric acid. The complexes immediately began to dissolve. The samples were allowed to stand overnight and then were diluted with 25 ml. of distilled water. A 10 ml. aliquot of each was taken and slowly titrated potentiometrically with 0.10 M sodium hydroxide. In both cases, at pH of 3 the solution turns green, and further addition of base results in the formation of a green precipitate. After filtering and drying both of the precipitates gave an X-ray powder pattern characteristic of the light green complex.

Other aliquots of the sample solutions when treated with excess alkali gave pale blue solutions.

The results given in Table 2 along with the fact that detectable amounts of carbon dioxide, ammonia, or hydrozoic acid are not found in the decomposition products and the fact that considerable quantities of the complex can be obtained upon neutralization of the acid solution, suggest that the amount of decomposition under the conditions described is slight.

Table 2. Amounts of Nitrogen Collected from Acid Decomposition of Copper-5-Aminotetrazole Complexes.

Sample	Sample Wt. (grams)	ml. N_2 Collected	Temperature °C	Pressure mm. Hg	g. N_2 Collected x 10^6	Per cent of Total N_2 From Sample
blank		0.00				
blank		0.00				
blank		0.01				
blank		0.01				
blank		-0.02				
blank		0.00				
lt. green	0.0540	0.00	26.0	744.0	0.00	0.00
lt. green	0.0361	0.08	26.0	747.0	90.2	0.54
lt. green	0.0268	0.10	26.0	736.5	113.0	0.92
lt. green	0.0750	0.05	27.0	741.0	54.0	0.16
dk. green	0.1335	0.03	26.5	738.5	33.2	0.04
dk. green	0.0707	0.04	26.0	734.1	44.1	0.11

The Effect of Anions on the Formation of Solid Complexes

When solutions of cupric perchlorate or cupric nitrate are mixed with solutions of 5-aminotetrazole clear, dark green solutions are produced from which $Cu(CN_5H_2)_2 \cdot \frac{1}{2}H_2O$ slowly crystallizes as a dark blue solid. However, if cupric sulfate or cupric chloride is used in place of the nitrate or perchlorate, a light green solid separates immediately after the solutions are mixed. However, these solids contain only small amounts of chloride or sulfate as the occluded copper salt.

Moreover, small amounts of sulfate or chloride added to solutions of cupric nitrate and 5-aminotetrazole cause the solutions to become turbid.

Qualitative Aspects of the Anion Effect

In order to determine which anions cause formation of solids (or turbidity) when present in solutions containing cupric ion and 5-aminotetrazole, some qualitative tests were made. For this study 0.10 M stock solutions of cupric nitrate and 5-aminotetrazole were prepared. The 5-aminotetrazole was recrystallized twice from deionized distilled water prior to use. The solvent used for all anion effect studies was deionized distilled water. In addition to the stock copper nitrate and 5-aminotetrazole solutions, 0.10 M stock solutions of sodium sulfate, sodium chloride, potassium bromide, sodium bicarbonate, sodium acetate, sodium phosphate and sodium nitrite were also prepared.

When 2 ml. of stock copper nitrate solution and 4 ml. of stock 5-aminotetrazole solution were mixed and diluted to 10 ml., no turbidity appeared even after 24 hours.

A series of samples was prepared by pipetting 2 ml. of copper nitrate solution and 4 ml. of 5-aminotetrazole solution into 10 ml.

volumetric flasks. The samples were diluted nearly to volume and 0.10 ml. of one of the test solutions was added to each flask. The samples were diluted to 10 ml. and the flasks were then stoppered and allowed to stand 24 hours. The results are summarized in Table 3.

Table 3. Qualitative Anion Effects at Low Concentrations of Anions.

Salt Added	Observation
Na_2SO_4	Turbidity on mixing
NaCl	Becomes very slightly turbid after 3-4 hours
KBr	Remains clear for 24 hours
$NaHCO_3$	Remains clear for 24 hours
$NaC_2H_3O_2$	Remains clear for 24 hours
$NaNO_2$	Becomes slightly turbid after 3-4 hours, definitely turbid after 6-8 hours
Na_3PO_4	Remains clear for 24 hours

Another series of samples was prepared using the same amount of copper and 5-aminotetrazole solutions. The samples were prepared in the same manner as previously described except that larger amounts of the anion test solutions were used. The results are given in Table 4.

From the data in Table 3, one can conclude that, at a given concentration, $SO_4^=$ is more effective, with respect to producing turbidity in copper nitrate-5-aminotetrazole solutions, than any of the other anions tested.

When NaOH is added to a solution of copper nitrate and 5-aminotetrazole a green solid precipitates which suggests that the anion effect may be an acid-base effect. However, any explanation based on the basicity of the anion involved fails to explain the poor effectiveness of phosphate ion. Moreover, the low effectiveness of the highly charged

Table 4. Qualitative Anion Effects at High Anion Concentrations.

Salt Added	Ml. of Soln. Used	Result
NaCl	2	Definitely turbid after 24 hours
KBr	2	Remains clear for 24 hours
$NaHCO_3$	2	Dark green precipitate forms on adding salt, ppt. dissolves on being shaken and soln. remains clear for 24 hours
$NaC_2H_3O_2$	2	Same as for $NaHCO_3$
Na_3PO_4	1.5	Dark green ppt. forms on adding salt, ppt. does not dissolve on being shaken or standing

phosphate ion suggests that the anion effect is not entirely one of coagulating colloidal particles.

The rather high degree of specificity observed suggests that the anion may be chemically involved in some intermediate complex.

The Effect of Added Sulfate on the Weight of Precipitate Formed

Relatively small amounts of sulfate present in solutions of copper nitrate and 5-aminotetrazole result in the rapid formation of weighable amounts of solids. For this and subsequent work on anion effects a stock solution of cupric nitrate approximately 0.10 M was prepared by dissolving a weighed amount of $Cu(NO_3)_2 \cdot 3H_2O$ and diluting it to the volume desired. This stock solution was standardized spectrophotometrically and was found to be 0.104 M. Standard 5-aminotetrazole solutions were prepared by weighing the $CN_5H_3 \cdot H_2O$ and dissolving it in sufficient solvent to give the desired volume. Standard sodium sulfate solutions were prepared by weighing and dissolving the salt, dried two hours at 110° prior to use.

Two types of samples were prepared. One type was prepared by pipetting, into a 25 ml. volumetric flask, the following solutions in the order given: an aliquot of copper nitrate solution, an aliquot of 5-aminotetrazole solution, an aliquot of sodium sulfate solution. The samples were rapidly diluted to volume. The second series of samples was prepared in a similar manner except that the order of mixing of the reagents was: copper nitrate, sodium sulfate, 5-aminotetrazole solution.

The samples became cloudy as soon as they were mixed and solid began separating within 4 or 5 hours. The samples were allowed to stand 24 hours and then were filtered through tared fine-porosity, sintered, glass crucibles. The sample flasks were rinsed with 5 ml. of water and the solids were rinsed with another 5 ml. portion of water. The samples were sucked as dry as possible and were dried for one hour in an oven at 110° (several checks revealed this was long enough to achieve constant weight). Addition of sulfate after the 5-aminotetrazole had been added always resulted in the formation of slightly more precipitate than the addition of sulfate before addition of the tetrazole. The results are given in Table 5.

Table 5. Weight of Solid Obtained as a Function of Sulfate Concentration.

Ml. 0.104 M $Cu(NO_3)_2$	Ml. 0.104 M CN_5H_3	Millimoles $SO_4^=$ Added	$SO_4^=$ Added Before or After CN_5H_3	Wt. ppt. Mg.
3	10	0.04	before	34.4
3	10	0.04	after	35.1
3	10	0.06	before	35.1
3	10	0.06	after	36.0
3	10	0.10	before	33.4
3	10	0.10	after	36.7
3	5	0.04	before	18.4
3	5	0.04	after	20.4
3	5	0.06	before	19.6

The Effect of Sulfate at Lower Sulfate Concentrations

The effect of added sulfate at low sulfate concentrations was evaluated by measuring the turbidity of solutions of copper nitrate to which sulfate had been added either prior to or after addition of 5-aminotetrazole solution. A Beckman model DU spectrophotometer was used to make the turbidity measurements.

The samples were prepared as described for higher sulfate concentrations. The samples were allowed to stand 24 hours and their absorbancies at 550 mμ were measured using one cm. silica cells. The reference cell was filled with a blank containing copper nitrate and tetrazole but no added sulfate. Any absorbancy of the sample as compared to the reference solution was assumed to be due to turbidity of the sample. Six series of samples were prepared using varying amounts of copper ion, 5-aminotetrazole, and sulfate. The results are given in Tables 6, 7, 8 and Figures 2, 3 and 4.

Table 6. Turbidity of $Cu(NO_3)_2 \cdot CN_5H_3$ Solutions as a Function of Sulfate Concentration.
$[Cu^{++}] = 1.65 \times 10^{-2}$ $\underline{M}$ $[CN_5H_3] = 4.12 \times 10^{-2}$ $\underline{M}$

Ml. of $4 \times 10^{-3}\underline{M}$ Na_2SO_4 Added per 25 ml.	Absorbancy of Samples 550 mμ $SO_4^=$ Added Before CN_5H_3	 $SO_4^=$ Added After CN_5H_3
0.5	0.006	0.003
1.0	0.005	0.005
1.5	0.007	0.008
2.0	0.014	0.012
2.5	0.022	0.034
3.0	0.054	0.086
3.5	0.112	0.105
4.0	0.139	0.114

Table 7. Turbidity of $Cu(NO_3)_2 \cdot CN_5H_3$ Solutions as a Function of Sulfate Concentration.
$[Cu^{++}] = 1.24 \times 10^{-2}$ M $[CN_5H_3] = 4.12 \times 10^{-2}$ M

Ml. of 4×10^{-3} M Na_2SO_4 Added per 25 ml.	Absorbancy of Samples 550 mμ	
	SO_4 Added Before CN_5H_3	SO_4 Added After CN_5H_3
0.5	0.003	0.002
1.0	0.003	0.004
2.0	0.011	0.011
2.5	0.022	0.030
3.0	0.059	0.083
3.5	0.117	0.104
4.0	0.149	0.113

Table 8. Turbidity of $Cu(NO_3)_2 \cdot CN_5H_3$ Solutions as a Function of Sulfate Concentration
$[Cu^{++}] = 1.65 \times 10^{-2}$ M $[CN_5H_3] = 2.06 \times 10^{-2}$ M

Ml. of 4×10^{-3} M Na_2SO_4 Added per 25 ml.	Absorbancy of Samples 550 mμ	
	$SO_4^=$ Added Before CN_5H_3	$SO_4^=$ Added After CN_5H_3
0.5	0.002	0.003
1.0	0.004	0.005
2.0	0.012	0.018
2.5	0.047	0.055
3.0	0.083	0.065

It is rather apparent from the data in Tables 6, 7 and 8 that small amounts of $SO_4^=$ added to copper nitrate solutions before or after the addition of 5-aminotetrazole produce turbidity in the solutions. For example, in Table 6, a solution containing 3.09×10^{-1} millimoles of copper ion and 10.3×10^{-1} millimoles of 5-amino-tetrazole definitely becomes turbid if as little as 8.0×10^{-6} moles of $SO_4^=$ is added as sodium sulfate.

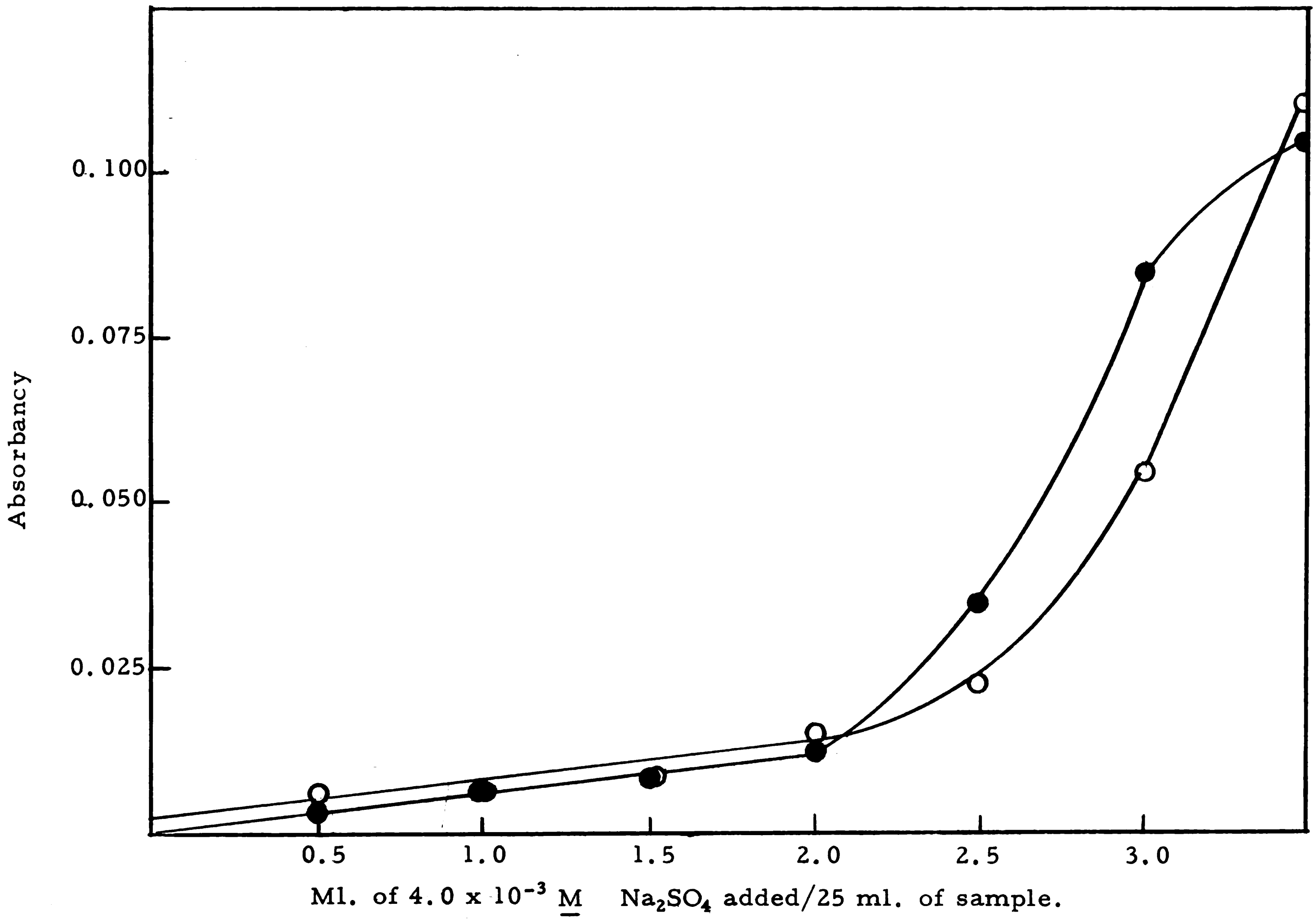


Figure 2. Turbidity versus sulfate concentration
$[Cu^{++}] = 1.65 \times 10^{-2}$ M, $[CN_5H_3] = 4.12 \times 10^{-2}$ M

○ = $SO_4^{=}$ added before CN_5H_3
● = $SO_4^{=}$ added after CN_5H_3

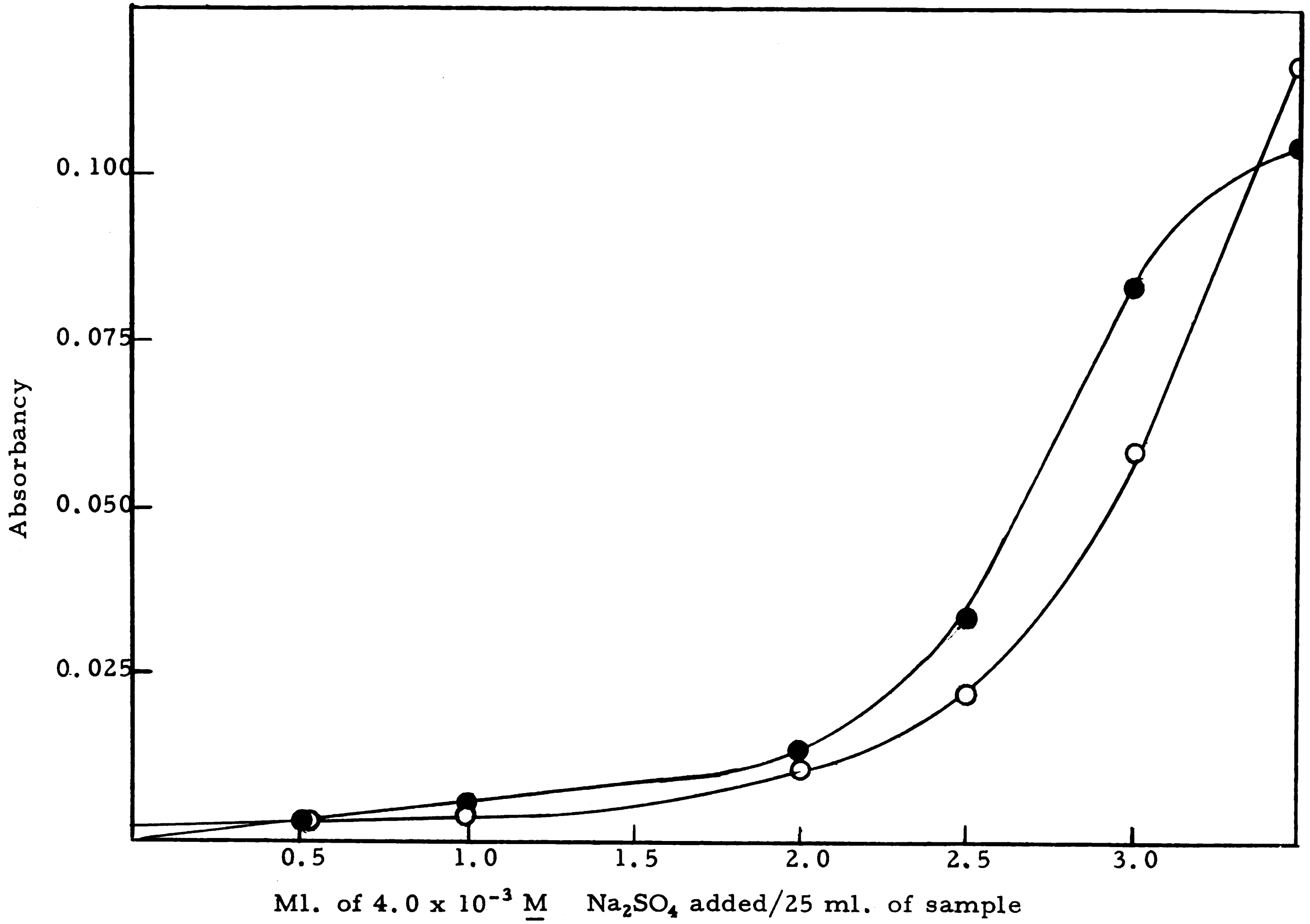


Figure 3. Turbidity versus Sulfate Concentration
$[Cu^{++}] = 1.24 \times 10^{-2}$ M $[CN_5H_3] = 4.12 \times 10^{-2}$ M

○ = $SO_4^=$ added before CN_5H_3
● = $SO_4^=$ added after CN_5H_3

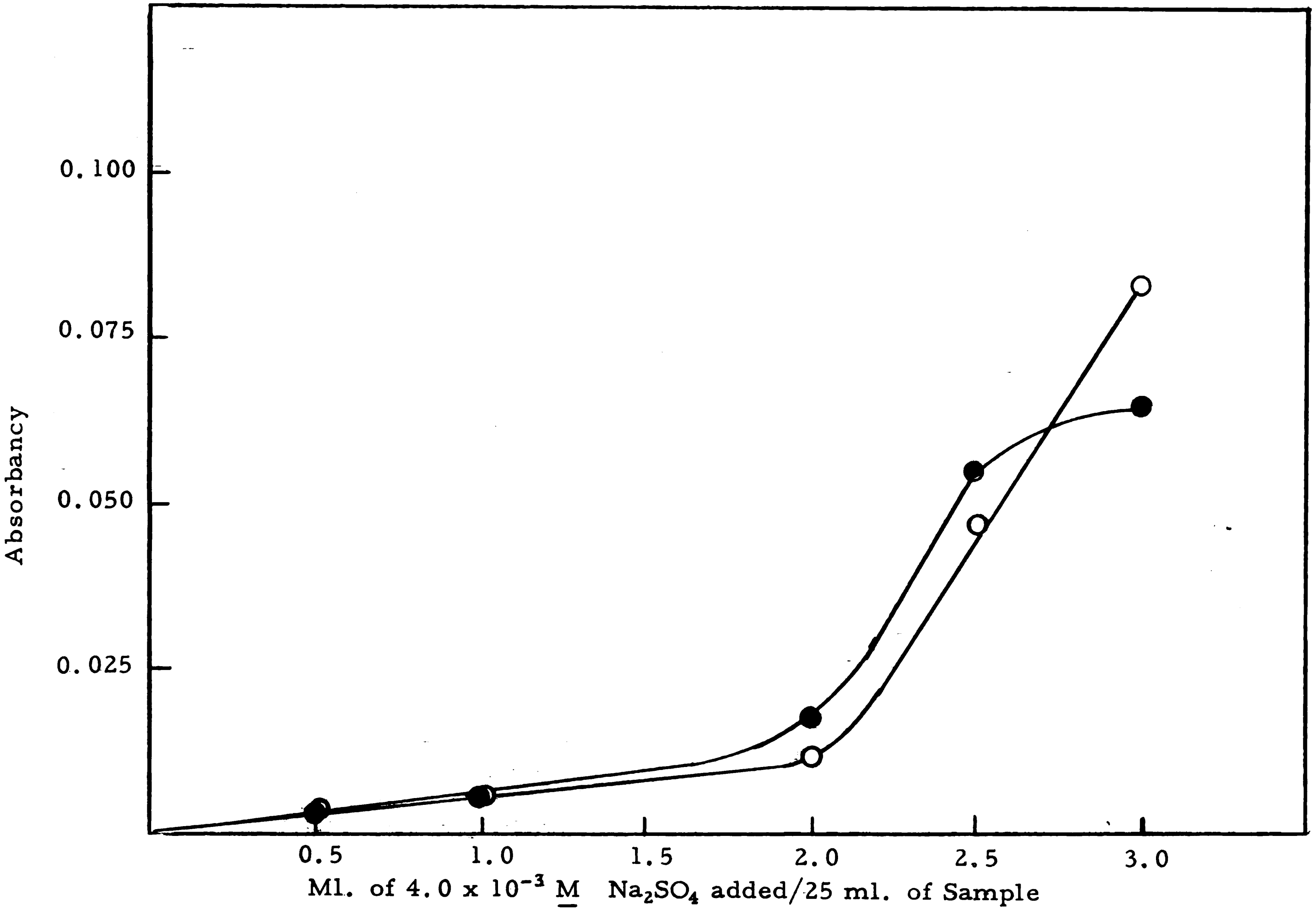


Figure 4. Turbidity versus sulfate concentration.
$[Cu^{++}] = 1.65 \times 10^{-2}$ M, $[CN_5H_3] = 2.06 \times 10^{-2}$ M

○ = $SO_4^=$ added before CN_5H_3
● = $SO_4^=$ added after CN_5H_3

The curves shown in Figures 2, 3, and 4 all have the same general shape. All of the curves rise slowly until the amount of sodium sulfate in the samples is about 8.0×10^{-3} millimoles (2 ml. of 0.004 M Na_2SO_4). The addition of larger amounts of sulfate causes the curves to rise sharply and then level out. The leveling out is probably due to coagulation of the solid and separation of a solid phase. The intersection of the "before" and "after" curves in each figure is probably due to separation of a solid phase at lower sulfate concentrations in the "after" case. This seems reasonable since at high sulfate concentrations (Table 5) the addition of sulfate "after" the addition of 5-aminotetrazole always produced more solid.

