1, 8-naphthyridine copper complexes
by Eric Lee Enwall

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in CHEMISTRY
Montana State University

Abstract:
Copper complexes of 1,8-naphthyridine were prepared and the structure of Bis-(1,8-naphthyridine)-copper (II) chloride determined. Procedures were developed to prepare 1,8-naphthyridine in amounts suitable for use as a ligand for the preparation of coordination compounds. A new preparation of 4-methyl-1,8-naphthyridine was developed.

140

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TABLE OF CONTENTS

Introduction

Experimental

Appendix A

Appendix B

Appendix C

List of Tables

LIST OF FIGURES

ABSTRACT

Copper complexes of 1,8-naphthyridine were prepared and the structure of Bis-(1,8-naphthyridine)-copper(II) chloride determined. Procedures were developed to prepare 1,8-naphthyridine in amounts suitable for use as a ligand for the preparation of coordination compounds. A new preparation of 4-methyl-1,8-naphthyridine was developed.

INTRODUCTION

I. GENERAL

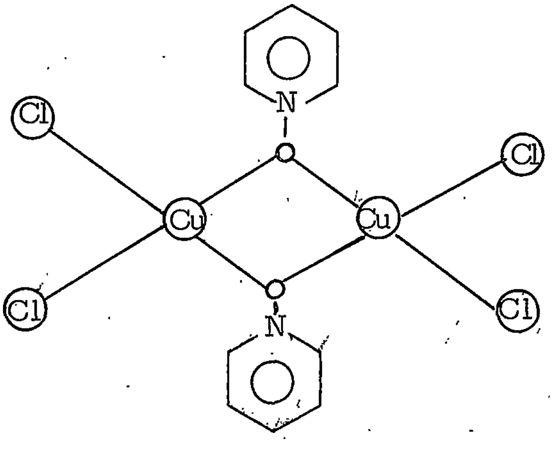
All copper(II) compounds exhibit paramagnetism because of the unpaired electron resulting from the electronic configuration ($3d^9$) of copper(II). If the only contribution to the magnetic moment for any compound containing an atom with unpaired electrons came from the electron spin, the magnetic moment for the atom with the unpaired electrons would be given by the expression:

$$\mu = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons on the atom
μ is the magnetic moment in Bohr magnetons

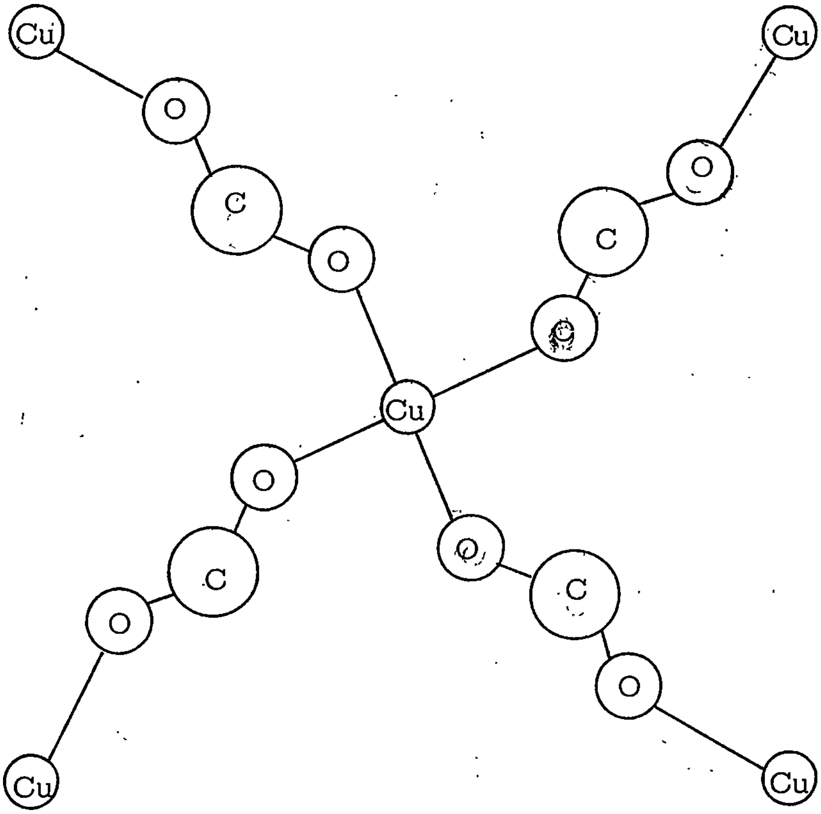
The "spin only" value for a copper(II) atom would then be 1.73 Bohr magnetons. The electron spin is not the only contribution to the magnetic moment. In most cases the spin orbit coupling must be considered. If the spin orbit coupling in copper(II) compounds is estimated from the values obtained for the free ion, the magnetic moment is expected to be about 1.9 Bohr magnetons (1). A third contribution to the magnetic moment may arise from the orbital momentum of the unpaired electron on the copper atom. The first two contributions are always expected for copper(II), but the third contribution may or may not be present depending on the symmetry of the copper coordination. If the crystal field surrounding the copper(II) atom is octahedral or of symmetry lower than cubic, the orbital contribution to the magnetic moment is expected to be quenched (1). If the symmetry is tetrahedral the orbital contribution is not entirely quenched, and the degree of quenching may depend on the degree of distortion from true tetrahedral symmetry. In any case the magnetic moment for copper(II) is expected to be 1.9 Bohr magnetons or greater.

A number of copper(II) compounds exhibit magnetic moments which are below 1.9 Bohr magnetons. These compounds with "subnormal" magnetic moments may be divided into two classes depending on their molecular and crystal structure (2). In one type of subnormal copper(II) compounds, the structures typically have two copper atoms bonded to a common non-copper atom, or to a common ligand molecule or ion. The non-copper atoms, ligand molecules, or ions are said to "bridge" the copper atoms. In many cases these bridges connect the copper atoms into long chains or planes. Bis-(pyridine-1-oxide) copper(II) chloride (Fig. 1) and copper formate tetrahydrate (Fig. 2) are typical of compounds with bridged structures which have subnormal magnetic moments.



Bis-(pyridine-1-oxide) copper(II) chloride (3)

Figure 1

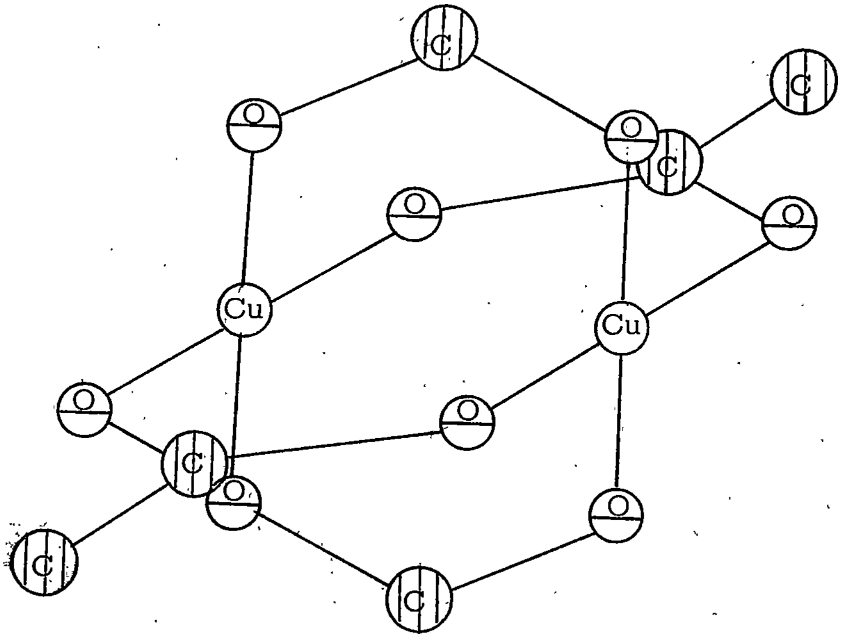


One Layer of Copper Formate Tetrahydrate Structure

(Water Molecules Omitted) (4)