At very low sulfate concentrations (less than 2 ml. of 0.004 M Na_2SO_4 added) the amount of turbidity produced is small and seems to be, within experimental error, almost independent of the concentration of both 5-aminotetrazole and copper ion. At higher sulfate concentrations (2-3.5 ml. of 0.004 M Na_2SO_4 added) and constant CN_5H_3 concentration the amount of turbidity produced is essentially independent of copper ion concentration (Figures 2 and 3). Comparison of Figures 3 and 4 indicates that decreasing the concentration of CN_5H_3 increases the amount of turbidity and allows separation of a solid phase at lower sulfate concentration.

The Effect of Added Chloride on the Formation of Solids in the Copper (II)-5-Aminotetrazole System

The addition of chloride ion to the copper nitrate-5-aminotetrazole system also causes turbidity and precipitation of solids, but much greater concentrations of chloride must be used than in the case of sulfate.

A turbidimetry study using the same methods as described for sulfate was carried out for chloride ion. The results are summarized in Table 9 and Figures 5 and 6.

Table 9. Turbidity as a Function of Chloride Concentration
$[Cu^{++}] = 1.24 \times 10^{-2}$ M Total volume of samples = 25 ml.

Ml. of 0.103 M CN_5H_3	Ml. of 0.10 M NaCl	Absorbancy at 550 mμ	
		Cl^- Added Before CN_5H_3	Cl^- Added After CN_5H_3
5	1.0	0.011	0.008
5	2.0	0.021	0.013
5	3.0	0.028	0.017
5	4.0	0.035	0.022
5	5.0	0.046	0.026
5	6.0	0.146	0.038
10	1.0	0.017	0.013
10	2.0	0.033	0.022
10	3.0	0.048	0.028
10	4.0	0.061	0.038
10	5.0	0.078	0.067
10	6.0	0.164	0.124

In the experiments involving addition of Cl^- to copper nitrate solutions either before or after the addition of 5-aminotetrazole, no significant turbidity was observed when the chloride concentrations were less than one-third of the copper concentration. The relationship between turbidity and amount of chloride added is nearly linear (in all of the cases studied) until the chloride concentration is 1.7-2.0 times greater than the copper concentration. In contrast to sulfate, the addition of Cl^- before the addition of CN_5H_3 to the copper nitrate favors formation of solids and also in contrast to $SO_4^{=}$, decreasing the concentration of CN_5H_3 decreases the amount of turbidity.

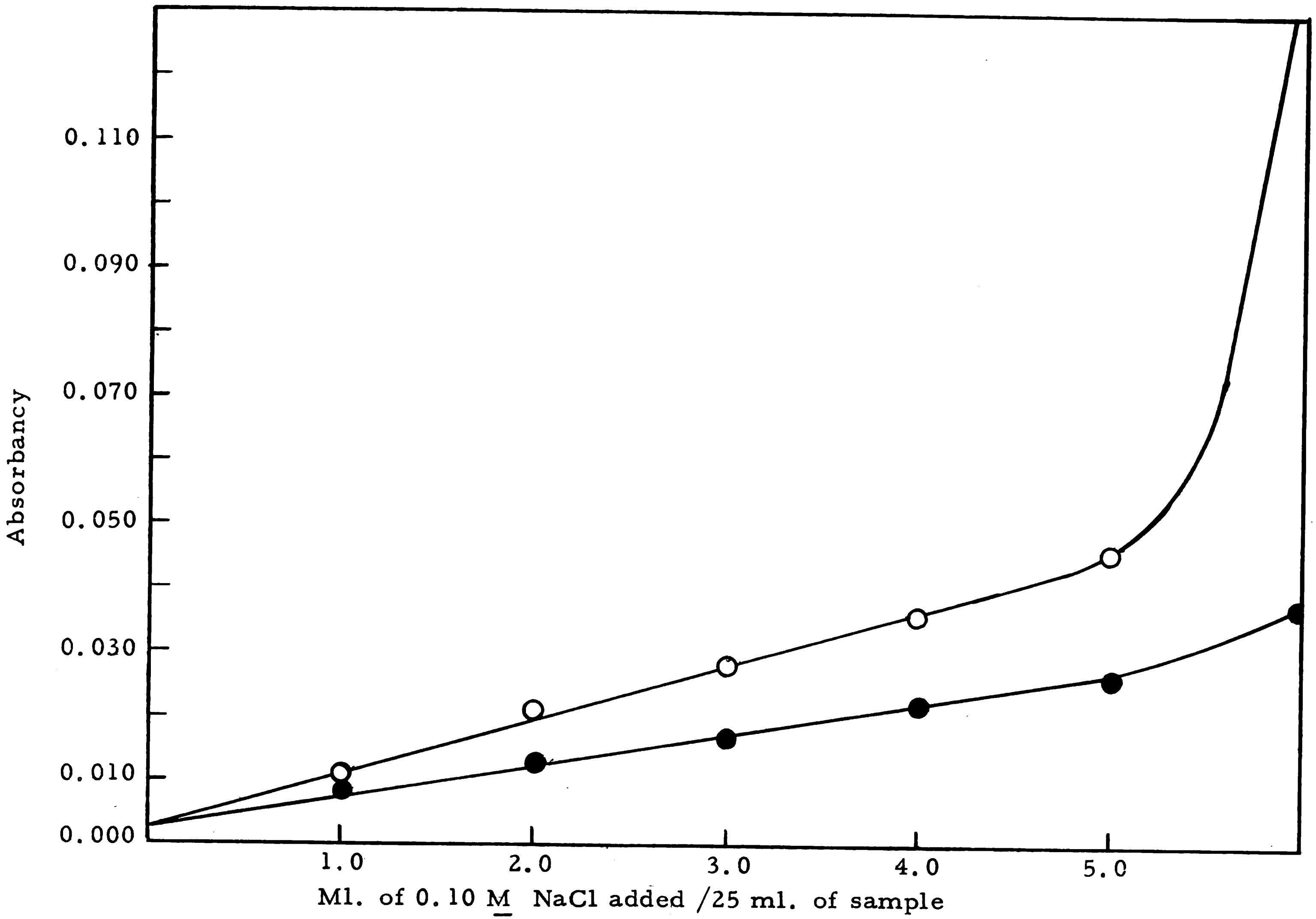


Figure 5. Turbidity versus chloride concentration
$[Cu^{++}] = 1.24 \times 10^{-2}$ M, $[CN_5H_3] = 2.06 \times 10^{-2}$ M

○ = Cl^- added before CN_5H_3
● = Cl added after CN_5H_3

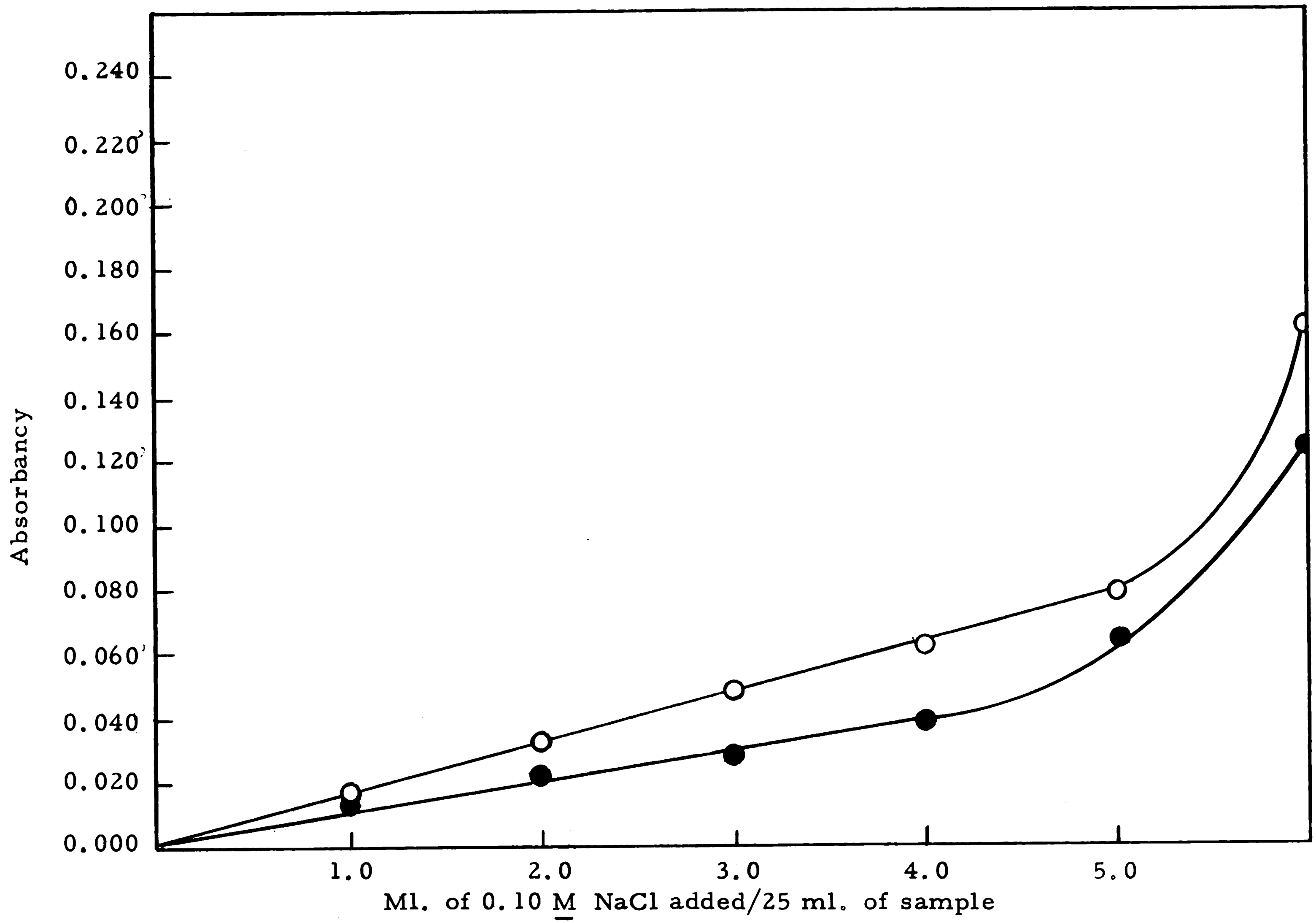


Figure 6. Turbidity versus chloride concentration
$[Cu^{++}] = 1.24 \times 10^{-2}$ M, $[CN_5H_3] = 4.12 \times 10^{-2}$ M
o = Cl^- added before CN_5H_3
● = Cl^- added after CN_5H_3

The Effect of Added Chloride on the Rate of Formation of Solids in the Copper Nitrate-5-aminotetrazole System

It was noted that chloride ion added to solutions of copper nitrate and 5-aminotetrazole caused the solutions to become turbid and, also, that the turbidity appeared to increase with time until a solid phase separated. It seemed desirable to determine whether the rate of formation of turbidity in the samples was a function of chloride concentration.

Stock solutions of copper nitrate, 5-aminotetrazole, sodium chloride and sodium nitrate were stored in a water bath, thermostated at 25°. A reference solution was made up immediately before a run by pipetting 3 ml. of 0.103 M copper nitrate, 10 ml. of 0.10 M sodium nitrate and 10 ml. of 0.10 M CN_5H_3 into a 25 ml. volumetric flask and diluting to volume. The sample solutions were prepared by pipetting 3 ml. of 0.103 M copper nitrate, 10-x ml. of 0.10 M sodium nitrate, x ml. of 0.10 M sodium chloride and 10 ml. of 0.10 M CN_5H_3 into a 25 ml. volumetric flask and quickly diluting to volume. The reagents were added in the order given.

The sample solutions were transferred as soon as possible to one cm stoppered silica cells and were placed in the cell compartment of a Beckman DU spectrophotometer thermostated at 25°. The absorbancy of the samples at 550 mμ compared to the reference solution was recorded as a function of time. When it was possible, the reaction was followed until the absorbancy readings reached a nearly constant value. A plot of absorbancy *versus* time for several chloride concentrations is shown in Figure 7.

The results of the kinetic runs as graphed in Figure 7 leave little doubt that increasing the concentration of added chloride increases the rate of formation of solids.

As mentioned previously, in some cases the reaction was followed until a nearly constant turbidity was reached. It is perhaps significant that in those runs where a constant turbidity was reached the final turbidity measurements are different. Moreover, increasing

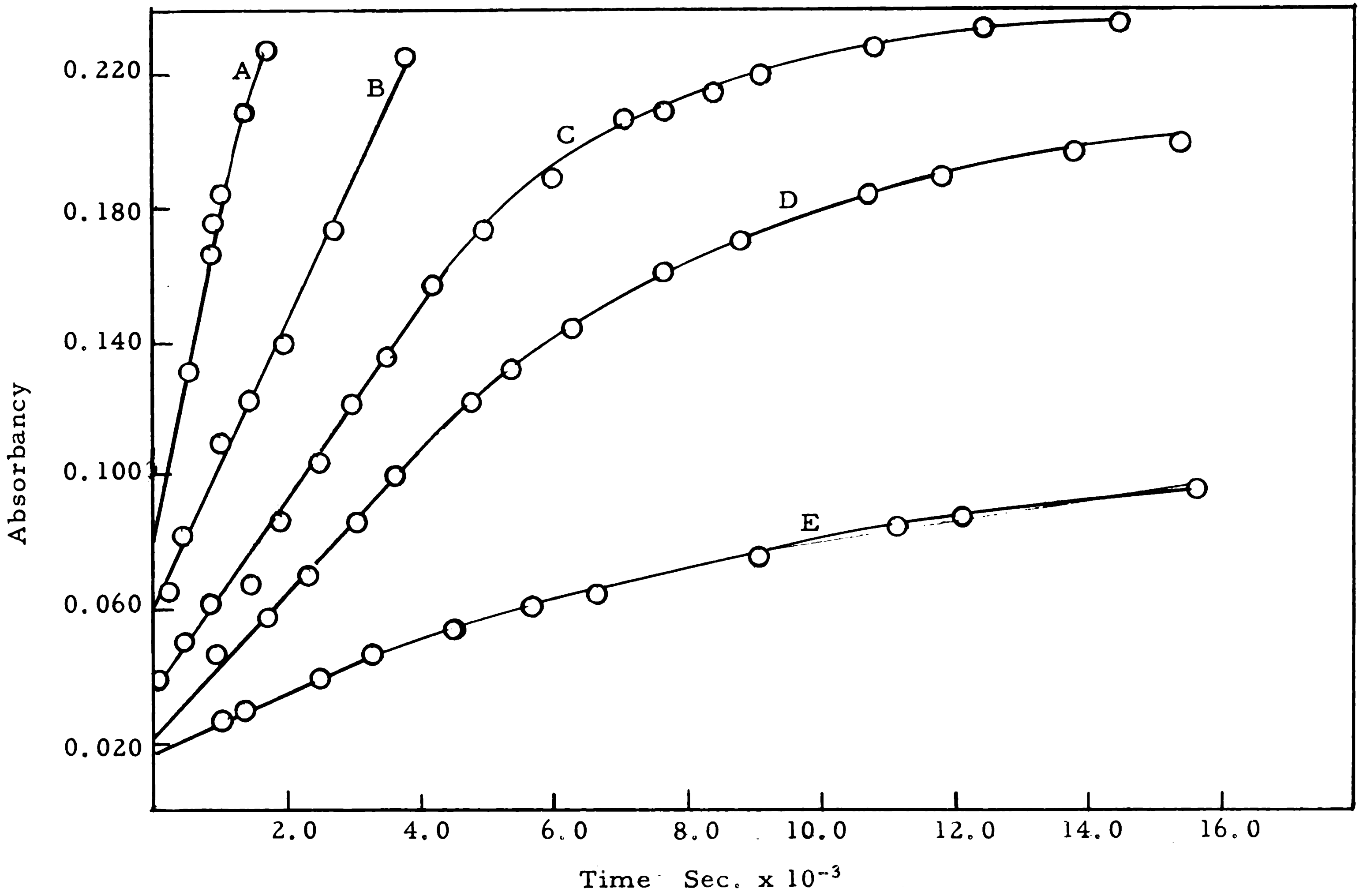


Figure 7. Rate of Turbidity Formation Dependence on Chloride Concentration. $[Cu^{++}] = 1.24 \times 10^{-2}\ \underline{M}$, $[CN_5H_3]$ $4.12 \times 10^{-2}\ \underline{M}$ $[Cl^-]$, Curve A, $2.80 \times 10^{-2}\ \underline{M}$; Curve B, $2.4 \times 10^{-2}\ \underline{M}$; Curve C, $2.0 \times 10^{-2}\ \underline{M}$; Curve D, $1.6 \times 10^{-2}\ \underline{M}$; Curve E, $1.2 \times 10^{-2}\ \underline{M}$.

the initial chloride concentration resulted in an almost proportional increase in the final turbidimetry reading.

Copper (II) - 5-Phenyltetrazole Complexes

Since 5-phenyltetrazole is but slightly soluble in water, non aqueous solvents were employed in the study of 5-phenyltetrazole complexes. The solvents most frequently used were absolute ethanol, 95% aqueous ethanol, and methanol. The reactions of cupric sulfate, cupric chloride, and cupric nitrate with 5-phenyltetrazole were investigated.

The Reaction of Copper Sulfate with 5-Phenyltetrazole in Methanol

When methanol is used as the solvent, mixing 200 ml. of 0.04 M copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, and 50 ml. of 0.20 M 5-phenyltetrazole solution gives a deep blue solution. After standing 5 hours in a stoppered flask, dark blue crystals begin to separate from the solution. After 24 hours much solid has separated from the solution leaving the supernate pale blue. Analysis for copper, carbon, hydrogen, and nitrogen after drying to constant weight over magnesium perchlorate, indicate that the blue solid is bis(5-phenyltetrazolato)copper(II) monohydrate. Calculated for $Cu(C_7H_5N_4)_2 \cdot H_2O$: Cu, 17.1%; C, 45.2%; H, 3.8%; N, 30.2%. Found: Cu, 17.1%; C, 45.7%; H, 3.7%; N, 29.7%.

Mixing methanol solutions of 5-phenyltetrazole and copper sulfate pentahydrate in any proportions gives deep blue solutions from which a dark blue crystalline material forms. The blue solids always contain 16.5-18.0% Cu after drying.

If the blue solid $Cu(C_7H_5N_4)_2 \cdot H_2O$ is heated at 110° for 2 or 3 days or is stored over magnesium perchlorate for several weeks, a bronze colored solid, containing 18.0% Cu and corresponding to anhydrous $Cu(C_7H_5N_4)_2$ is produced. When the anhydrous $Cu(C_7H_5N_4)_2$ is exposed to moist air, it rapidly turns blue.

When the blue methanol solution resulting from mixing 10 ml. of 0.25 M $CuSO_4 \cdot 5H_2O$ and 20 ml. of 0.25 M 5-phenyltetrazole, was diluted with 400 ml. of water, a pale blue solid separated at once. The mixture was filtered, the solid residue was washed three times with methanol, and was dried over magnesium perchlorate. The dried solid contained 16.5% Cu and gave an X-ray powder pattern identical to the one obtained from $Cu(C_7H_5N_4)_2 \cdot H_2O$.

However, if methanol solutions in which the molar ratio of tetrazole to copper is slightly less than 1:1 are diluted with water, a blue solid separates which gives an X-ray powder pattern different from $Cu(C_7H_5N_4)_2 \cdot H_2O$ and contains 28.5% Cu. Analyses indicate that this solid is probably hydroxo(5-phenyltetrazolato) copper (II). Calculated for $Cu(C_7H_5N_4)OH$: Cu, 28.2%; C, 37.3%; H, 2.7%; N, 24.8%. Found: Cu, 28.5%; C, 38.2%; H, 2.8%; N, 24.8%.

The Hydrolysis of $Cu(C_7H_5N_4)_2 \cdot H_2O$

A sample of $Cu(C_7H_5N_4)_2 \cdot H_2O$ weighing 0.1857 g. (5.0×10^{-4} moles) was placed in a 100 ml. round bottom flask and 50 ml. of water was added. The flask was stoppered and the mixture was stirred magnetically for 20 hours. At the end of the reaction period the mixture consisted of a blue solid suspended in the water with a film of white solid floating on the surface of the water. The blue solid was collected on a medium-porosity filtering crucible. Any film sticking to the flask or crucible was discarded. An X-ray powder pattern of the dried product is similar to the pattern of $Cu(C_7H_5N_4)OH$ but also shows some lines characteristic of the pattern of $Cu(C_7H_5N_4)_2 \cdot H_2O$.

The product contains 22.1% Cu and 75.8% $C_7H_5N_4$. These values are intermediate between the amounts calculated for $Cu(C_7H_5N_4)_2$ (18.0% Cu; 82.1% $C_7H_5N_4^-$) and $Cu(C_7H_5N_4)OH$ (28.2% Cu; 64.3% $C_7H_5N_4^-$). It appears that the product is a mixture of these two compounds.

Calculated for 59.8% $Cu(C_7H_5N_4)_2$ and 40.2% $Cu(C_7H_5N_4)OH$; Cu, 22.1%; $C_7H_5N_4^-$, 75.1%. Found: Cu, 22.1%; $C_7H_5N_4^-$, 75.8%.

The Reaction of $Cu(C_7H_5N_4)_2 \cdot H_2O$ with 3.0 M H_2SO_4

Samples of $Cu(C_7H_5N_4)_2 \cdot H_2O$ weighing 70-80 mg. were treated with 4 ml. of 3.0 M H_2SO_4. The samples were allowed to stand 8 hours at the end of which time the samples had reacted to give a white solid suspended in a pale blue solution. The samples were diluted with 20 ml. of water causing most of the white solid to dissolve. The samples were neutralized dropwise with 6 N NaOH. The pH change was followed by means of a Beckman model G pH meter. At pH of ~ 3, the solutions turned a deeper blue and addition of more base caused the precipitation of a pale blue solid. After drying, the solid gave an X-ray powder pattern identical with the pattern given by $Cu(C_7H_5N_4)OH$.

The Visible Spectra of Methanol Solutions of $CuSO_4 \cdot 5H_2O$ and $C_7H_6N_4$

The addition of 5-phenyltetrazole to methanol solutions of copper sulfate pentahydrate shifts the 830 mμ peak of the copper solution to a shorter wavelength. A 20:1 tetrazole to copper ratio gives a peak with maximum at 730 mμ, but it appears as if further addition of tetrazole would shift the maximum to a still shorter wavelength. The addition of the tetrazole produces a very strong absorption in the ultra violet (Figure 8).

Continuous Variation Experiments in the $CuSO_4 \cdot 5H_2O$-$C_7H_6N_4$ System

Continuous variation studies of copper sulfate pentahydrate and 5-phenyltetrazole in methanol solution were carried out at both 720 mμ and 380 mμ.

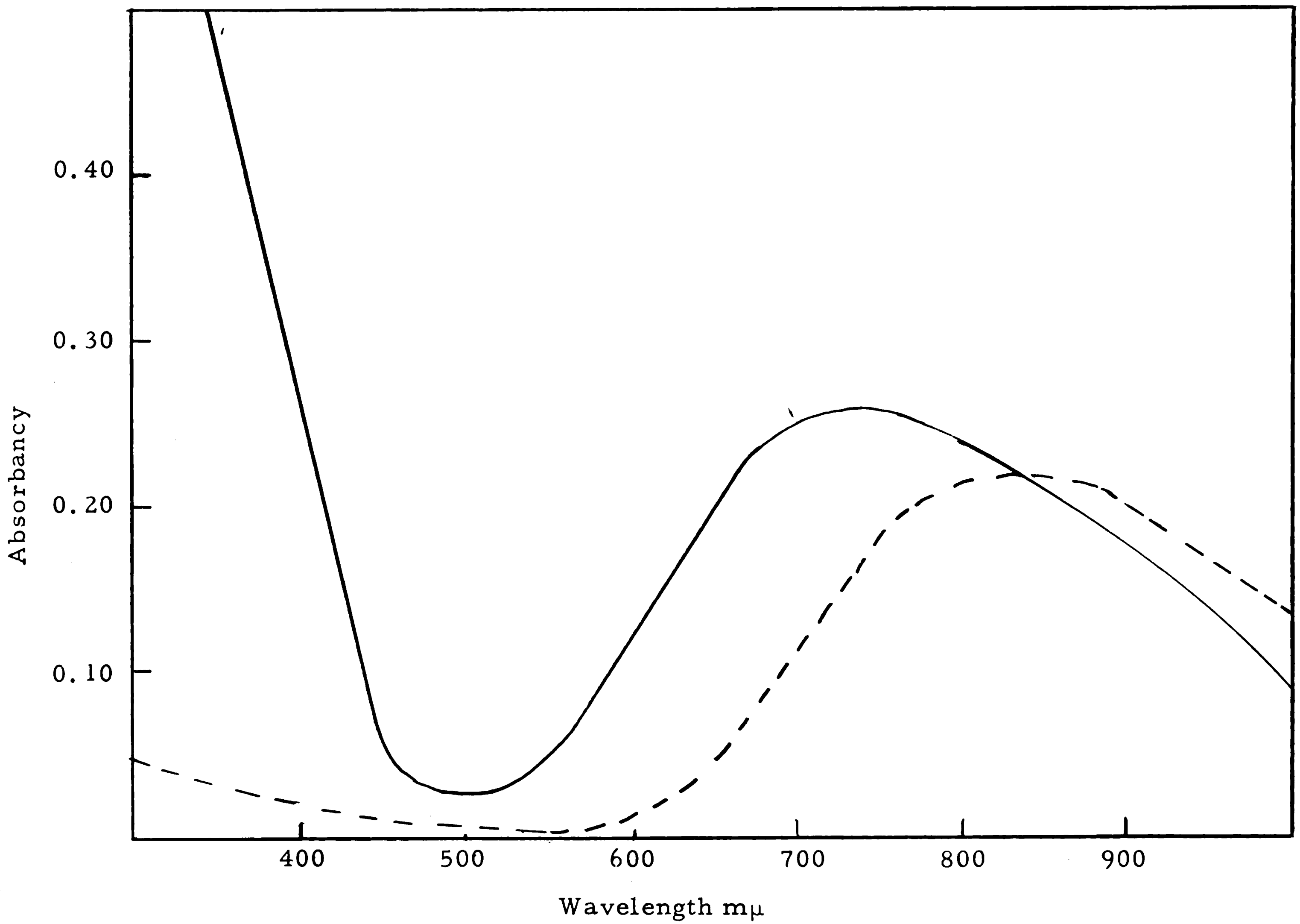


Figure 8. Visible Spectra in Methanol
8.0×10^{-3} $\underline{M}$ $CuSO_4 \cdot 5H_2O$ (broken line)
8.0×10^{-3} $\underline{M}$ $CuSO_4 \cdot 5H_2O$ and also 160×10^{-3} $\underline{M}$ in $C_7H_6N_4$ (solid line)

Samples for continuous variation measurements at 380 mμ were prepared from 0.04 M stock solutions. The samples were made up by pipetting the required amount of copper solution into a 25 ml. volumetric flask and adding the required amount of 5-phenyltetrazole solution. The samples were diluted to volume and allowed to stand 30 minutes. The absorbancies of the samples at the desired wavelength were measured using one cm. stoppered silica cells in a Beckman model DU spectrophotometer. Methanol was used in the reference cell.

Samples for measurements at 720 mμ were made up from 0.05 M stock solutions using the same technique. In both cases no change in absorbancy with time could be detected over a period of several hours. The results are given in Tables 10 and 11.

Table 10. Continuous Variation of $CuSO_4 \cdot 5H_2O$ and $C_7H_6N_4$ in Methanol at 380 mμ. Total Molarity = 1.6×10^{-2}.

$\frac{[C_7H_6N_4]}{[Cu^{++}]}$	Absorbancy Observed	Excess Absorbancy
0.5	0.205	0.176
1.0	0.218	0.196
1.5	0.203	0.185
2.0	0.186	0.171
2.5	0.172	0.159
4.0	0.132	0.123
0 (Cu only)	0.044	-
(only $C_7H_6N_4$)	0.000	-

Table 11. Continuous Variation of $CuSO_4 \cdot 5H_2O$ and $C_7H_6N_4$ in Methanol at 720 mμ. Total Molarity =, 2.0×10^{-2}.

$\frac{[C_7H_6N_4]}{[Cu^{++}]}$	Absorbancy Observed	Excess Absorbancy
0.5	0.271	0.058
1.0	0.220	0.060
1.5	0.182	0.054
2.0	0.158	0.051
2.5	0.135	0.044
Cu only	0.320	-

Although both experiments indicate a 1:1 copper-tetrazole interaction, it should be mentioned that optimum conditions for continuous variation studies do not exist at either wavelength. At the higher wavelength (720 mμ) the absorption peak of the complex overlaps considerably the absorption peak of uncomplexed copper ion. The lower wavelength (380 mμ) does not correspond to an absorption maximum but is only a convenient wavelength at which the complex is the only strongly absorbing species.

The Reactions of Cupric Chloride with 5-Phenyltetrazole

When 0.10 M solutions of cupric chloride dihydrate, $CuCl_2 \cdot 2H_2O$, and 5-phenyltetrazole in 95% ethanol are mixed in a 2:1 tetrazole to copper molar ratio, no visible color change occurs. However, after standing 30 minutes the solution becomes cloudy and a pale blue solid slowly begins to precipitate. The solid was collected on a sintered glass filter and washed with 95% ethanol until the washings gave no precipitate with silver nitrate. The dried solid gave the X-ray powder pattern of $Cu(C_7H_5N_4)OH$. Calculated for $Cu(C_7H_5N_4)OH$, Cu, 28.2%; $C_7H_5N_4^-$, 64.3%. Found: Cu, 27.7%; $C_7H_5N_4^-$, 62.9%.

In another experiment, using absolute ethanol as the solvent, 40 ml. of 0.10 M $CuCl_2 \cdot 2H_2O$ and 80 ml. of 0.10 M 5-phenyltetrazole were mixed. No color change occurred. The alcohol solution was diluted with one liter of water which caused the immediate separation of a pale blue solid. The solid was collected on a sintered glass funnel and washed repeatedly with water until the washings were chloride free. The dried solid gave an X-ray powder pattern characteristic of $Cu(C_7H_5N_4)OH$ and contained 26.5% Cu. Elimination of any washing of the precipitate, in a repeat experiment, gives a solid containing 16.9% Cu and having an X-ray pattern very similar to that of $Cu(C_7H_5N_4)_2 \cdot H_2O$.

Similarly, dilution of methanol solutions of $CuCl_2 \cdot 2H_2O$ or anhydrous $CuCl_2$ and 5-phenyltetrazole, mixed in a 2:1 tetrazole to copper molar ratio, with water and collection of the solids without washing produces blue solids containing 16-18.5% Cu.

On the other hand, if 40 ml. of 0.10 M $CuCl_2$ and 80 ml. of 0.10 M 5-phenyltetrazole in absolute ethanol are mixed and allowed to stand in a closed container, a week after mixing a brown film can be detected on the sides and bottom of the flask. The amount of solid slowly increases and then appears to reach a constant amount after four weeks. The solid was separated by suction filtration and washed several times with small portions of absolute alcohol. After drying, the coffee-colored solid contains 30.4% Cu. Sodium fusion of the brown solid yields a solution which, when acidified, gives a white precipitate with silver nitrate. The X-ray powder pattern of the brown solid is not similar to the pattern of any other copper-5-phenyltetrazole complex. The sample was sent out for carbon, hydrogen, and nitrogen analyses. The sample exploded on analysis; the results reported were: C, 30.9%; H, 2.2%; N, 20.0%.

These analytical results suggested that the solid might be a mixture of chloro(5-phenyltetrazolato)copper(II), $Cu(C_7H_5N_4)Cl$ and cupric chloride. Calculated for 90.7% $Cu(C_7H_5N_4)Cl$ and 9.3% $CuCl_2$: Cu, 30.4%; C, 31.2%; H, 1.9%; N, 20.8%. Found: Cu, 30.4%; C, 30.9%, H, 2.2%; N, 20.0%.

Further evidence for this suggested composition is given by the following experiment, a sample of the dried, brown solid weighing 9.60 mg. was warmed with 5 ml. of 1.0 $\underline{M}$ NaOH until decomposition occurred. The supernatant, clear liquid was separated from the black copper oxide by filtration and the oxide was washed several times with distilled water. The filtrate and washings were acidified to pH 6.5 with dilute nitric acid. A calculated excess of 0.02 $\underline{M}$ $AgNO_3$ was added, precipitating any chloride or 5-phenyltetrazole present as the silver salts. The precipitate was coagulated by digestion on the steam bath for one hour, the sample was cooled, and was filtered through a tared, fine-porosity sintered glass crucible. The precipitate was washed with water and dried to constant weight at 90°. The weight of the silver salts was 15.91 mg. The combined weight of AgCl and $AgC_7H_5N_4$ that could be obtained from 9.60 mg. of a mixture of 90.7% $Cu(C_7H_5N_4)Cl$ and 9.3% $CuCl_2$ was calculated to be 16.02 mg.

The reactions of anhydrous cupric chloride and 5-phenyltetrazole in anhydrous methanol and aqueous methanol were compared. A 0.25 $\underline{M}$ stock solution of anhydrous $CuCl_2$ in methanol was prepared by weighing 2.6311 g. of the dihydrate (1.25×10^{-2} moles) into a 50 ml. volumetric flask, heating the flask at 110° for 48 hours, and dissolving the solid in sufficient dry methanol to give 50 ml. of solution.

Samples were prepared by pipetting 5.00 ml. of stock $CuCl_2$ solution into clean, dry 25 ml. volumetric flasks. Then 10 ml. of 0.25 $\underline{M}$ 5-phenyltetrazole in dry methanol was added and the contents of the flasks were diluted almost to volume with dry methanol. Then, various amounts of water were added to the samples, the samples were diluted to volume with methanol, the flasks were tightly stoppered, and the samples were allowed to stand 50 hours. Any changes in the appearance of the samples were noted. In order to determine relative copper content of the supernates, about 10 ml. of each sample was filtered and 4 ml. of the filtrate was pipetted into a 50 ml. beaker. The solutions were evaporated to dryness on a steam bath and the residues were redissolved in dilute nitric acid. The solutions were transferred to 50 ml. volumetric flasks, 20 ml. of NH_3-NH_4Cl buffer was added to each, the samples were diluted to 50 ml., and the absorbancies of the samples were measured at 620 mμ using one cm. silica cells in a Beckman DU spectrophotometer. The data are summarized in Table 12.

Enough solid was obtained from sample number 7 to obtain an X-ray powder pattern which was identical to the pattern of $Cu(C_7H_5N_4)OH$.

Two facts seem to be apparent from a consideration of the data in Table 12. One of these is that although the water content of samples 3 through 6 varies over a four-fold concentration range, the concentration of copper in the supernate is essentially constant and the solids in samples 3 through 6 are all brown colored. However, sample 7, which contained 50% more water than 6, produced a blue solid and the supernate of 7 definitely contained less copper than any other sample. Secondly, it is of interest to note that in sample 6 (brown solid) the molar ratio of water to Cu^{++} is 88:1, suggesting that rather large amounts of water are needed to produce the blue solid.

In another experiment using methanol as the solvent, 2 ml. of 0.25 $\underline{M}$ $CuCl_2 \cdot 2H_2O$ and 4 ml. of 0.25 $\underline{M}$ 5-phenyltetrazole were combined in a 10 ml. volumetric flask. The volume was diluted to 10 ml. with methanol, the flask was stoppered, and was allowed to stand 2 weeks. No solid separated from the solution during this period.

Table 12. The Effect of Water in the Reaction of $CuCl_2$ and $C_7H_6N_4$ in Methanol

Sample Number	Ml. 0.25 $\underline{M}$ $CuCl_2$ Added	Ml. 0.25 $\underline{M}$ $C_7H_6N_4$ Added	Ml. of H_2O Added	Observations	Color of Solid in Flask	Absorbancy at 620 mμ of samples taken for Cu anal.
1	5.0	0.0	0.0	Soln. remains clear	none	0.297
2	5.0	10.0	0.0	A small amt. of brown solid present after 50 hours	brown	0.293
3	5.0	10.0	0.5	A small amt. of brown solid present after 14 hours	brown	0.288
4	5.0	10.0	1.0	Begins to get cloudy after 11 hours	brown	0.288
5	5.0	10.0	1.5	Begins to get cloudy after 9 hours	brown	0.288
6	5.0	10.0	2.0	Begins to get cloudy after 4 hours	brown	0.289
7	5.0	10.0	3.0	Begins to get cloudy after 2 hours	blue	0.272

Visible Spectra of Anhydrous Cupric Chloride with Added 5-Phenyltetrazole

Addition of 5-phenyltetrazole to anhydrous cupric chloride in absolute ethanol or methanol does not alter the cupric chloride spectrum.

The Reactions of Cupric Nitrate and 5-Phenyltetrazole

A 0.10 M solution cupric nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$ in methanol was prepared and 20 ml. of this solution were mixed with 40 ml. of a 0.10 M 5-phenyltetrazole solution. No apparent reaction occurred at the time of mixing. The mixture was allowed to stand in a stoppered flask. After standing an hour, a very small amount of solid had separated. After standing overnight more of the solid had crystallized from solution, but the total amount of solid was very small. Leaving the solution stand for several weeks longer produced no significant additional amount of solid.

The solid was separated, washed and dried. The bluish-purple crystals gave an X-ray powder pattern different from any copper complex previously prepared.

In another experiment, 95% ethanol was used as the solvent. When 20 ml. of 0.10 M $Cu(NO_3)_2 \cdot 3H_2O$ solution and 40 ml. of 0.10 M 5-phenyltetrazole solution were mixed the blue color of the copper solution became more intense and within seconds the solution became turbid. A green solid separated within 5 minutes after the solutions had been mixed. After standing 10 more minutes the green solid turned blue.

The blue solid was separated by suction filtration and was washed three times with 95% ethanol. After the solid had been dried, it contained 30.5% Cu and gave an X-ray powder pattern identical with that of $Cu(C_7H_5N_4)OH$.

During a duplicate experiment, the green solid first formed in the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ and 5-phenyltetrazole in 95% ethanol, was removed by filtration as soon as it was formed. The green solid started to turn blue as it was sucked dry in the filter and turned completely blue a few minutes after being placed in a desiccator. The dried solid contained 17.9% Cu and its X-ray powder pattern was identical with that of the bluish-purple solid prepared from methanol.

In an attempt to reduce the possibility of hydrolysis, the reaction was next carried out in absolute ethanol. In addition, a reaction temperature of 0° was employed in an attempt to decrease the rate of reaction and/or precipitation in order to lower the probability of occluding unreacted starting materials.

When the copper and tetrazole solutions were mixed, a grass green solution resulted. The flask containing the green solution was stoppered and the temperature maintained by an ice-water bath. Eight hours after the time of mixing, a finely divided purple-blue solid began to form on the bottom of the flask. The flask was stored overnight in the freezer compartment of a refrigerator.

The flask was allowed to stand 24 hours during which time more of the purple solid crystallized from the green solution. The solid was separated from the green supernatant solution by filtration, was washed with absolute alcohol, and was dried. The dried purple-blue crystals also gave an X-ray powder pattern identical to the pattern of the solid prepared from methanol. Copper and tetrazolate analyses were performed giving the following results: 17.9% Cu, 73.1% $C_7H_5N_4^-$ or a tetrazolate: copper molar ratio of 1.79.

Infra-red Spectra

The infra-red spectra of $Cu(C_7H_5N_4)_2 \cdot H_2O$, $Cu(C_7H_5N_4)OH$ (copper sulfate preps.) and $Cu(C_7H_5N_4)Cl$ are offered in Table 13.

Table 13. Infra-red Absorption Bands (in cm^{-1}) of 5-Phenyltetrazole, Sodium-5-phenyltetrazolate, and Copper (II) Complexes of 5-Phenyltetrazole. Potassium Bromide Discs.

$C_7H_6N_4$	$NaC_7H_5N_4$	$Cu(C_7H_5N_4)_2\cdot H_2O$	$Cu(C_7H_5N_4)OH$	$Cu(C_7H_5N_4)Cl$
3571 mw	3690 s		3636 ms	3571 m
	3509 s	3484 s		3448 m
3226 mw	3279 s			3390 m
3155 m		3125 m	3125 m	
3077 m				3049 m
2985 ms			2985 m	
2915 ms				
2755 s				
2653 s				
2584 s				
2519 s				
	2309 w			
2000 mw	1972 w		1961 w	1961 w
1923 m	1908 w		1898 w	1905 w
1880 m				
1776 w				
1754 w				
1724 w	1704 m			
1675 w	1658 w	1650 m		
1623 ms		1626 m	1639 w	
1577 s			1613 w	1613 m
1497 ms		1538 mw	1531 mw	1527 m
1479 ms	1479 ms			
1443 w	1453 s		1453 s	1456 s
1391 s	1391 s	1398 ms	1389 s	1381 mw
	1374 ms	1376 m	1366 mw	1366 m
				1339 w
				3112 w

Continued

Table 13 - Continued

$C_7H_6N_4$	$NaC_7H_5N_4$	$Cu(C_7H_5N_4)_2\cdot H_2O$	$Cu(C_7H_5N_4)OH$	$Cu(C_7H_5N_4)Cl$
1294 m	1285 mw	1287 mw	1282 mw	1285 m
1255 m	1266 w	1267 mw	1266 mw	1253 w
				1242 w
	1215 w	1217 m	1209 m	1209 ms
1167 s	1149 m	1183 m	1181 mw	1195 m
				1178 mw
	1134 m	1161 mw		1156 mw
	1127 m	1130 m	1127 m	1135 m
1103 w	1105 w	1101 w	1096 mw	
1087 ms	1096 w	1081 m	1075 m	1073 m
1057 ms	1075 m			1066 m
				1044 w
1036 m	1027 mw	1036 w	1031 mw	1033 mw
1015 m	1012 mw	1014 m	1008 m	1015 ms
994 ms	996 w			
959 mw				
924 mw	917 w	922 mw	956 broad band (s)	929 mw
	909 w		914 m	
792 m	786 mw	789 m	781 mw	784 m
783 mw	725 s	731 s	722 s	745 s
725 s	704 s	694 s	698 ms	699 ms
703 s				694 ms

The bands occurring in the 2940-2500 cm^{-1} region of the 5-aminotetrazole spectrum have been assigned to the ring N-H group by Brubaker (41). Several bands in the region 3077-2519 cm^{-1} are found in the spectrum of 5-phenyltetrazole and since these bands do not appear in the spectrum of $NaC_7H_5N_4$ they apparently are due to the ring N-H group. The bands in the region 3077-2519 cm^{-1} are also missing in the spectra of the complexes, indicating loss of the ring hydrogen during complex formation. Analytical results also indicate loss of H^+ during complex formation.

Lieber *et al.* (48) have examined the infra-red spectra of some tetrazoles and have attributed bands in the 1100-900 cm^{-1} region to tetrazole ring vibrations. The spectra of the complexes differ from the spectrum of the simple sodium salt in this region.

Other 5-Aryltetrazole Complexes of Copper

Copper complexes of 5-o-chlorophenyltetrazole, 5-m-chlorophenyltetrazole, 5-p-chlorophenyltetrazole, 5-p-nitrophenyltetrazole and 5-p-methoxyphenyltetrazole were all prepared in an identical manner. A 0.20 *M* stock solution of $CuSO_4 \cdot 5H_2O$ in methanol was prepared and 12 ml. of this solution was added to 10^{-2} moles of each of the tetrazoles dissolved in 100 ml. of methanol. The flasks containing the copper-tetrazole solutions were stoppered and allowed to stand until crystallization of the complex had occurred. The crystals were collected on a sintered glass funnel and washed with dry methanol until the washings were free of sulfate. The solids were dried in a vacuum desiccator over magnesium perchlorate. The solid complexes of the tetrazoles are described below.

5-o-Chlorophenyltetrazole

Methanol solutions of $CuSO_4 \cdot 5H_2O$ and 5-o-chlorophenyltetrazole when mixed give a dark blue solution from which dark blue crystals form after a week to 10 days. The dried crystals are bronze colored and contain 15.0% Cu and 84.3% $C_7H_4N_4Cl^-$. Calculated for bis(5-ortho-chlorophenyltetrazolato)copper (II), $Cu(C_7H_4N_4Cl)_2$: Cu, 15.0%; $C_7H_4N_4Cl^-$, 85%. Found: Cu, 15.0%; $C_7H_4N_4Cl^-$, 84.3%.

5-m-Chlorophenyltetrazole

Dark blue crystals of the complex precipitate 12-16 hours after mixing methanol solutions of the starting materials. The color of the solid changes to blue-grey upon drying. Analyses indicate that the material probably is impure $Cu(C_7H_4N_4Cl)_2 \cdot H_2O$. Calculated for $Cu(C_7H_4N_4Cl)_2 \cdot H_2O$: Cu, 14.4%; C, 38.0%; H, 2.3%; N, 25.4%. Found: Cu, 15.5%; C, 37.0%; H, 2.5%, N, 24.8%.

5-p-Chlorophenyltetrazole

Mixing methanol solutions of $CuSO_4 \cdot 5H_2O$ and 5-p-chlorophenyltetrazole results in the formation of a blue solution. After 48 hours, pale blue crystals begin to separate from the solution. When the crystals are sucked dry on a funnel, the color changes to green. After drying the solid contains 20.4% Cu, 58.0% $C_7H_4N_4Cl^-$, and 15.3% sulfate. The molar ratios of copper: tetrazolate: sulfate are 2:2:1. Calculated for $Cu_2(C_7H_4N_4Cl)_2SO_4 \cdot 2H_2O$: Cu, 20.6%; $C_7H_4N_4Cl^-$, 58.2%; $SO_4^=$, 15.5%. Found: Cu, 20.4%; $C_7H_4N_4Cl^-$, 58.0%; $SO_4^=$, 15.3%.

The infra-red spectrum of the complex shows a broad band in the region from 1210 cm^{-1} to 1051 cm^{-1} which corresponds to the assigned band for inorganic sulfate (1130 cm^{-1} to 1080 cm^{-1}).

5-p-Nitrophenyltetrazole

Bright blue crystals precipitate from methanol solutions of $CuSO_4 \cdot 5H_2O$ and 5-p-nitrophenyltetrazole about 48 hours after mixing. When the crystals are collected by filtration and washed with methanol until the washings are sulfate free, the dried crystals contain 14.9%

sulfate, 19.3% Cu, and 59.9% $C_7H_4N_5O_2^-$. As in the case of the 5-p-chlorophenyltetrazole complex, the molar ratio of copper: tetrazolate: sulfate is 2:2:1. Calculated for $Cu_2(C_7H_4N_5O_2)_2SO_4 \cdot 2H_2O$: Cu, 19.9%; $C_7H_4N_5O_2^-$, 59.5%; $SO_4^=$, 15.0%. Found: Cu, 19.3%; $C_7H_4N_5O_2^-$, 59.9%, $SO_4^=$, 14.9%.

The infra-red spectrum of this complex also shows an intense band in the region 1210 cm^{-1} to 1050 cm^{-1}.

5-p-Methoxyphenyltetrazole

Addition of a methanol solution of 5-p-methoxyphenyltetrazole to a solution of $CuSO_4 \cdot 5H_2O$ in the same solvent produces a green solution from which a green solid precipitates within 24 hours. After washing and drying, the solid contains 20.1% Cu, 61.8% $C_8H_7N_4O^-$, and 11.3% $SO_4^=$. This composition corresponds to a copper: tetrazolate: sulfate molar ratio of 2.8:3.0:1. Although the solid appears to be homogeneous, it is probably a mixture of compounds. No definite formula can be assigned on the basis of the analytical results, but it is interesting to note that the results are in fair agreement with the composition calculated for $Cu(C_8H_7N_4O)OH \cdot Cu_2(C_8H_7N_4O)_2SO_4 \cdot 2H_2O$ (Cu, 22%; $C_8H_7N_4O^-$, 60.7%; $SO_4^=$, 11.1%).

Copper Sulfate Pentahydrate and 5-o-Tolyltetrazole

A solution of $CuSO_4 \cdot 5H_2O$ was prepared by dissolving 1.25 g. of the salt (5.0 x 10^{-3} moles) in 50 ml. of dry methanol. The copper solution was poured into a solution of 1.60 g. (10 x 10^{-3} moles) of 5-o-tolyltetrazole dissolved in 100 ml. of dry methanol. The resulting solution was deep blue and began to deposit dark blue crystals 12 hours after the solutions had been mixed.

The dark blue crystals were filtered, washed, and dried. After having been dried over magnesium perchlorate the color of the solid changed to brown. The brown solid is very hygroscopic and turns blue on brief exposure to moist air. Drying the brown solid to constant weight at 110° results in a weight loss of 2.1% and produces an ash green solid. Analysis of the brown solid shows that it contains 16.3% Cu, 81.3% $C_8H_7N_4^-$. These analytical results plus the weight loss on heating suggest that the brown solid is $Cu(C_8H_7N_4)_2\cdot\frac{1}{2}H_2O$. Calculated for $Cu(C_8H_7N_4)_2\cdot\frac{1}{2}H_2O$: Cu, 16.3%; $C_8H_7N_4^-$, 81.3%; H_2O, 2.3%. Found: Cu, 16.3%; $C_8H_7N_4^-$, 81.3%, weight loss on heating 2.1%.

5-p-Tolyltetrazole and 5-Cyclohexyltetrazole Copper Complexes

Solid of complexes of these two tetrazoles were prepared by the same method as described for 5-o-tolyltetrazole. Both tetrazoles give complexes that appear to be homogeneous solids, but definite formulas can not be assigned on the bases of analytical results.

The copper complex of 5-p-tolyltetrazole is a light green solid which contains 20.8% Cu, 69.9% $C_8H_7N_4^-$ and 7.5% $SO_4^=$. The molar ratio of tetrazolate to copper is 1.34:1 and the molar ratios of tetrazolate: copper: sulfate are 5.64:4.20:1.

The copper complex of 5-cyclohexyltetrazole is bright blue containing 21.1% Cu, 73.2% $C_7H_{10}N_4^-$ and 9.3% $SO_4^=$ and having a tetrazolate to copper molar ratio of 1.46.

Nickel Complexes of 5-Aminotetrazole

Preparation of Solid Complexes

Mixing aqueous solutions of nickel chloride or nickel nitrate with aqueous 5-aminotetrazole solutions in any proportions produces purple solutions which can be stored for over a year without separation of a solid phase. On the other hand, if nickel sulfate is used in place of the nitrate, the purple solution produced rapidly becomes cloudy and a purple precipitate forms. The gelatinous purple solid can not be washed free of the last traces of sulfate. Nickel, carbon, hydrogen and nitrogen analyses indicate that there are 1.5-1.7 tetrazoles per nickel atom in the solid.

A solid nickel-5-aminotetrazole complex also was obtained by slowly adding 50 ml. of 0.10 M $Ni(NO_3)_2 \cdot 6H_2O$ in absolute ethanol to 100 ml. of 0.10 M 5-aminotetrazole in absolute alcohol. The solid that precipitated from the reaction mixture was separated by centrifuging. The gelatinous solid was washed with alcohol several times and was dried in a vacuum desiccator over magnesium perchlorate. The dried purple solid contained 23.9% Ni and 56.0% $CN_5N_2^-$ which corresponds to a tetrazole to nickel molar ratio of 1.64.

Nickel Complexes of 5-Aminotetrazole in Solution

Visible Spectra. When aqueous solutions of 5-aminotetrazole are added to aqueous solutions of nickel nitrate or nickel chloride the color of the nickel solution changes from green to purple. Since such solutions remain clear indefinitely, they are suitable for spectrophotometric examination. The visible spectrum of 0.03 M $NiCl_2$ and 0.03 M $NiCl_2$ in the presence of 5-aminotetrazole is shown in Figure 9.

Continuous Variation Study at 540 mμ

A continuous variation study of the reaction of $Ni(NO_3)_2$ and 5-aminotetrazole in aqueous solution was carried out. A stock $Ni(NO_3)_2$ solution was prepared approximately 0.125 M by weighing and dissolving the hexahydrate. The stock $Ni(NO_3)_2$ solution was standardized gravimetrically with dimethylglyoxime and was found to be 0.128 M. A stock solution of 0.128 M 5-aminotetrazole was prepared by weighing 1.31 g. of the monohydrate and dissolving the compound in sufficient water to give 100 ml. of solution.

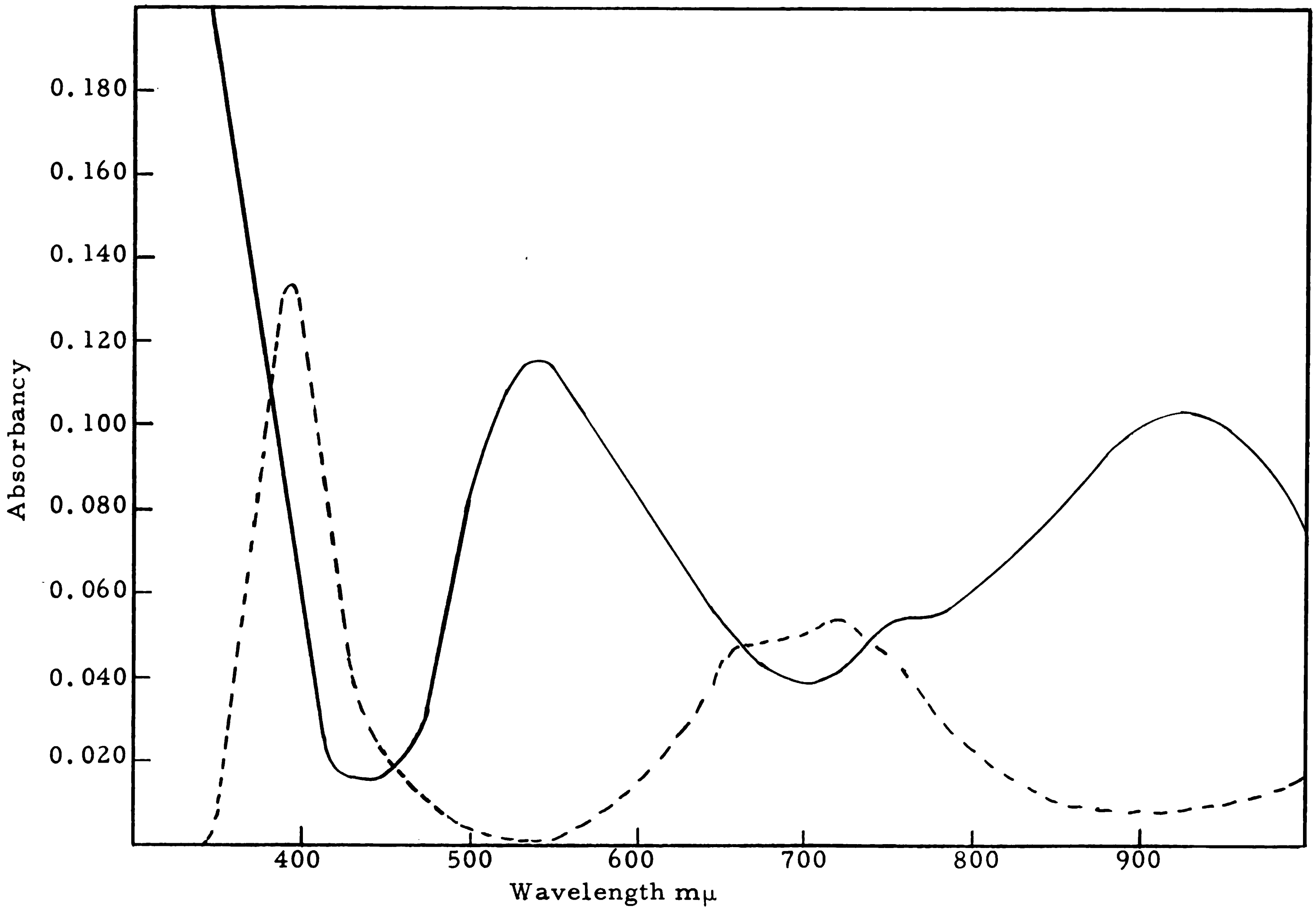


Figure 9. Visible Spectra (in H_2O)
3.0×10^{-2} $\underline{M}$ $NiCl_2$ (broken line)
3.0×10^{-2} $\underline{M}$ $NiCl_2$ and also 15.0×10^{-2} $\underline{M}$ in 5-aminotetrazole (solid line)

Samples for the study were prepared by delivering x ml. of stock nickel solution into a 25 ml. volumetric flask from a 10 ml. buret. Then, 10-x ml. of 0.128 M stock 5-aminotetrazole solution were added. The samples were mixed by swirling the flasks and the samples were diluted to volume with distilled water. The samples were allowed to stand 24 hours before any measurements were taken.

After the samples had aged 24 hours, the absorbancy of each sample was determined at 540 mμ using one cm cells in a Beckman DU spectrophotometer. A graph of excess absorbancy *versus* tetrazole to nickel molar ratio exhibits a broad maximum extending from a ratio of 0.8 to 2.4. No conclusions can be drawn concerning the stoichiometry of the complex, but the complex is apparently a rather weak one.

Attempted continuous variation studies with the sodium salt of 5-aminotetrazole and nickel nitrate hexahydrate failed in both water and N, N-dimethylformamide (DMF) because precipitates formed at all tetrazole to nickel molar ratios greater than 1.5.

Attempted Determination of Formation Constant for 5-Aminotetrazole Complexes of Nickel

When 5-aminotetrazole coordinates with nickel ion the hydrogen bonded to the ring nitrogens is released as a proton and, as mentioned previously, the nickel solution changes color. Attempts to determine formation constants for the complex were made using spectrophotometric and pH measurements, but satisfactory results could not be obtained. The results of these experiments are discussed in the Appendix.

Nickel Complexes of 5-Aryltetrazoles

Nickel Complexes of 5-Aryltetrazoles in Solution

The reactions of nickel nitrate hexahydrate, $Ni(NO_3)_2 \cdot 6H_2O$, with various 5-aryltetrazoles in several solvents were studied qualitatively in order to find a solvent suitable for quantitative spectrophotometric studies employing $Ni(NO_3)_2 \cdot 6H_2O$ and 5-aryltetrazoles or their sodium salts. In general, the reaction of 5-phenyltetrazole and $Ni(NO_3)_2 \cdot 6H_2O$ was examined and if a solvent appeared to be suitable for this tetrazole, the reactions of other tetrazoles and their sodium salts with $Ni(NO_3)_2 \cdot 6H_2O$ were examined.

If methanol is used as the solvent, mixing solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and 5-phenyltetrazole gives pale blue solutions which remain clear. The solutions are not suitable for spectrophotometric study because the color is of low intensity even when large excesses of tetrazole are used. When the sodium salt of 5-phenyltetrazole is used in place of the tetrazole, clear, purple solutions of sufficient intensity are produced. However, when the sodium salts of other tetrazoles, particularly the salts of 5-p-methoxyphenyltetrazole, and 5-p-nitrophenyltetrazole, are used, the purple solutions rapidly become turbid and precipitates soon form.

The reaction of $Ni(NO_3)_2 \cdot 6H_2O$ and 5-phenyltetrazole in absolute alcohol imparts a rather intense blue color to the solution. Although the solution becomes dark blue as soon as ethanol solutions of the reactants are mixed, maximum absorbancy of the solution is not attained until at least 24 hours after mixing. Unfortunately, other 5-aryltetrazoles react with $NiNO_3 \cdot 6H_2O$ in ethanol to produce solids within a short time after mixing solutions of the reactants.

Mixing solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and 5-phenyltetrazole dissolved in 95% ethanol results in the formation of a pale blue solution which slowly becomes more intensely colored. Other 5-aryltetrazoles react with $Ni(NO_3)_2 \cdot 6H_2O$ in 95% ethanol to produce gelatinous solids.

The most satisfactory solvent used was N, N-dimethylformamide (DMF). In this solvent, 5-aryltetrazoles react with $Ni(NO_3)_2 \cdot 6H_2O$ to yield pale blue to purple solutions. The sodium salts of 5-aryltetrazoles react to give more intensely colored solutions which remain clear indefinitely. The absorbancy of the solutions reaches a maximum constant value in less than 24 hours after the solutions are prepared. Moreover, the nickel salt and the tetrazoles are very soluble in DMF and the sodium salts of the tetrazoles are moderately soluble, which permits studying the reactions over a range of concentrations. Since the density of DMF is very temperature dependent, temperature control is necessary in the preparation of standard solutions in DMF.

Visible Spectra of Nickel-5-phenyltetrazole Complexes in DMF Solution

When the sodium salt of 5-phenyltetrazole dissolved in DMF is added to a DMF solution of $Ni(NO_3)_2 \cdot 6H_2O$, the color of the solution changes from green to purple. The visible spectra of $Ni(NO_3)_2 \cdot 6H_2O$ in DMF and $Ni(NO_3)_2 \cdot 6H_2O$ in DMF with the sodium salt of 5-phenyltetrazole added are shown in Figure 10.

Continuous Variation Studies of 5-Phenyltetrazole Complexes of Nickel

Continuous variation studies of the reaction of $Ni(NO_3)_2 \cdot 6H_2O$ with both 5-phenyltetrazole and the sodium salt of 5-phenyltetrazole were made with DMF as the solvent.

Standard nickel solutions were prepared by weighing approximately the amount of $Ni(NO_3)_2 \cdot 6H_2O$ required and dissolving the salt in DMF. The nickel solution was diluted almost to volume and was then stored at 25° in a constant temperature bath for at least 24 hours. After thermal equilibrium was established, the solutions were diluted to volume with DMF that had also been stored at 25° in the bath. The nickel solutions were standardized by the following procedure. Aliquots of the solution (at 25°) were pipetted into 50 ml. beakers and the solutions were evaporated to dryness on the steam bath.

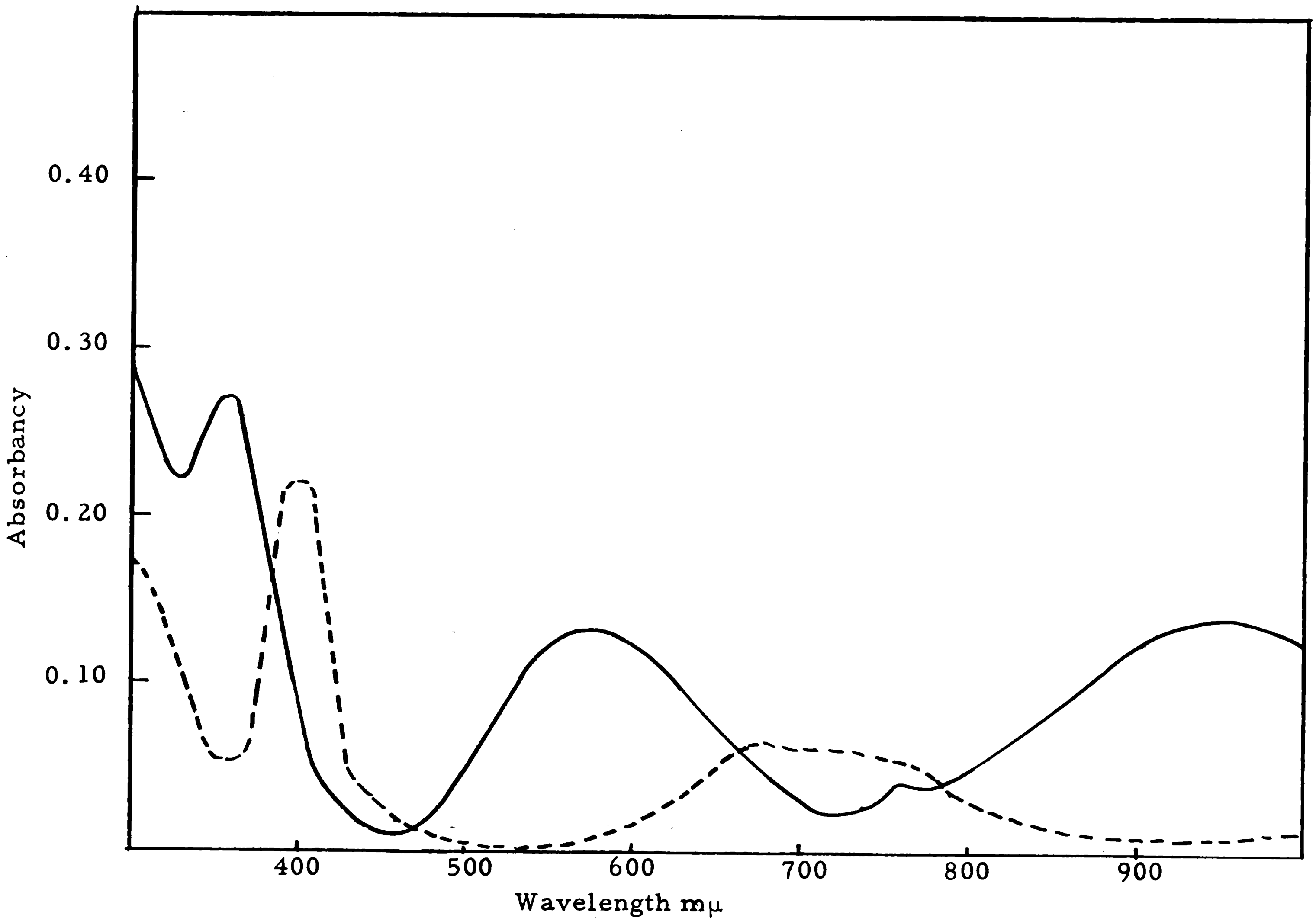


Figure 10. Visible Spectra in DMF
1.37×10^{-2} M $Ni(NO_3)_2 \cdot 6H_2O$ (broken line)
1.37×10^{-2} M $Ni(NO_3)_2 \cdot 6H_2O$ and also 8.0×10^{-2} M in $NaC_7H_5N_4$ (solid line)

The residues were dissolved in distilled water, slightly acidified with nitric acid. The nickel content of the sample solutions was determined gravimetrically as the dimethylglyoxime precipitate.

Standard DMF solutions of the tetrazoles and their sodium salts were prepared by a similar technique after weighing the exact amount of tetrazole required.

The reaction of $Ni(NO_3)_2 \cdot 6H_2O$ and sodium 5-phenyltetrazolate was investigated spectrophotometrically by the method of continuous variation. Samples for the study were prepared from standard nickel and tetrazolate solutions prepared at 25°. The standard solutions were removed from the constant temperature bath at least 12 hours before continuous variation samples were to be prepared in order to insure that both solutions would be at room temperature at the time of sample preparation. The samples were prepared by combining x ml. of the nickel solution and 10-x ml. of the tetrazolate solution in a 25 ml. volumetric flask and diluting the sample to 25 ml. with DMF. The volumes of the nickel and tetrazolate solutions were conveniently measured by using a 10 ml. buret. The sample flasks were then stoppered and allowed to stand 48 hours before the absorbancy of each samples was measured at 570 mμ. The measurements were made using five cm. absorption cells in a Beckman DU spectrophotometer.

The excess absorbancy, i.e. the absorbancy of the sample minus the absorbancy of a $Ni(NO_3)_2 \cdot 6H_2O$ solution of equal nickel concentration, was calculated for the samples. A graph was prepared by plotting excess absorbancy versus tetrazolate/nickel molar ratio. The results of this study are shown in Figure 11.

The use of a hydrated nickel salt in the continuous variation experiment described above introduces a varying amount of water in the samples. It was desirable to determine whether this varying

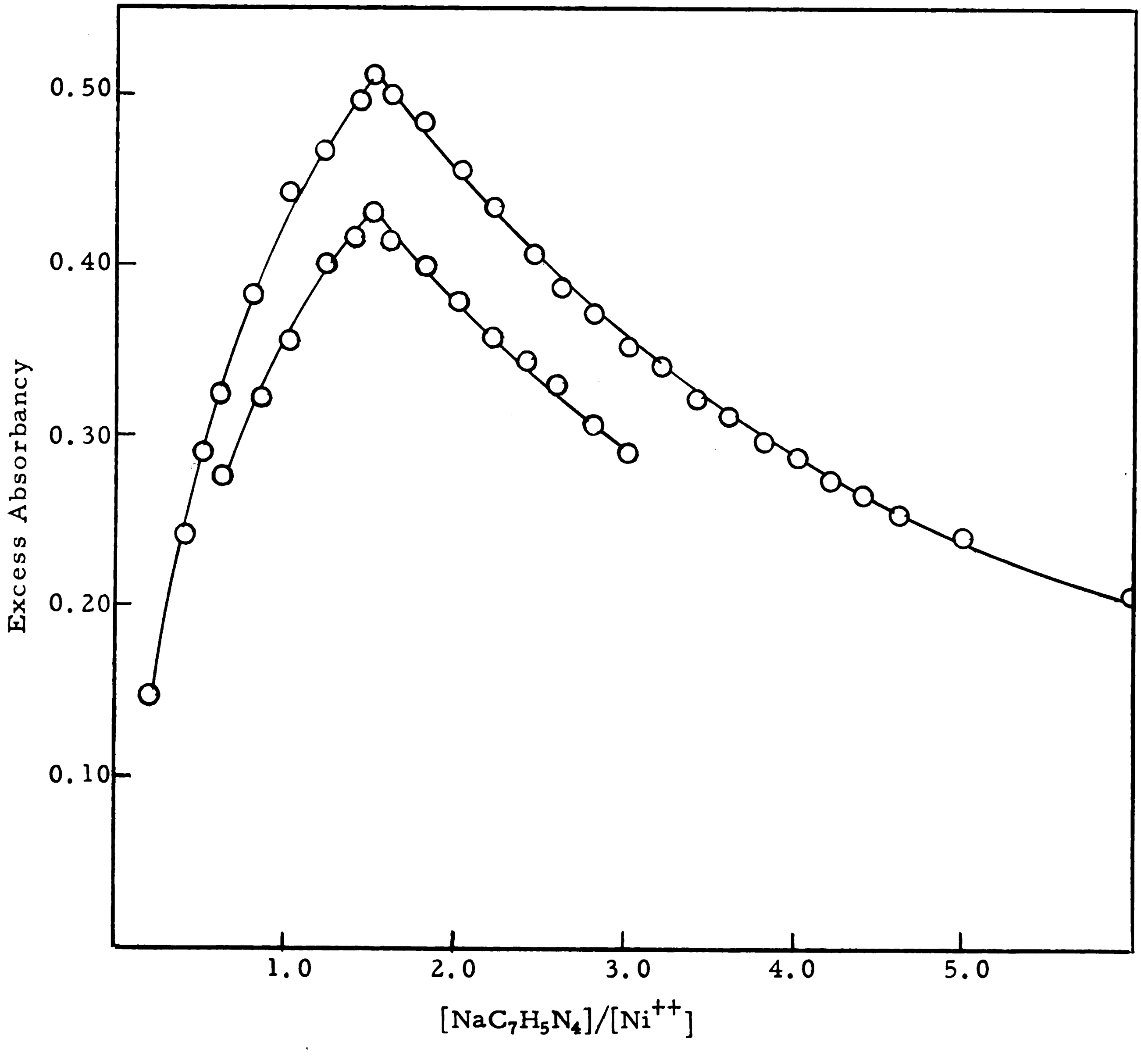


Figure 11. Continuous variation study of $Ni(NO_3)_2 \cdot 6H_2O$ and sodium 5-phenyltetrazolate. Total molarity = 3.44×10^{-2} $\underline{M}$. Upper Curve - DMF solvent. Lower Curve - 96% Aqueous DMF solvent.

amount of water had any influence on the position of the maximum observed in the graph of excess absorbancy versus tetrazolate/nickel mole ratio. Therefore, another set of samples was prepared containing the same amounts of nickel and tetrazolate solutions as previously, but also containing one ml. of water. As can be seen by Figure 11, addition of water to the samples decreases the absorbancy of the samples but does not change the position of maximum absorbancy. The graph of excess absorbancy versus tetrazolate to nickel mole ratio shows a single, rather sharp, maximum at a ratio of 1.5, suggesting that the complex in solution has the formula $[Ni_2(C_7H_5N_4)_3]_x^+$.

The reaction of $Ni(NO_3)_2 \cdot 6H_2O$ and 5-phenyltetrazole in DMF was also studied by the method of continuous variation. The technique described for the experiments using the sodium salt was also employed with 5-phenyltetrazole. Since the color of the sample solutions is less intense when the tetrazole is used in place of its sodium salt, higher concentrations of metal and tetrazole were used in the preparation of the samples containing added water. A graph of the mole ratio of tetrazole/nickel versus excess absorbancy shows a broad maximum extending from a $[C_7H_6N_4]/[Ni^{++}]$ of 1.0 to 2.4.

The Absorbancy of $Ni(NO_3)_2 \cdot 6H_2O$ Solutions in DMF as a Function of the Concentration of Various Tetrazoles and Their Sodium Salts

The absorbancies of nickel solutions in DMF as a function of the concentration of various tetrazoles and their sodium salts were measured in an attempt to determine formation constants for the nickel complexes.

Standard solutions were prepared in the manner described for the continuous variation studies. The standard solutions were stored in a water bath maintained at 25°.

Samples were prepared by pipetting an aliquot of standard nickel solution stored at 25° into a 25 ml. volumetric flask. An aliquot of the tetrazole (or sodium tetrazolate) solution also stored at 25° was pipetted into the flask. The sample was diluted to within a few drops of 25 ml., was stoppered, and was placed in the bath for 24 hours. After 24 hours, the sample was removed from the bath and immediately diluted to volume. The samples were then placed back in the bath for another 24 hours.

The absorbancies of the samples were measured at the desired wavelength 48 hours after the samples had been prepared. The measurements were made with a Beckman DU spectrophotometer using five cm. absorption cells. Because five cm. cells were used, the cell compartment was not thermostated, but all measurements were made within 120 ± 5 seconds after a sample was removed from the bath. Duplicate runs gave excellent agreement. Spectrophotometric data for various concentrations of the sodium salts of some 5-aryltetrazoles added to $Ni(NO_3)_2 \cdot 6H_2O$ in DMF are given in Tables 14 and 15. The wavelengths at which the measurements were taken are the wavelengths of maximum absorption in the region 500-600 $m\mu$ as determined from the visible spectrum of a solution 1.03×10^{-2} $\underline{M}$ in $Ni(NO_3)_2 \cdot 6H_2O$ and 4.0×10^{-2} $\underline{M}$ in the sodium salt of each tetrazole.

Attempts to calculate stability constants from the spectrophotometric data in Tables 14 and 15 were unsuccessful. These attempts will be discussed in the Appendix. If the data in Table 15 is presented in the form of a graph of absorbancy versus concentration of the sodium tetrazolates (Figures 12, 13, 14, and 15) it is interesting to note that a linear relationship exists in each case for tetrazolate/nickel molar ratios of 1.5 or less, but that the relationship rapidly departs from linearity after the 1.5 ratio is reached.

Table 14. Absorbancies of 6.87×10^{-3} $\underline{M}$ $Ni(NO_3)_2 \cdot 6H_2O$ and Various Quantities of Sodium 5-Aryltetrazolates in DMF at 25°. Tetrazole Salt Concentrations are Given in Molarity x 10^3.

Concn. of Na 5 φ CN_4	Absorbancy 570 mμ	Concn. of Na 5-p-Cl-φ CN_4	Absorbancy 560 mμ	Concn. of Na 5-o-Cl-φ CN_4	Absorbancy 570 mμ
0.00	0.013	0.00	0.008	0.00	0.013
2.00	0.063	2.00	0.051	2.00	0.062
3.00	0.088	3.00	0.069	3.00	0.088
4.00	0.113	4.00	0.092	4.00	0.114
5.00	0.140	5.00	0.113	5.00	0.143
6.00	0.165	6.00	0.136	6.00	0.162
7.00	0.192	7.00	0.156	7.00	0.187
8.00	0.216	8.00	0.183	8.00	0.210
10.00	0.269	10.00	0.225	10.00	0.260
14.00	0.295	14.00	0.287	14.00	0.284
20.00	0.300	20.00	0.312	20.00	0.287
30.00	0.306	30.00	0.319	30.00	0.300
40.00	0.307	40.00	0.321	40.00	0.305

Table 15. Absorbancies of 1.03 x 10^{-2} $\underline{M}$ $Ni(NO_3)_2 \cdot 6H_2O$ and Various Quantities of Sodium 5-Aryltetrazolates in DMF at 25°. Tetrazole Salt Concentrations Given in Molarity x 10^3.

Concn. of Na ϕ CN_4	Absorbancy 570 mμ	Concn. of Na o-Cl-ϕ CN_4	Absorbancy 570 mμ	Concn. of Na p-Cl-ϕ CN_4	Absorbancy 560 mμ	Concn. of Na p CH_3O-ϕ CN_4	Absorbancy 560 mμ
0.00	0.021	0.00	0.020	0.00	0.012	0.00	0.013
2.50	0.082						
3.00	0.095	3.00	0.091	3.00	0.077	3.00	0.076
3.50	0.110						
4.00	0.120	4.00	0.116	4.00	0.101	4.00	0.098
4.50	0.135						
5.00	0.147	5.00	0.138	5.00	0.118	5.00	0.131
6.00	0.171						
7.50	0.210	7.00	0.185	7.00	0.160	7.00	0.168
8.50	0.239	8.00	0.211	8.00	0.186	8.00	0.190
10.00	0.281	10.00	0.260	10.00	0.222	10.00	0.235
12.00	0.328	12.00	0.308	12.00	0.273	12.00	0.278
14.00	0.380	14.00	0.356	14.00	0.320	14.00	0.326
16.00	0.420	16.00	0.400	16.00	0.365	16.00	0.369
18.00	0.432	18.00	0.411	18.00	0.396	18.00	0.408
20.00	0.442	20.00	0.418	20.00	0.422	20.00	0.432
24.00	0.451	24.00	0.425	24.00	0.455	24.00	0.455
30.00	0.453	30.00	0.432	30.00	0.466	30.00	0.466
40.00	0.453	40.00	0.442	40.00	0.471	40.00	0.475

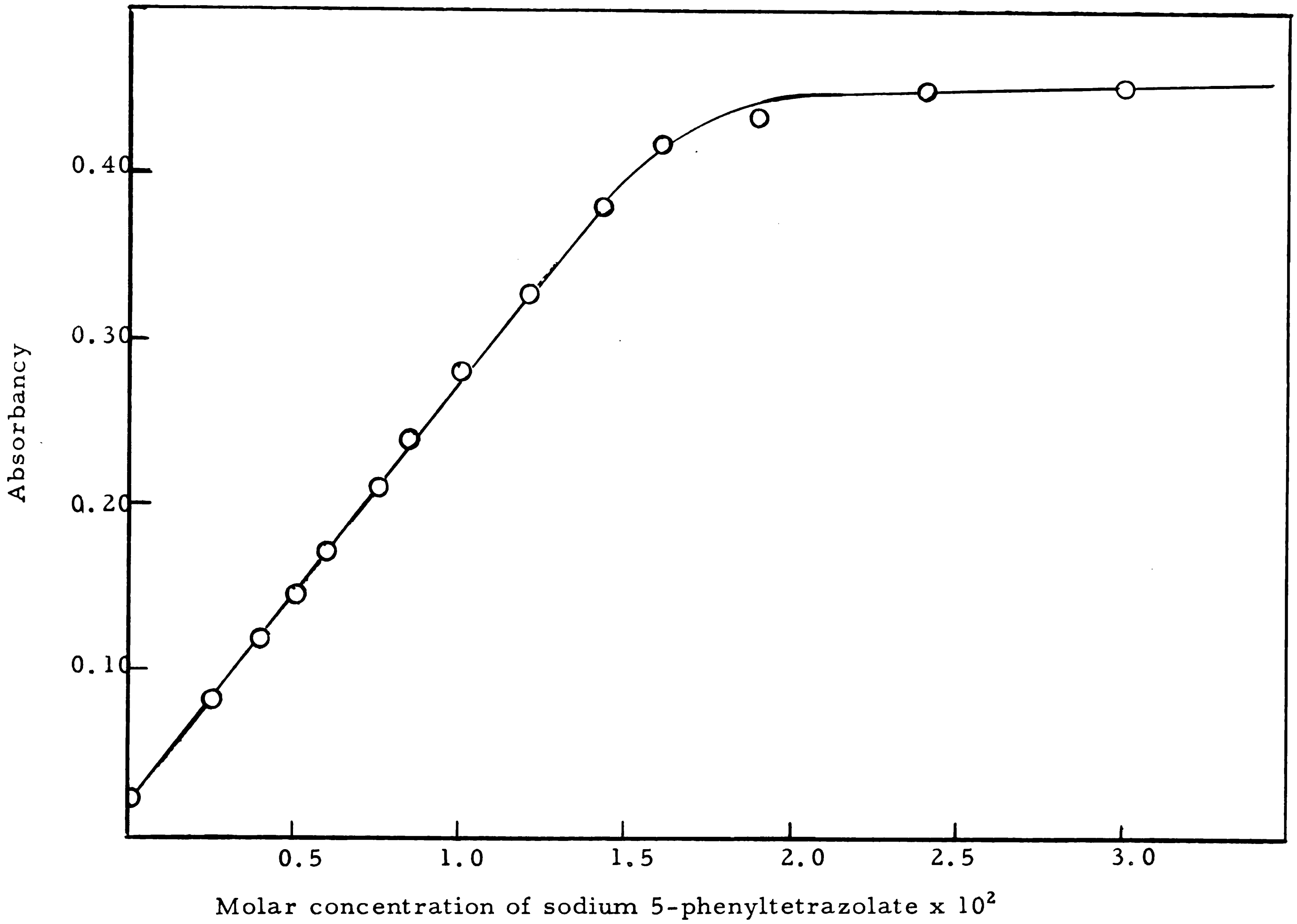


Figure 12. Absorbancy of 1.03 x 10^{-2} $\underline{M}$ $Ni(NO_3)_2 \cdot 6H_2O$ in DMF with Various Concentrations of Sodium 5-phenyltetrazolate.

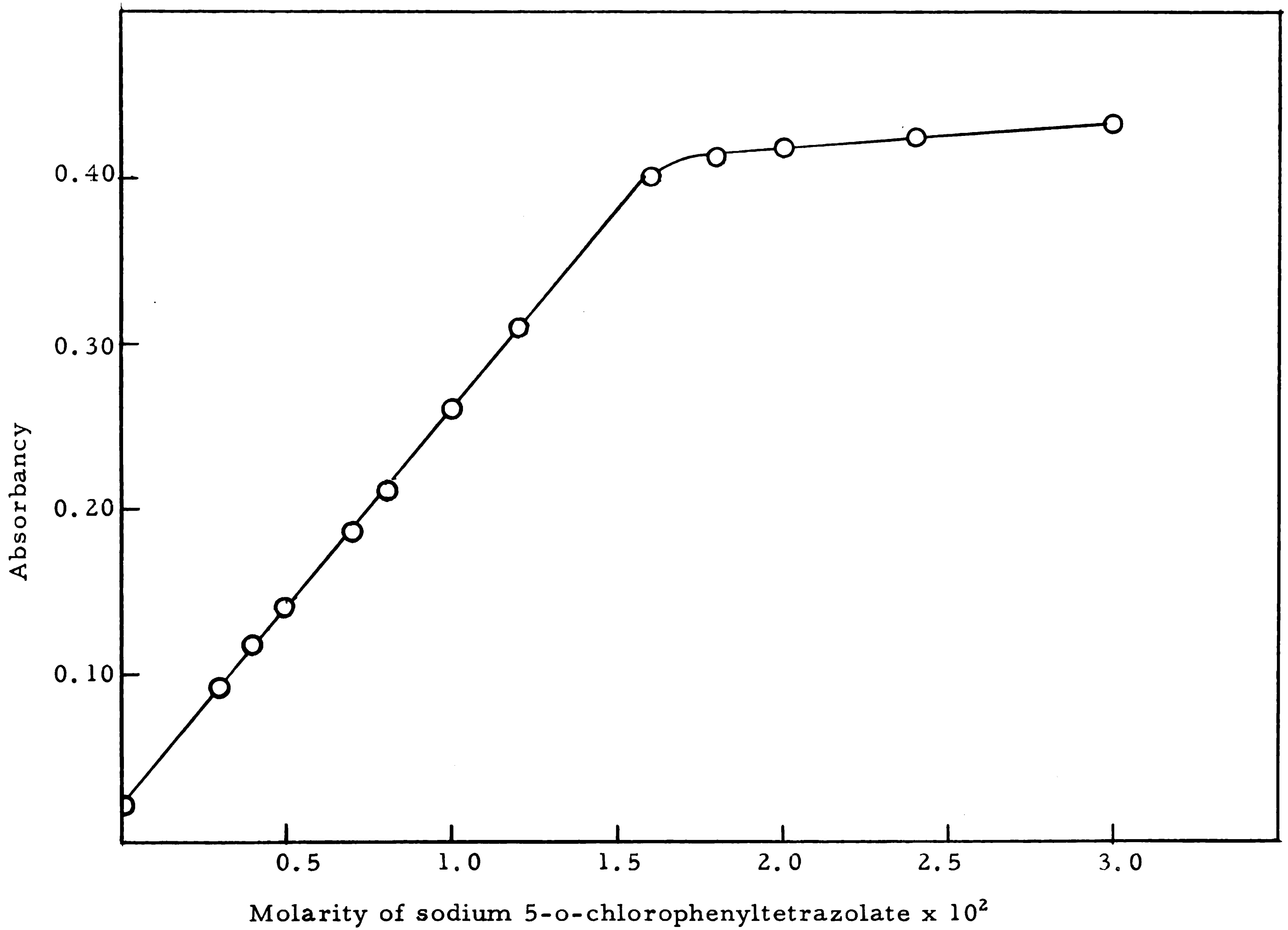


Figure 13. Absorbancy of 1.03 x 10^{-2} $\underline{M}$ $Ni(NO_3)_2 \cdot 6H_2O$ in DMF with Various Concentrations of Sodium 5-o-chlorophenyltetrazolate.

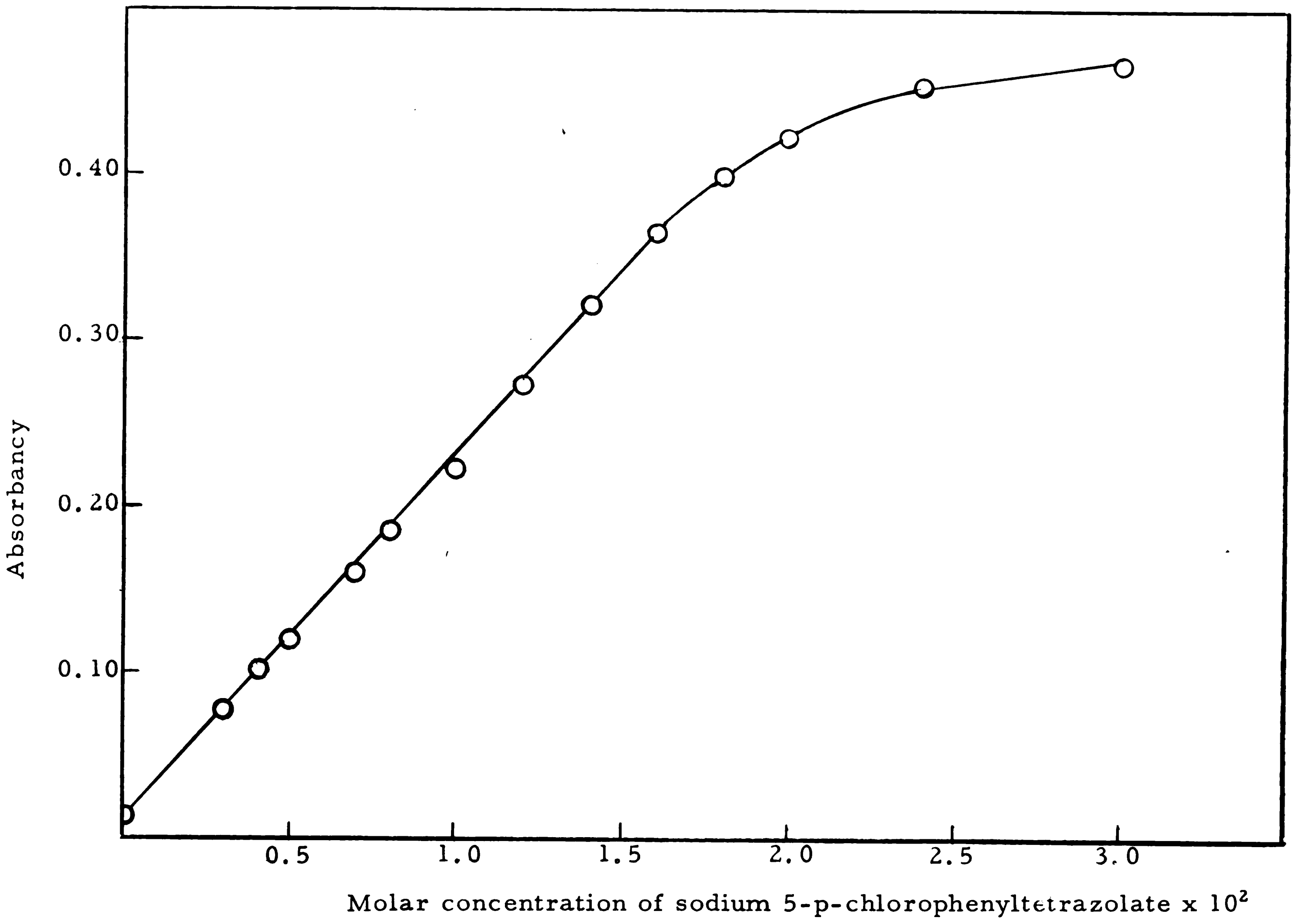


Figure 14. Absorbancy of 1.03 x 10^{-2} $\underline{M}$ $Ni(NO_3)_2 \cdot 6H_2O$ in DMF with Various Concentrations of Sodium 5-p-chlorophenyltetrazolate.

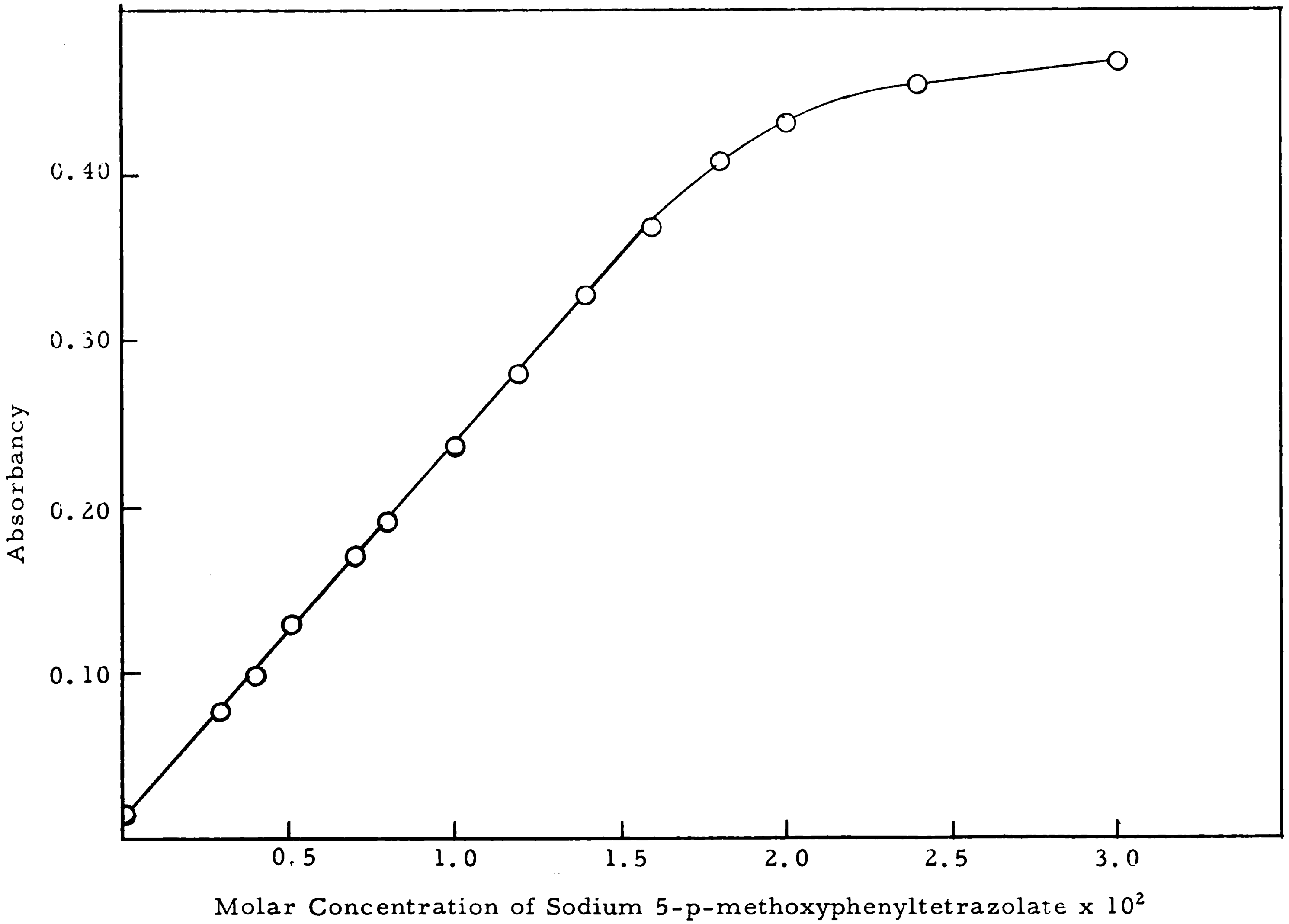


Figure 15. Absorbancy of 1.03 x 10^{-2} $\underline{M}$ $Ni(NO_3)_2 \cdot 6H_2O$ in DMF with Various Concentrations of Sodium 5-p-Methoxyphenyltetrazolate.

Similar spectrophotometric data were obtained using the tetrazoles in place of their sodium salts. The results are given in Table 16. The absorbancies were calculated from per cent transmissions obtained experimentally.

Although 5-phenyltetrazole and sodium 5-phenyltetrazolate both react with $Ni(NO_3)_2 \cdot 6H_2O$ in DMF to produce purple solutions, the complexes formed in the two reactions are not necessarily the same. It is possible that 5-phenyltetrazole could coordinate with nickel ion without losing the hydrogen (as H^+) bonded to the tetrazole ring. If coordination of 5-phenyltetrazole with nickel ion does occur without producing H^+ as one of the products, then the nickel complex produced from the reaction of $Ni(NO_3)_2 \cdot 6H_2O$ and 5-phenyltetrazole is different from the complex formed from $Ni(NO_3)_2 \cdot 6H_2O$ and sodium 5-phenyltetrazolate. Therefore it was of interest to determine whether $Ni(NO_3)_2 \cdot 6H_2O$ reacts with 5-phenyltetrazole in DMF to produce H^+.

Although pH meter readings in DMF can not be used directly to calculate the molar concentration of H^+, meter readings for DMF containing a few drops of dilute HCl are much lower than meter readings taken in pure DMF. Therefore, a pH meter could be used to detect changes of H^+ concentration in DMF.

A series of sample pairs was prepared (in DMF) in which one member of a given pair was 1.03×10^{-2} $\underline{M}$ in $Ni(NO_3)_2 \cdot 6H_2O$ and contained a given amount of 5-phenyltetrazole and the other member of the pair contained only an equal amount of 5-phenyltetrazole. The "pH"s of the samples were measured using a Beckman model G pH meter. The electrodes were rinsed with DMF and wiped dry with absorbent tissue between each reading. For each sample pair, the sample containing $Ni(NO_3)_2 \cdot 6H_2O$ as well as 5-phenyltetrazole had a lower "pH."

The samples which contained nickel ion also contained small amounts of water. It was calculated that the amount of water in the samples containing nickel ion was about 0.03 ml. of water/25 ml. sample.

'able 16. Absorbancies of 1.03 x 10^{-2} $\underline{M}$ $Ni(NO_3)_2 \cdot 6H_2O$ and Various Quantities of 5-Aryltetrazoles in DMF at 25°. Tetrazole Concentrations are Molarity x 10^2.

ncn. of -ϕ CN_4H	Absorbancy 570 mμ	Concn. of 5-o-Cl ϕ CN_4H	Absorbancy 570 mμ	Concn. of 5-p Cl ϕ CN_4H	Absorbancy 560 mμ	Concn. of 5-p CH_3O ϕ CN_4H	Absorbancy 560 mμ
0.00	0.020	0.00	0.020	0.00	0.013	0.00	0.013
2.00	0.063	2.00	0.093	2.00	0.063	2.00	0.046
2.80	0.071	2.80	0.109	2.80	0.073	2.80	0.048
3.20	0.075	3.20	0.118	3.20	0.077	3.20	0.050
3.60	0.077	3.60	0.120	3.60	0.081	3.60	0.052
4.00	0.082	4.00	0.131	4.00	0.086	4.00	0.057
5.20	0.091	5.20	0.148	5.20	0.095	5.20	0.058
6.00	0.095	6.00	0.154	6.00	0.100	6.00	0.061
8.00	0.101	8.00	0.172	8.00	0.114	8.00	0.072

It was possible that the samples containing nickel ion had lower "pH"s than the samples containing only an equal amount of the tetrazole (but no nickel ion) because of the presence of water in those samples which contained $Ni(NO_3)_2 \cdot 6H_2O$. However, when 0.05 ml. of water was added to 10 ml. of 2.80×10^{-2} M 5-phenyltetrazole in DMF, the "pH" decreased only 0.10 "pH" unit. The results of the experiment are given in Table 17.

Table 17. Qualitative Determination of H^+ Production in the Reaction of $Ni(NO_3)_2 \cdot 6H_2O$ and 5-Phenyltetrazole in DMF.

10^2 x Concentration of $Ni(NO_3)_2 \cdot 6H_2O$ (Molar)	10^2 x Concentration of 5-Phenyltetrazole (Molar)	pH Meter Reading
1.03	0.00	8.49
0.00	2.00	6.28
1.03	2.00	3.04
0.00	2.80	6.02
1.03	2.80	2.95
0.00	4.00	5.85
1.03	4.00	2.85
0.00	0.00	11.95

There seems to be little doubt that the reaction of $Ni(NO_3)_2 \cdot 6H_2O$ with 5-phenyltetrazole produces H^+ as one of the products.

Solid Nickel (II) Complexes

Solid Nickel-5-phenyltetrazole Complexes

Solid complexes of nickel and 5-phenyltetrazole were prepared by two different methods. Neither method yielded a well characterized solid.

The starting materials for one preparation were 0.10 M solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and 5-phenyltetrazole dissolved in isopropyl alcohol. When 100 ml. of 0.10 M 5-phenyltetrazole solution was mixed with 50 ml. of 0.10 M $Ni(NO_3)_2 \cdot 6H_2O$, a dark blue solution was produced which turned cloudy within a few seconds. The mixture was allowed to stand 24 hours during which time a dark blue gelatinous precipitate separated. The solid was separated from the supernatant solution by centrifugation. The solid was washed with small portions of isopropyl alcohol and recentrifuged several times, but the solid could not be washed free of nitrate.

After being dried the solid was light blue and was analyzed for metal and tetrazolate content. The results were 16.7% Ni and 72.2% $C_7H_5N_4^-$ indicating 1.76 tetrazoles per nickel.

The second method of preparation involved the use of the sodium salt of 5-phenyltetrazole and $Ni(NO_3)_2 \cdot 6H_2O$ in DMF. In a 100 ml. flask 45 ml. of 0.190 M $NaC_7H_5N_4$ and 30 ml. of 0.190 M $Ni(NO_3)_2 \cdot 6H_2O$ were combined. A dark blue solution was obtained. The solution remained clear and no solid separated up to 24 hours after mixing. The solution was then evaporated to dryness under an air jet. The dry residue consisted of a dark blue solid and a white solid.

The dry residue was extracted twice with 25 ml. portions of acetone. The acetone extracts were filtered yielding a dark blue filtrate and a white insoluble residue. The dark blue filtrate was slowly evaporated to dryness by placing the solution in a beaker, covering the beaker with a watch glass, and allowing it to stand overnight at room temperature. Evaporation of the acetone left a dark blue solid which covered the sides and bottom of the beaker in a continuous sheet. This extraction, filtration, and evaporation procedure was repeated three times using successively 25, 20, and 15 ml. of dry acetone. The final evaporation left a dark blue solid which turned light blue after being dried in vacuo over magnesium perchlorate. The solid contained 16.8% Ni and 76.5% $C_7H_5N_4^-$ indicating a composition of 1.84 tetrazoles per nickel.

These two solids, prepared by different methods, have similar solubilities; they both are soluble in DMF, acetone, and methyl cellosolve (monomethyl ether of ethyleneglycol), and are insoluble in water, ethanol, glacial acetic acid, ethylacetate, benzene, dioxane, and chloroform. Not only do the solids have similar analyses, and solubilities, but their infra-red spectra are nearly identical, suggesting that the two solids are the same.

Other Nickel-Tetrazole Complexes Obtained as Solids

Solid nickel complexes of tetrazole, 5-methyltetrazole, 5-p-methoxyphenyltetrazole, and 5-p-nitrophenyltetrazole were prepared. All of the complexes were prepared by mixing 100 ml. of absolute ethanol, containing .010 mole of the tetrazole, with 50 ml. of 0.10 M $Ni(NO_3)_2 \cdot 6H_2O$ in absolute alcohol. In each case, the blue solution produced, rapidly became cloudy and a solid phase separated. The gelatinous solids were separated from the mother liquor by centrifuging and were washed several times with small portions of absolute ethanol. The solids could not be washed free of nitrate. The solids were dried in vacuo over magnesium perchlorate. All of the complexes were obtained as amorphous solids and were rather poorly characterized. Their infra-red spectra generally showed broad bands rather than the sharp peaks observed with copper complexes.

The Nickel Complex of Tetrazole

The nickel complex of tetrazole was obtained as a purple solid containing 27.0% Ni and 56.0% CN_4H^- which indicates there are 1.66 tetrazoles bound per nickel ion. The complex is slightly soluble in water and is insoluble in ethanol, DMF, acetone, acetic acid, methylcellosolve, acetonitrite, ethylacetate, benzene, dioxane and chloroform.

The Nickel Complex of 5-p-Nitrophenyltetrazole

The dried complex is a pale green solid which is very hygroscopic and turns purple after a few seconds contact with moist air. A tetrazole to nickel molar ratio of 1.88 is calculated from the composition of 13.5% Ni, 82.3% $C_7H_4N_5O_2^-$.

The green solid is soluble in DMF, acetone, methylcellosolve, and acetonitrile. It is insoluble in water ethanol, acetic acid, ethylacetate, benzene, dioxane, and chloroform.

The Nickel Complex of 5-p-Methoxyphenyltetrazole

Nickel nitrate reacts with 5-p-methoxyphenyltetrazole in ethanol to give a light blue-grey solid in poor yield. After drying, analysis of the solid gives a composition of 15.5% Ni and 88.5% $C_8H_7N_4O^-$ corresponding to a tetrazole to nickel molar ratio of 1.91.

The Nickel Complex of 5-Methyltetrazole

The complex was obtained as a powder-blue solid. Analysis of the dried sample for nickel and tetrazolate gives a composition which closely corresponds to a formula of $Ni_2(C_2N_4H_3)_3NO_3$. Calculated for $Ni_2(C_2N_4H_3)_3NO_3$: Ni, 26.4%; $C_2N_4H_3^-$, 55.8%. Found: Ni, 26.4%; $C_2N_4H_3^-$, 56.1%. An aqueous solution of the solid does give a positive test for nitrate which lends feeble support for suggesting the formula $Ni_2(C_2N_4H_3)_3NO_3$. However, since most of the nickel complexes are poorly characterized, the nitrate may very well be present simply as occluded nickel salt and the agreement of the analytical data with the proposed formula is probably fortuitous. The solid soluble in water, and insoluble in ethanol, DMF, acetone, acetic acid, methylcellosolve, acetonitrile, ethylacetate, benzene, dioxane, and chloroform.

III. RESULTS AND DISCUSSION

As a part of this study, the crystalline, copper complexes of several 5-substituted tetrazoles were prepared and characterized. Some of these solids, such as the complexes of 5-phenyltetrazole, are well characterized and have a definite stoichiometry. On the other hand, the exact nature of the copper complexes of 5-cyclohexyltetrazole and 5-p-tolyltetrazole is unknown.

One of the experimental difficulties in producing pure, solid complexes is that no method for purification of the solids has yet been found. The solids can not be recrystallized because they are insoluble in a wide variety of solvents such as water, alcohols, DMF, benzene, dioxane, acetone, acetonitrile, chloroform, and ethylacetate. The complexes are soluble in acids and aqueous or liquid ammonia but dissolve with destruction of the complex. The solids decompose when heated and can not be distilled or sublimed. Even washing the solids with excess solvent has been known to convert one crystalline form of a complex to another (41) or to result in extensive hydrolysis of the complex.

The type of preparation which gives the purest product is one in which the complex slowly crystallizes from a solution produced by mixing solutions of a copper salt and the desired tetrazole. If deposition of the solid is too rapid, the product almost always contains occluded impurities which are difficult to remove. The choice of the copper salt and of the solvent is important. Moreover, a particular copper salt and solvent may give a pure product with a given tetrazole, but may not be at all useful in the preparation of complexes of a different tetrazole. For example, $CuSO_4 \cdot 5H_2O$ and 5-phenyltetrazole react in methanol to give a well characterized product, but $CuSO_4 \cdot 5H_2O$ and 5-aminotetrazole react in water or methanol to give impure products containing occluded $CuSO_4$.

The hydrogen, bound to the ring nitrogens of a 5-monosubstituted tetrazole, is weakly acidic. Examination of analytical results for the complexes as well as comparison of the infra-red spectra of the complexes with the spectra of the free tetrazoles and their sodium salts clearly indicates that 5-monosubstituted tetrazoles coordinate as the anion. However, Brubaker (41) and Popov (40) have reported that tetrazoles which have the ring hydrogen replaced by an alkyl group also coordinate with metal ions. Therefore, loss of the ring hydrogen is not necessary in order for coordination to occur.

The sensitivity of the reactions of cupric ion and tetrazoles to slight changes in the nature of the solvent and to the anion of the copper salt suggests that these reactions may be rather complicated. The exact mechanism of the coordination reaction is unknown, but some interesting observations have been made.

The maximum number of tetrazoles that can coordinate to a cupric ion appears to be two. Most likely coordination occurs stepwise with the formation of an intermediate 1:1 copper-tetrazole complex. Continuous variation experiments in the $CuSO_4 \cdot 5H_2O$-5-phenyltetrazole system point to the formation of a 1:1 complex in solution. In fact, one such complex, chloro(5-phenyltetrazolato)copper (II) has been isolated as a solid. Some of the data on anion effects can also best be interpreted in terms of the formation of a mixed chloro-tetrazolato complex. However, Brubaker (41) reported that he could find no evidence for the formation of a 1:1 copper-5-aminotetrazole complex.

The effects of various anions in producing turbidity in solutions containing 5-aminotetrazole and $Cu(NO_3)_2$ were investigated.

Although the anion effect is not well understood, there seems to be little doubt that it is neither an acid-base phenomena nor is it entirely a coagulation phenomena.

The addition of chloride ion to $Cu(NO_3)_2$ solutions before the addition of 5-aminotetrazole is more effective in producing turbidity than the addition of chloride ion to solutions of $Cu(NO_3)_2$ which already contain 5-aminotetrazole. Increasing the concentration of chloride added to $Cu(NO_3)_2$ solutions before the addition of 5-aminotetrazole, increases both the rate of formation of turbidity and the total amount of turbidity. The fact that increasing chloride concentration increases the amount of solid suspended suggests that chloride ion is contained in the solid. Chloride ion forms a weak complex with cupric ion, the stability constant for the first chloro complex being 6.3×10^2 (49). It is possible that the addition of chloride ion to $Cu(NO_3)_2$-CN_5H_3 solutions produces turbidity due to the formation of an insoluble, mixed chloro-5-aminotetrazolate complex according to the reactions

$$(1)\quad Cu^{++} + Cl^- \rightleftarrows CuCl^+$$

$$(2)\quad CuCl^+ + CN_5H_3 \rightleftarrows \underline{Cu(CN_5H_2)Cl} + H^+$$

The above reaction sequence is purely speculative, but it does fit the experimental facts. It is known that the equilibrium constant for reaction (1) is rather small. If the magnitude of the equilibrium constant for reaction (2) is also not very large, then one would expect that fairly large quantities of chloride ($[Cl^-] \geq [Cu^{++}]$) would be needed to produce much turbidity. One would also expect that increasing the chloride ion concentration would drive both reactions to the right and would increase the amount of solid.

If the CN_5H_3 is added before chloride is added to the system, most of the copper ion and tetrazole are bound as $Cu(CN_5H_2)_2$. Formation of the mixed chloro-tetrazolato complex could take place either by a dissociative mechanism

$$(3)\quad Cu(CN_5H_2)_2 \rightleftarrows Cu(CN_5H_2)^+ + CN_5H_2^-$$

$$(4)\quad Cu(CN_5H_2)^+ + Cl^- \rightleftarrows \underline{Cu(CN_5H_2)Cl}$$

or by direct attack of Cl^- on the $Cu(CN_5H_2)_2$ complex

$$(5)\ Cu(CN_5H_2)_2 + Cl^- \rightleftarrows Cu(CN_5H_2)Cl + CN_5H_2^-$$

A difference in the rates of reactions (1) and (2) as compared to reactions (3) and (4), or (5) may explain the greater apparent effectiveness of adding chloride ion before CN_5H_3 is added. If the samples had been observed for longer periods of time, the amounts of solid produced in the "before" and "after" cases might have been equal.

It is quite likely that the effect of added chloride is a much more complicated process. For example, mixing solutions of $CuCl_2$ and CN_5H_3 immediately produces a solid which appears to be mostly $Cu(CN_5H_2)_2$. Perhaps then, chloride ion produces turbidity in solutions of $Cu(NO_3)_2$ and CN_5H_3 by first producing an insoluble intermediate which also may act as a nucleation site for the crystallization of $Cu(CN_5H_2)_2$.

The effect of adding $SO_4^=$ to solutions of $Cu(NO_3)_2$ and CN_5H_3 is even more difficult to explain. Since the addition of $SO_4^=$ "after" the addition of CN_5H_3 seems to be more effective in the formation of solids and also because $SO_4^=$ is effective in much smaller amounts than chloride, it is possible that $SO_4^=$ produces turbidity by a different mechanism than the mechanism for chloride.

It should be pointed out that the anion effect is not limited to the reactions of cupric ion and 5-aminotetrazole. For example, $Cu(NO_3)_2 \cdot 3H_2O$ and 5-phenyltetrazole react in 95% ethanol to immediately produce a solid but the reaction of $CuCl_2 \cdot 2H_2O$ and 5-phenyltetrazole in the same solvent takes several hours to produce any significant amount of solid (neither solid contains more than a trace of the anion of the copper salt used). The anion effect seems to be a widely distributed phenomena in the reaction of metal salts and tetrazoles.

In those reactions in which solutions of the reactants are mixed to yield an intensely colored, clear, solution from which the complex crystallizes after several hours or days, it is interesting to note that the color of the solution reaches a maximum constant intensity during the time required to mix the reactant solutions. It appears as if a complex is fully formed at once and then may slowly rearrange to the insoluble, crystalline form. In the case of 5-phenyltetrazole where a 1:1 interaction in solution is indicated by continuous variation, it is possible that a soluble 1:1 copper:tetrazole complex is formed rapidly, followed by the slow coordination of a second tetrazole to give an insoluble complex.

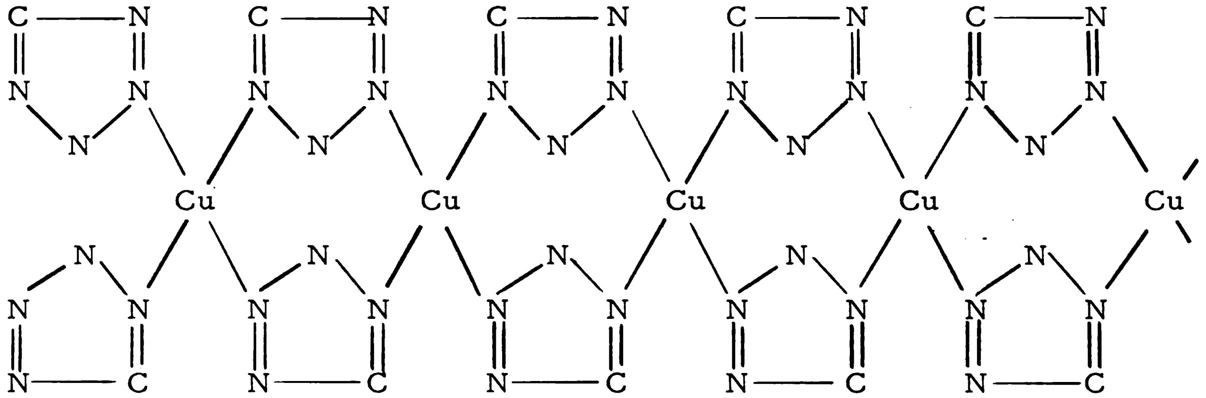
The structure of the crystalline tetrazole complexes of copper is unknown. The X-ray powder patterns of the solids indicate that the unit cell is large. A complete structure determination from X-ray data is beyond the scope of the present investigation. However, a consideration of some possible structures is interesting.

There are a number of ways that coordination between metal ions and tetrazoles could occur. Perhaps the simplest type of bonding would be simple donation of an electron pair by one of the nitrogen atoms of the tetrazole ring to the metal ion. If bonding occurred in this manner, one might expect copper to exhibit a coordination number of four in these complexes. The maximum coordination number observed for copper in tetrazole complexes is two; although copper ion readily coordinates with four imidazole molecules.

The tetrazolate anion seems to satisfy two coordination sites on the copper ion. Coordination may involve two distinct nitrogen atoms of the tetrazole ring. Coordination probably would not involve two adjacent nitrogen atoms of the tetrazole ring which means that the tetrazole ring probably is not coplanar with the copper ion.

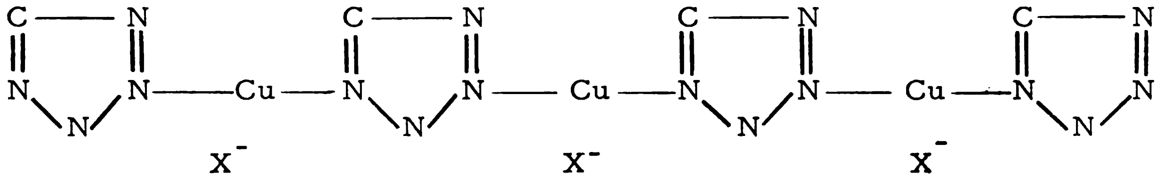
Another possible mode of bonding, similar to the bonding in ferrocene, is coordination of the metal ion to the π electron system of the tetrazolate ion. If this type of bonding were encountered, one might expect the copper complexes to be soluble in organic solvents.

In fact, the almost complete lack of solubility of the copper complexes in a wide variety of solvents might suggest a polymeric structure in the solid. Complexes of the general formula CuT_2, where T represents a tetrazolate anion, can be visualized as forming ribbon or sheet polymers. The ribbon structure could be pictured as



in which each tetrazolate ion is shared by two copper ions.

In a similar manner the mixed hydroxo or chloro-5-phenyltetrazole complexes of copper might be pictured as a copper ion-tetrazolate chain in which the chloride or hydroxide ion is present simply to neutralize the charge.



Of course, these polymeric structures are purely speculative, but it seems as if such structures are not beyond the realm of possibility.

Magnetic measurements on the dark green copper complex of 5-aminotetrazole, $Cu(CN_5H_2)_2 \frac{1}{2}H_2O$, indicate the presence of one unpaired electron on the copper ion.

It is difficult to account for the unusual reactions of 5-p-nitrophenyltetrazole and 5-p-chlorophenyltetrazole with $CuSO_4 \cdot 5H_2O$ in methanol solution. Under similar reaction conditions, 5-o-chlorophenyltetrazole, 5-phenyltetrazole and other 5-aryltetrazoles react to give complexes of the formula CuT_2, but 5-p-chloro and 5-p-nitrophenyltetrazole react to give complexes of the general formula $Cu_2T_2SO_4 \cdot 2H_2O$. The acidities of the latter two tetrazoles does not differ greatly from the acidities of the other tetrazoles nor is it readily apparent how a group in the para position on the phenyl ring could influence sterically coordination to the tetrazole ring.

The copper complexes of tetrazoles are at least partially soluble in acids. The complexes are reprecipitated upon neutralization of the acid. The reaction involved is probably the reverse reaction of complex formation

$$CuT_2 + 2H^+ \rightleftarrows Cu^{++} + 2HT$$

The equilibrium is shifted to the right by the addition of excess H^+. The only complex which appears to react in an unusual manner with acids is the light green copper complex of 5-aminotetrazole. Treatment of this complex with dilute acids at room temperature evolves a small amount of HCN, pointing to cleavage of the tetrazole ring. Although the amount of decomposition apparently is small, it should be pointed out that this is an unusual reaction. It has been reported (50) that 5-aminotetrazole is stable when treated with concentrated hydrochloric acid at 160-170°, but decomposes at 200-210° in the presence of concentrated hydrochloric acid to give CO_2, NH_3, N_2, and N_2H_4. Thiele (51) also has reported that 5-aminotetrazole reacts to give HCN and CO_2 when treated with alkaline permanganate.

The nickel complexes of several tetrazoles were obtained as poorly characterized, amorphous solids. All of the solids were obtained as gelatinous precipitates from which impurities could not easily be removed. One of the experimental difficulties in the attempted preparation of pure, solid, nickel complexes was that a suitable solvent could not be found. In the case of the copper complexes, a judicious choice of solvent and copper salt led to solutions containing the complex from which the complex slowly crystallized in a fairly pure form. In the case of nickel, two situations prevailed. The complex would not crystallize from solution or the complex rapidly precipitated as an impure, gelatinous solid. Evaporation of solutions containing the complex gave heterogeneous mixtures of solids.

Although some of the nickel complexes are soluble in certain solvents, recrystallization is not very efficient because the only way that recrystallization can be accomplished is by almost total evaporation of the solvent. When the nickel complex of 5-phenyltetrazole was recrystallized several times from acetone, the final product appeared to be of no greater purity than when the complex was obtained as a gelatinous solid.

Analytical results show that the solids contain 1.5-1.9 tetrazoles per nickel. The expected tetrazole to nickel ratio was 2:1. Since the solids were generally obtained as gelatinous solids, deviations from the expected tetrazole to nickel ratio can be explained by the presence of occluded nickel salts. However, there is good evidence that in solution species corresponding to the formula $Ni_2T_3^+$ (T = tetrazolate ion) exist. If this and other types of polymeric units also exist in the solid state, tetrazole to nickel ratios of 1.5-1.9 are not unreasonable. Unfortunately the purity of the solids is doubtful and the analytical methods are not sufficiently accurate for definite conclusions to be drawn.

Anion effects similar to those investigated in the $Cu(NO_2)_2$-CN_5H_3 system also were observed in the reactions of tetrazoles with nickel salts.

Analytical results for the complexes and the comparison of the infra-red spectra of the nickel complexes with the spectra of the free tetrazoles and their sodium salts show that tetrazoles also coordinate to nickel as the tetrazolate anion.

The magnetic moment of the nickel complex of 5-aminotetrazole was measured by use of the Gouy technique. The magnetic moment of the complex was calculated to be 3.9 Bohr Magnetons. This value is in considerable doubt because the exact composition of the sample is unknown and the measured density of the sample may not be correct. There is little doubt, however, that the complex is paramagnetic.

A study of some tetrazole complexes of nickel in solution was made. Tetrazoles react with nickel ion in solution to yield blue to purple solutions which are suitable for spectrophotometric examination. When large excesses of a tetrazole are added to a nickel solution, the limiting absorbancy of the solution is not attained. However, by the use of the sodium salts of the tetrazoles limiting absorbancies are easily reached. Although water, ethanol, and methanol can be used in some cases, the most useful solvent employed was N, N-dimethylformamide (DMF).

The addition of $Ni(NO_3)_2$ to aqueous solutions of 5-aminotetrazole results in a decrease in the pH of the solution. Experiments with $Ni(NO_3)_2$ and 5-phenyltetrazole in DMF indicate that H^+ is produced in the coordination reaction. No evidence exists for the coordination of tetrazoles as neutral molecules.

A continuous variation study of the reaction between $Ni(NO_3)_2$ and 5-aminotetrazole in aqueous solution was carried out spectrophotometrically. A graph of excess absorbancy <u>versus</u> $[CN_5H_3]/[Ni^{++}]$ shows a broad maximum extending from a tetrazole to nickel ratio of 1.2 to a ratio of 2.2. No valid conclusions concerning the nature of the species in solution can be drawn from these data. It seems apparent that the complex formed between Ni^{++} and 5-aminotetrazole is a rather weak complex. An attempt was made to prepare samples for a continuous variation study using the sodium salt of 5-aminotetrazole in both water and DMF. Unfortunately, solids immediately precipitated from all solutions in which the tetrazolate to nickel ratio was greater than 1.5.

The reaction of the sodium salt of 5-phenyltetrazole, $NaC_7H_5N_4$, and $Ni(NO_3)_2 \cdot 6H_2O$ in DMF solution was studied by the method of continuous variation. The experiments gave unexpected results. A graph of excess absorbancy versus [tetrazolate]/[Ni^{++}] shows a single sharp maximum at a [tetrazolate]/[Ni^{++}] of 1.5. The position of the maximum is not altered by the addition of small amounts of water to the system.

According to Katzin (52), if a single, well-defined, maximum is obtained in a continuous variation study, the position of the maximum corresponds to the formula of the complex. One, then, must conclude from the continuous variation data that in solution the complex has the empirical formula $[Ni_2(C_7H_5N_4)_3]^+$. Continuous variation experiments using 5-phenyltetrazole in place of its sodium salt gave inconclusive results similar to those obtained for 5-aminotetrazole.

Further evidence for the existence of $[Ni_2(C_7H_5N_4)_3]^+$ in solution is given by the spectrophotometric titration of $Ni(NO_3)_2 \cdot 6H_2O$ in DMF with a standard solution of $NaC_7H_5N_4$. The titration was carried out by measuring the absorbancies of a series of samples containing a constant amount of $Ni(NO_3)_2 \cdot 6H_2O$ and various concentrations of $NaC_7H_5N_4$. A graph of absorbancy versus amount of $NaC_7H_5N_4$ added is linear until the [tetrazolate]/[Ni^{++}] is slightly greater than 1.5. After this tetrazolate to nickel ion ratio has been reached, the curve rapidly flattens out and reaches a constant absorbancy value. Similar results are obtained when $Ni(NO_3)_2 \cdot 6H_2O$ in DMF is titrated spectrophotometrically with the sodium salts of 5-o-chlorophenyltetrazole, 5-p-chlorophenyltetrazole, or 5-p-methoxyphenyltetrazole. Leussing (53, 54) has used this type of data to prove the existence of nickel complexes of 1,2 ethanedithiol and 2, 3-dimercapto-1-propanol having the general formula $Ni_2X_3^{=}$, where X represents the anion of the ligand. Recently, pyrocatechol-3, 5-disulfonate complexes of Th(IV) having this same general formula have been prepared and characterized (55, 56, 57).

The absorbancies of DMF solutions of constant nickel ion concentration and various concentrations of 5-aryltetrazoles were also measured. A comparison of the absorbancies of solutions 1.02×10^{-2} M in $Ni(NO_3)_2 \cdot 6H_2O$ and 8.0×10^{-2} M in 5-aryltetrazole is given in Table 18. Limiting absorbances for 1.03×10^{-2} M $Ni(NO_3)_2$ solutions containing excesses of the sodium salts of the tetrazoles are also given as well as acid dissociation constants for the tetrazoles.

Table 18. Comparison of the Absorbancies of DMF Solutions 1.03×10^{-2} M in $Ni(NO_3)_2 \cdot 6H_2O$ and 8.0×10^{-2} M in Various 5-Aryltetrazoles.

Tetrazole	Absorbancy of 1.03×10^{-2} M Soln of $NI(NO_3)_2 \cdot 6H_2O$ and 8.0×10^{-2} M in Tetrazole	Limiting Abs. from Excess Na salt and 1.03×10^{-2} M $Ni(NO_3)_2 \cdot 6H_2O$	Ka x 10^6 Tetrazole in 75% Methanol (58)	Ka x 10^6 of Tetrazole in 50% Dioxane
5-phenyl	0.101	0.453	13.0	15.8
5-0-Chloro-phenyl	0.172	0.442	25.0	26.7
5-p-Chloro-phenyl	0.114	0.471	32.0	-
5-p-Methoxy-phenyl	0.072	0.475	-	14.0

If one assumes that both 5-phenyltetrazole and sodium 5-phenyltetrazolate react with $Ni(NO_3)_2 \cdot 6H_2O$ to give the same complex, the data in Table 18 are interesting. The purple color of the solutions described in Table 18 is a measure of the amount of complex present. Moreover, for a given concentration of 5-phenyltetrazole and $Ni(NO_3)_2 \cdot 6H_2O$ one can calculate the degree of formation of the complex by use of the following relationship

$$\alpha = \frac{A - A_0}{A_\infty - A_0}$$

α = degree of formation

A = absorbancy of a solution 1.03×10^{-2} M in $Ni(NO_3)_2 \cdot 6H_2O$ containing 5-phenyltetrazole

A_∞ = limiting absorbancy

A_0 = absorbancy of 1.03×10^{-2} M $Ni(NO_3)_2 \cdot 6H_2O$

The degree of complex formation for solutions 1.03×10^{-2} M in $Ni(NO_3)_2 \cdot 6H_2O$ and 8.0×10^{-2} M in 5-aryltetrazole was calculated from the data in Table 18. For a 1.02×10^{-2} M solution of $Ni(NO_3)_2 \cdot 6H_2O$ which is also 8.0×10^{-2} M in 5-phenyltetrazole the degree of complex formation is 0.22. For the other tetrazoles the degrees of complex formation were: 5-o-chlorophenyltetrazole, 0.39; 5-p-chlorophenyltetrazole 0.24; 5-p-methoxyphenyltetrazole, 0.15. This data suggests that the relative stability of the nickel complexes of these 5-aryltetrazoles is 5-o-chlorophenyltetrazole > 5-p-chlorophenyltetrazole > 5-phenyltetrazole > 5-p-methoxyphenyltetrazole. Examination of the acid dissociation constants of these tetrazoles would predict the order of stability to be: 5-p-methoxyphenyltetrazole > 5-phenyltetrazole > 5-o-chlorophenyltetrazole > 5-p-chlorophenyltetrazole.

Examination of the visible absorption spectra of the nickel complexes of 5-aminotetrazole and 5-phenyltetrazole points to the conclusion that the complexes in solution have cubic symmetry. The position, number, and intensity of the absorption bands are in good agreement with those observed for known octahedral nickel complexes. The position and intensities of the absorption bands in the visible spectra of the nickel complexes of 5-aminotetrazole and 5-phenyltetrazole are given in Table 19. The spectra as reported by Jϕrgensen (59) of other nickel complexes known to be octahedral are also given in Table 19.

The other configurations that are known for nickel complexes are square planar and tetrahedral.

The visible spectra of square planar nickel complexes have, at most, three bands the first of which appears in the range 15000-18000 cm^{-1}. The second and third bands often are not observed due to intense absorption of the ligands in the ultra violet. The intensity of the bands are rather high being in the range 90-350.

The spectra of the tetrazole complexes have well defined bonds at frequencies much lower than 15000-18000 cm^{-1} and the intensities of the bands are much lower than the band intensities of known square-planar, nickel complexes.

It has recently been shown that there are very few tetrahedral complexes of nickel. One complex of nickel that has been shown to be tetrahedral occurs as $Ni(Cl)_4^{=}$ in a fused salt mixture of LiCl and $NiCl_2$ (60). The visible spectrum of this complex has two absorption bands at 655 and 705 mμ both of which have intensities of 160. Recently Cotton (61) has reported the preparation of tetrahedral nickel complexes of triphenylphosphine oxide. These complexes have 4 or 5 rather intense absorption bands in their visible spectra. For example, the visible spectrum of diiodo bis(triphenylphosphine oxide) nickel (II), $[(C_6H_5)_3PO]_2NiI_2$, in acetone has absorption bands at the following wavelengths (intensities given in parenthesis) 515 mμ (535), 590 mμ (shoulder), 715 mμ (136), 775 mμ (shoulder), 1365 mμ (19.2).

Table 19. Spectra of Octahedral Nickel Complexes

Compound or Ligand	Absorption Band	mμ	V cm^{-1}	Intensity	V_3/V_1
$CN_5H_2^-$ (a)	V_1	930	10740	3.3	1.73
	V_2	725	13800	1.7	
	V_3	540	18540	3.8	
	V_4	385	26000	4.9	
$C_7H_5N_4^-$ (b)	V_1	940	10630	10.2	1.66
	V_2	770	13000	3.1	
	V_3	565	17700	9.8	
	V_4	356	28100	19.7	
$Ni(enta)NH_3^=$	V_1	980	10200	16.6	1.69
	V_2	788	12700	3.4	
	V_3	582	17200	10.9	
	V_4	372	26900	20.2	
$Ni(tetren)NH_3$	V_1	900	11100	25.0	1.68
	V_2	800	12500	4.7	
	V_3	535	17300	8.1	
	V_4	350	27100	10.8	
$Ni(H_2O)_6^{++}$	V_1	1175	8500	2.0	1.81
	V_2	740	13500	1.8	
	V_3	650	15400	1.5	
	V_4	396	25300	5.2	
$Ni(NH_3)_6^{++}$	V_1	930	10750	4.0	1.63
	V_2	760	13150	5.0	
	V_3	572	17500	4.8	
	V_4	355	28200	6.3	

(a) = obtained from $NiCl_2$ and 5-aminotetrazole in H_2O
(b) = obtained from $Ni(NO_3)_2 \cdot 6H_2O$ and $NaC_7H_5N_4$ in DMF
enta = ethylenediaminetetraacetate
tetren = tetraethylenepentamine

Neither the positions nor the intensities of the bands observed in the spectra of the tetrazole complexes suggest that these complexes are tetrahedral.

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APPENDICES

APPENDIX I

Attempts to Determine Formation Constants for the Complexes

As part of this investigation, several attempts were made to determine formation constants for the complexes. Formation constants for a given metal ion and various tetrazoles might elucidate the role that basicity of the ligand and steric factors play in complex formation. A knowledge of formation constants for the complexes may have led to a better general understanding of the nature of the complexes. Unfortunately, none of the attempts to determine formation constants was successful.

Most of the attempts were made using nickel as the metal ion because fewer solubility problems occurred than when copper ion was used. A series of 5-aryltetrazoles was chosen for this study. The reasons for this choice of tetrazoles are twofold: these tetrazoles are easily synthesized in high purity and good yield; altering the nature and position of the substituent on the phenyl ring allows one to vary the acidity and possibly the steric requirements of the ligand. A disadvantage of using 5-aryltetrazoles is that they are water insoluble. Some attempts were also made to determine the formation constants for the nickel complexes of 5-aminotetrazole and tetrazole.

Brubaker (41) has used spectrophotometric and pH measurements to determine the formation constant of the copper complex of 5-aminotetrazole. 'Several attempts to determine formation constants were based on Brubaker's method or on slight modifications of it. Therefore, his method will be described. A series of solutions 0.02 M in $Cu(NO_3)_2$ and containing various concentrations of 5-aminotetrazole were prepared. The samples at high tetrazole concentrations contained sufficient tetrazole to enable one to determine the limiting absorbancy. The absorbancies of the sample solutions were measured at a wavelength at which the complex absorbs strongly. The pH's of the solutions were also measured.

If the limiting absorbancy is taken as that of 0.02 M $Cu(CN_5H_2)_2$, the degree of formation, α, can be calculated from $A-A_0/A_\infty - A_0$. A is the absorbancy of any solution of 0.02 M Cu^{++} and CN_5H_3, A_0 is the absorbancy of 0.02 M $Cu(NO_3)_2$, and A_∞ is the absorbancy of 0.02 M $Cu(CN_5H_2)_2$.

Then $\bar{n}$, the average number of ligands bound per metal ion, is given as

$$(1)\quad \bar{n} = 2\,\alpha = 2 \times \frac{A - A_0}{A_\infty - A_0}$$

Consider the equilibria:

$$HT \rightleftarrows H^+ + T^- \qquad K_A$$

$$\underline{Cu^{++} + 2T^- \rightleftarrows CuT_2} \qquad K_1$$

$$(2)\quad Cu^{++} + 2HT \rightleftarrows CuT_2 + 2H^+ \qquad K_A{}^2K_1 = K$$

$$HT = CN_5H_3\,, \quad T^- = CN_5H_2^-$$

We also may write:

$$(3)\quad \bar{n} = \frac{2[CuT_2]}{[Cu^{++}] + [CuT_2]} = \frac{2K[Cu^{++}]\,[HT]^2/[H^+]^2}{[Cu^{++}]\,(1 + K[HT]^2/[H^+]^2)}$$

$$(4)\quad \bar{n} = \frac{2K[HT]^2/[H^+]^2}{1 + K\,[HT]^2/[H^+]^2}$$

and

$$(5)\quad \frac{1}{\bar{n}} = \frac{1\,[H^+]^2}{2K[HT]^2} + \frac{1}{2}$$

Then a graph of $[H^+]^2/[HT]^2$ versus $\frac{1}{\bar{n}}$ should give a straight line with slope $\frac{1}{2K}$ and intercept $\frac{1}{2}$. The concentration of H^+ can be measured by the use of a pH meter.

The concentration of tetrazole not bound to metal ion is given by

(6) $(HT)' = C_{HT} - \bar{n}\ C_M$

where C_{HT} and C_M are total tetrazole and total metal ion concentrations respectively. Due to the presence of the amino group in the 5-aminotetrazole molecule, some of the H^+ produced in equation (2) is bound by uncoordinated 5-aminotetrazole as $CN_5H_4^+(H_2T^+)$ and the concentration of free HT, CN_5H_3, is given by

(7) $(HT) = (HT)' - (H_2T^+)$

The concentration of H_2T^+ can be calculated from

(8) $(H_2T^+) = (H^+)' - (H^+)$

where $(H^+)'$ is given by the relationship

(9) $(H^+)' = \bar{n}\ C_M$

and (H^+) is measured (H^+).

Then by spectrophotometric measurements, pH measurements, and by use of the above relationships; the quantities $\bar{n}$, (H^+) and (HT) can be determined. The above treatment assumes that the concentration of any CuT^+ can be neglected. There is evidence that no CuT^+ is formed (41).

The formation constant for the 5-aminotetrazole complex of nickel can not be determined by the method outlined above. A series of solutions 0.01 $\underline{M}$ in $Ni(NO_3)_2$ and containing various concentrations of 5-aminotetrazole, up to 0.144 $\underline{M}$, was prepared. The pH's and absorbancies (at 540 mμ) of these solutions were measured. The limiting absorbancy, A_∞, could not be determined from the data. Attempts to determine A_∞ by the use of lower nickel ion concentrations failed.

Several estimates of A_∞ were made and, based on these estimates, $\bar{n}$, (H^+) and (HT) were calculated. In each case a graph of $1/\bar{n}$ versus $(H^+)^2/(HT)^2$ was not linear.

If the complex in solution is NiT^+, an equation analogous to equation (5) can be derived which gives the relationship

$$\text{(10)} \qquad \frac{1}{\bar{\bar{n}}} = \frac{1}{K}\,\frac{(H^+)}{(HT)} + 1$$

Graphs of $\frac{1}{\bar{\bar{n}}}$ versus $(H^+)/[HT]$ based on various estimates of A_∞ were not linear. Since A_∞ could not be determined, the data was not subjected to further treatment.

It seems reasonable to assume that any complex NiT_2 forms by stepwise addition of ligands forming NiT^+ as an intermediate species. Conditions that favor the formation of NiT^+ are high concentration of Ni^{++} and a low concentration of 5-aminotetrazole.

Hume (62) has derived a relationship which is valid when the metal ion concentration is sufficiently high so that only free metal ion and the first complex exist. If both species are colored, the relationship is

$$\text{(11)} \qquad \log\left(\frac{A - E\,M_t}{E_1}\right) = q \log\left[X_t - q\left(\frac{A - E\,M_t}{E_1}\right)\right] + \log K_1$$

where

A = observed absorbancy

E = absorbancy index of the metal ion

E_1 = absorbancy index of the complex

M_t = total metal ion concentration

X_t = total ligand concentration

q = number of ligands/metal ion in the first complex

K_1 = formation constant for the first complex

A graph of $\log\left(\frac{A - E\,M_t}{E_1}\right)$ versus $\log\left[X_t - q\left(\frac{A - E\,M_t}{E_1}\right)\right]$ should be linear with a slope of one and an intercept $\log K_1$.

The absorbancy index of the first complex was calculated from spectrophotometric measurements at 540 mμ (complex peak) and 730 mμ (nickel ion peak) using 0.386 M $NI(NO_3)_2$ solutions containing CN_5H_3 in the concentration range 1.8×10^{-2} M to 6.0×10^{-2} M. The absorbancy index for NiT^+ calculated from these data was 2.74. The absorbancy index for $Ni(NO_3)_2$ at 540 mμ was calculated to be 0.129.

A series of samples was prepared for determination of the formation constant for the first complex. The samples were 0.024 M in CN_5H_3 and the Ni^{++} concentration varied from 0.774 M to 0.0774 M. The absorbancies of the samples were measured at 540 mμ and from the measurements the quantities $\frac{A - E\,M_t}{E_1}$ and $X_t - (\frac{A - E\,M_t}{E_1})$ were calculated. It turns out that the difference $X_t - (\frac{A - E\,M_t}{E_1})$ is small or even negative. A graph of log $(\frac{A - E\,M_t}{E_1})$ versus log $(X_t - \frac{A - E\,M_t}{E_1})$ is not linear.

In order to make the difference $X_t - \frac{A - E\,M_t}{E_1}$ large, one would need to use larger CN_5H_3/Ni^{++} ratios which introduces the possibility of formation of NiT_2 making equation (11) invalid.

The formation constant for the nickel complex of tetrazole, CN_4H_2, could not be determined spectrophotometrically because solutions containing $Ni(NO_3)_2$ and CN_4H_2 rapidly became turbid. Recrystallization of the tetrazole did not remedy the situation, although recrystallization of the $Ni(NO_3)_2$ seemed to help, the solutions were still too turbid for spectrophotometric measurements. The turbidity may have been caused by trace amounts of sulfate present in the $Ni(NO_3)_2$.

It was also observed that, with 5-aryltetrazoles and $Ni(NO_3)_2 \cdot 6H_2O$, the limiting absorbancy could not be attained. However, when one used the sodium salts of 5-aryltetrazoles in DMF, the limiting absorbancy could easily be determined.

If the sodium salt of a tetrazole is used in place of the tetrazole, the coordination reaction is

$$(12) \quad M^{++} + 2T^{-} \rightleftharpoons MT_2 \qquad K$$

where M^{++} is Ni^{++} or Cu^{++}

and equation (5) simplifies to

$$(13) \quad \frac{1}{\bar{\bar{n}}} = \frac{1}{2K} \frac{1}{[T^-]^2} + \frac{1}{2}$$

The degree of formation and $\bar{n}$ can be found according to equation (1) from spectrophotometric measurements.

The concentration of unbound tetrazolate is given by

$$(14) \quad [T^-] = C_T - \bar{n}\, C_M$$

where C_T is total concentration of sodium tetrazolate and C_M is total metal ion concentration. Then a graph of $\frac{1}{\bar{\bar{n}}}$ versus $\frac{1}{[T^-]^2}$ should be linear with slope of $\frac{1}{2K}$ and intercept $\frac{1}{2}$.

It seemed possible that the type of data given in Tables 14 and 15 might be used to calculate $\bar{n}$ and $[T^-]$ and that by graphing $\frac{1}{\bar{\bar{n}}}$ versus $\frac{1}{[T^-]^2}$ a value for the formation constant might be obtained.

The quantities $\bar{n}$ and $\frac{1}{[T^-]^2}$ were calculated by equations (1) and (14) for the data obtained by the use of sodium 5-p-chlorophenyltetrazolate and $Ni(NO_3)_2 \cdot 6H_2O$ in DMF. The quantity $[T^-]$ is rather small for samples containing small amounts of the sodium salt. As a result, the values of $\frac{1}{[T^-]^2}$ cover too wide a range to conviently be graphed. However, examination of equation (13) shows that a graph of log $(\frac{1}{\bar{\bar{n}}} - \frac{1}{2})$ versus log $(\frac{1}{[T^-]^2})$ should be linear with a slope of one. A graph of log $(\frac{1}{\bar{\bar{n}}} - \frac{1}{2})$ versus log $(\frac{1}{[T^-]^2})$ from the data obtained for the sodium salt of 5-p-chlorophenyltetrazole is reasonably linear.

However, when the sodium salts of other 5-aryltetrazoles were used, the above method of treating the data was not successful. The use of equation (14) often resulted in negative concentrations of unbound tetrazolate ion. This result strongly suggested that the complex in solution did not have the formula NiT_2.

If the complex in solution corresponds to the formula NiT^+, $\bar{n}$ is given by $A - A_0/A_\infty - A_0$ and equation (14) gives reasonable values for the concentration of unbound tetrazolate ion. For the reaction

$$(15) \quad Ni^{++} + T^- \rightleftarrows NiT^+ \qquad K$$

an equation can be derived relating $\bar{n}$ and $[T^-]$ and has the form

$$(16) \quad \frac{1}{\bar{n}} = \frac{1}{K}\,\frac{1}{[T^-]} + 1$$

A graph of $\frac{1}{\bar{n}}$ versus $\frac{1}{[T^-]}$ should be linear with slope of $\frac{1}{K}$ and intercept one. The quantities $\bar{n}$ and $[T^-]$ were calculated from the data in Table 12 for the sodium salts of 5-phenyl, 5-o-chlorophenyl, and 5-p-chlorophenyltetrazole. In no case was a graph of $\frac{1}{\bar{n}}$ versus $\frac{1}{[T^-]}$ linear.

Continuous variation experiments with $Ni(NO_3)_2 \cdot 6H_2O$ and sodium 5-phenyltetrazolate indicate that the complex in solution has the formula $Ni_2T_3^+$. Spectrophotometric titration of $Ni(NO_3)_2 \cdot 6H_2O$ with the sodium salts of several 5-aryltetrazoles also suggest the existence of a complex $Ni_2T_3^+$.

The reaction is

$$(17) \quad 2Ni^{++} + 3T^- \leftrightarrows Ni_2T_3^+ \qquad K_1$$

and

$$(18) \quad \bar{n} = 3/2\ \alpha = 3/2\ \frac{A - A_0}{A_\infty - A_0}$$

furthermore we may write

$$(19) \quad \bar{n} = \frac{3[Ni_2T_3^+]}{[Ni^{++}] + 2[Ni_2T_3]} = \frac{3K[Ni^{++}]\,[T^-]^3}{1 + 2K[Ni^{++}]\,[T^-]^3}$$

and

$$(20) \quad \frac{1}{\bar{n}} = \frac{1}{3K[Ni^{++}][T^-]^3} + 2/3$$

Unbound tetrazolate is given by equation (14) and bound metal is given by the product of α and C_M, assuming that $Ni_2T_3^+$ is the only complex formed. Unbound metal then can be calculated by taking the difference of C_M and αC_M.

A graph of $\frac{1}{\bar{n}_2}$ versus $\frac{1}{[Ni^{++}][T^-]^3}$ should be linear with slope $\frac{1}{3K}$ and intercept $\frac{2}{3}$.

For the cases studied, the concentrations of unbound tetrazolate calculated by the use of equation (14) are very small and slight errors in absorbancy measurements result in large errors in tetrazolate concentrations. If the complex does have the formula $Ni_2T_3^+$, it appears to be a rather strong complex and the experimental methods used are not sufficiently accurate to be of use in the determination of formation constants.

The absorbancies of 1.03×10^{-2} M $Ni(NO_3)_2 \cdot 6H_2O$ solutions in DMF containing various quantities of 5-aryltetrazoles were measured and are recorded in Table 16. It seems reasonable to assume that when the sodium salts of the tetrazoles are used coordination occurs nearly quantitatively and that from a graph of absorbancy versus moles of tetrazolate added, the number of moles of tetrazolate coordinated could be determined for a given absorbancy. For the absorbancies recorded in Table 16, the corresponding moles of coordinated tetrazolate were estimated from a graph of absorbancy versus moles of sodium tetrazolate added (at the same Ni^{++} concentration).

The number of moles of unbound tetrazole could then be calculated from the difference between total number of moles of tetrazole present and the number of moles of bound tetrazolate. By assuming various formulas for the complexes in solution, the concentrations of bound and unbound metal ion can be calculated and $\bar{n}$ can also be calculated. Finally the H^+ produced by the coordination reaction can be calculated from the product of $\bar{n}$ and C_M. The quantities $\bar{n}$, $[H^+]$, $[HT]$, and $[Ni^{++}]$ were calculated assuming the complex to be NiT_2,

NiT^+ or $Ni_2T_3^+$ and attempts were made to fit these data to the types of equations discussed previously. None of the attempts were successful. Straight line graphs could not be obtained when any single complex was assumed to be present.

Since the reactions of tetrazoles and metal ions produce H^+ as one of the products, it seemed feasible to be able to determine stability constants by measurement of the H^+ concentration of solutions of $Ni(NO_3)_2$ and tetrazoles. A major problem was to find a solvent in which pH could be measured and also in which the metal salt, the tetrazole and the complex were all moderately soluble. Fernelius (63) has reported that pH meter readings in 50% aqueous dioxane are an accurate measure of the molar concentration of H^+. The metal salt and the tetrazoles were found to be moderately soluble in 50% dioxane and if the total concentrations were kept low ($\sim 10^{-2}$) the complexes formed also were soluble. It was also shown that the pH's of 50% aqueous dioxane solutions 8.0×10^{-3} $\underline{M}$ in the desired tetrazole and 0.20 $\underline{M}$ in $NaNO_3$ were measurably lowered by the addition of $Ni(NO_3)_2 \cdot 6H_2O$. The acid dissociation constants for several tetrazoles in 50% dioxane were determined by potentiometric titration with standard alkali.

If a single complex, NiT_2, is formed, simultaneous equations relating $[H^+]$, $[T^-]$, C_M, C_{HT}, and $[Ni^{++}]$ can be written. The symbols have the same meanings as previously.

The equations are:

(21) $[H^+] = 2[NiT_2] + [T^-]$

(22) $C_M = [NiT_2] + [Ni^{++}]$

(23) $C_T = 2[NiT_2] + [T^-] + [HT]$

(24) $Ka = [H^+][T^-]/[HT]$

Experimentally, the pH's of solutions containing known amounts of metal salt, $NaNO_3$, and tetrazole are measured. The quantities,

$[H^+]$, $]NiT_2]$, $[HT]$, and $[Ni^{++}]$ are calculated for each solution by simultaneous solutions of equations (21-24), and an equilibrium constant for the coordination reaction can be calculated from the data for each solution.

When this treatment was used, the equilibrium constants calculated for a series of solutions containing $Ni(NO_3)_2 \cdot 6H_2O$ and a given tetrazole varied greatly from sample to sample. The observed variation in K strongly suggests that the above treatment is not correct.

If one assumes that a single complex of the formula NiT^+ is formed in the reaction, a set of equations similar to equations 21-24 can be written and by the use of the methods outlined above, equilibrium constants for each of a series of sample solutions can be calculated. When the data were treated in this manner, the calculated equilibrium constants also varied from sample to sample.

Equations can be derived for a situation in which both NiT^+ and NiT_2 are produced, but the set of equations contains too many unknowns to be solved.

The very fact that several quantities are calculated from a single experimental observation makes methods such as these somewhat unappealing. It seems fairly clear that no single, simple approach is sufficient to determine formation constants for the reactions of these metal ions and tetrazoles.

APPENDIX II

Miscellaneous

Determination of Acid Dissociation Constants for Some Tetrazoles in 50% Aqueous Dioxane at 30°

The acid dissociation constants for some 5-substituted tetrazoles in 50% aqueous dioxane at 30° were determined by potentiometric titration of weighed samples with standard alkali. All of the titrations were carried out at 30° in a constant temperature bath. All sample solutions were 0.20 M in $NaNO_3$. The pH change during a titration was followed by the use of a Beckman model G pH meter. Typical weak acid titration curves were obtained.

The dissociation constants were calculated by the use of the relationship

$$K = [H^+] \frac{X}{X_e - X}$$

where $[H^+]$ is H^+ concentration calculated from the pH corresponding to the addition of X ml, of alkali. The number of ml. of alkali required for neutralization is given by X_e. The equivalent weights of the tetrazoles were also calculated from the titration data. The dissociation constants reported in Table 20 are an average of at least five measurements taken near the neutralization point for each tetrazole.

Table 20. Acid Dissociation Constants in 50% Dioxane at 30°.

Tetrazole	Eq. Wt. Calc.	Eq. Wt. Found	Ka x 10^6
5-phenyltetrazole	146	147	15.8
5-o-chlorophenyltetrazole	181	181	26.7
5-o-tolyltetrazole	160	160	8.72
5-p-methoxyphenyltetrazole	176	178	7.10
5-methyltetrazole	84.1	84.5	1.12
5-cyclohexyltetrazole	152	151	0.76
5-aminotetrazole	85.7	86.4	0.22
tetrazole	70.7	70.7	7.98

The Reaction of $Co(NO_3)_2 \cdot 6H_2O$ with Sodium 5-Phenyltetrazolate in DMF

In DMF solution, $Co(NO_3)_2 \cdot 6H_2O$ and the sodium salt of 5-phenyltetrazole react to give orange-red or deep red solutions depending upon the concentrations. The visible spectrum of a DMF solution 8.0×10^{-4} $\underline{M}$ in $Co(NO_3)_2 \cdot 6H_2O$ and 8.0×10^{-3} $\underline{M}$ in $NaC_7H_5N_4$ shows no absorption maxima, but rather the solution shows an absorbancy starting at ~620 mμ which slowly increases at shorter wavelengths.

Qualitative Reactions of Copper and Nickel Salts with Tetrazoles in a Variety of Solvents

The reactions of various copper and nickel salts with tetrazoles were studied qualitatively in various solvents. The observations are summarized in Table 21. The reactions were carried out by mixing dilute solutions of the reactants.

Table 21. Reactions of Copper and Nickel Salts with Tetrazoles in A Variety of Solvents.

Tetrazole	Metal Salt	Solvent	Observation
5-amino	$Cu(NO_3)_2 \cdot 3H_2O$	75% dioxane	green soln. which rapidly becomes cloudy
5-amino	$Cu(Cl_2)_2 \cdot 2H_2O$	75% dioxane	green soln. which rapidly becomes cloudy
5-amino	$NiCl_2 \cdot 6H_2O$	75% dioxane	blue soln. which rapidly becomes cloudy
5-amino	$Ni(NO_3) \cdot 6H_2O$	75% dioxane	clear blue solution
5-phenyl	$Cu(NO_3)_2 \cdot 3H_2O$	75% dioxane	no apparent reaction
5-phenyl	$CuCl_2 \cdot 2H_2O$	75% dioxane	no apparent reaction
5-phenyl	$NiCl_2 \cdot 6H_2O$	75% dioxane	no apparent reaction
5-phenyl	$Ni(NO_3)_2 \cdot 6H_2O$	75_ dioxane	no apparent reaction
5-phenyl	$Cu(NO_3)_2 \cdot 3H_2O$	cyclohexanone	deep green solution
5-phenyl	$CuCl_2 \cdot 2H_2O$	cyclohexanone	no apparent reaction
5-phenyl	$Cu(NO_3)_2 \cdot 3H_2O$	methyl isobutyl ketone	blue solid forms at once
5-phenyl	$CuCl_2 \cdot 2H_2O$	methyl isobutyl ketone	the yellow color of the solution becomes more intense
5-phenyl	$Cu(NO_3)_2 \cdot 3H_2O$	ethylacetate	green soln. which rapidly becomes cloudy
5-phenyl	$Cu(NO_3)_2 \cdot 3H_2O$	acetic acid	green solution
5-p-nitrophenyl	$Cu(NO_3)_2 \cdot 3H_2O$	acetic acid	green solid forms