Figure 2

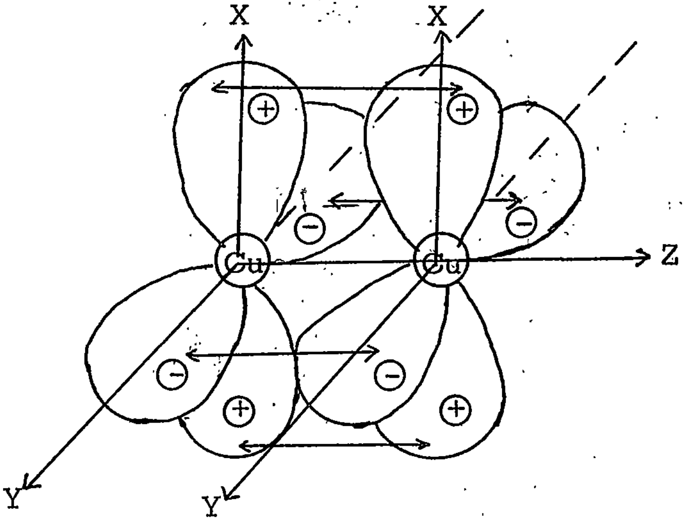
Copper acetate monohydrate (Fig. 3) is typical of the second type of copper (II) compounds with subnormal moments. In this type of structure the copper atoms are also bridged, but they occur as isolated, multiply bridged pairs with a short copper-copper distance. The number of compounds in this second class is very small, with the binuclear structure clearly demonstrated in few compounds other than copper (II) carboxylates, and not in all copper (II) carboxylates.



The Structure of Copper Acetate Monohydrate

Figure 3

In both types of structure, some form of spin correlation must occur to lower the magnetic moment. In copper formate tetrahydrate, Martin (5) has suggested that the π system of the formate ions can overlap with the d orbitals of the copper atoms providing a pathway for spin correlation. This type of interaction is known as "superexchange". In copper acetate monohydrate, a similar kind of superexchange could occur, but there is a second pathway as well. The copper-copper distance in copper acetate monohydrate is 2.64 Å, which is close to the separation in copper metal (6). The short distance could allow the overlap of d orbitals on the two atoms to form a partial chemical bond. Bond formation is accompanied by spin pairing which would reduce the magnetic moment. A direct copper-copper interaction could take two forms: the d_{z^2} orbitals of the copper atoms could overlap to form a partial sigma bond, or the $d_{x^2-y^2}$ orbitals could overlap to form a weak delta bond (Fig. 4).

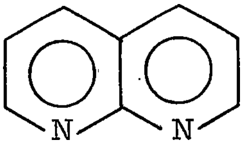


Cu-Cu Delta Bond Formed by Overlap of $d_{x^2-y^2}$ Orbitals

Figure 4

The sigma bond proposal has been supported by Forster and Ballhausen (7) and the delta bond supported by Figgis and Martin (8), who proposed it, and more recently by Kokoszka (9).

No definitive experiment has been proposed to decide between the possible modes of interaction in copper acetate monohydrate as correct. One possible approach to the solution of the problem is to synthesize compounds which have isolated pairs of copper atoms bridged in a manner similar to the bridging in copper acetate monohydrate and which have similar copper-copper distances. Study of the magnetic properties of such compounds should help to determine the true path of interaction. If such compounds are to be synthesized, ligand molecules or ions are required which meet certain geometric requirements. The ligand must be bidentate with the coordinating atoms approximately 2.6 Å apart. Two immediate possibilities would be acetamide and acetamidine which might form the copper acetate structure with the slight modification that nitrogen atoms would occupy some or all of the oxygen positions in copper acetate. Attempts to prepare copper acetamide and copper acetamidinate have been reported (10, 11), but no compounds with the desired geometry have been obtained. Another ligand which might form the desired binuclear structure is 1,8-naphthyridine (Fig. 5).



1,8-Naphthyridine

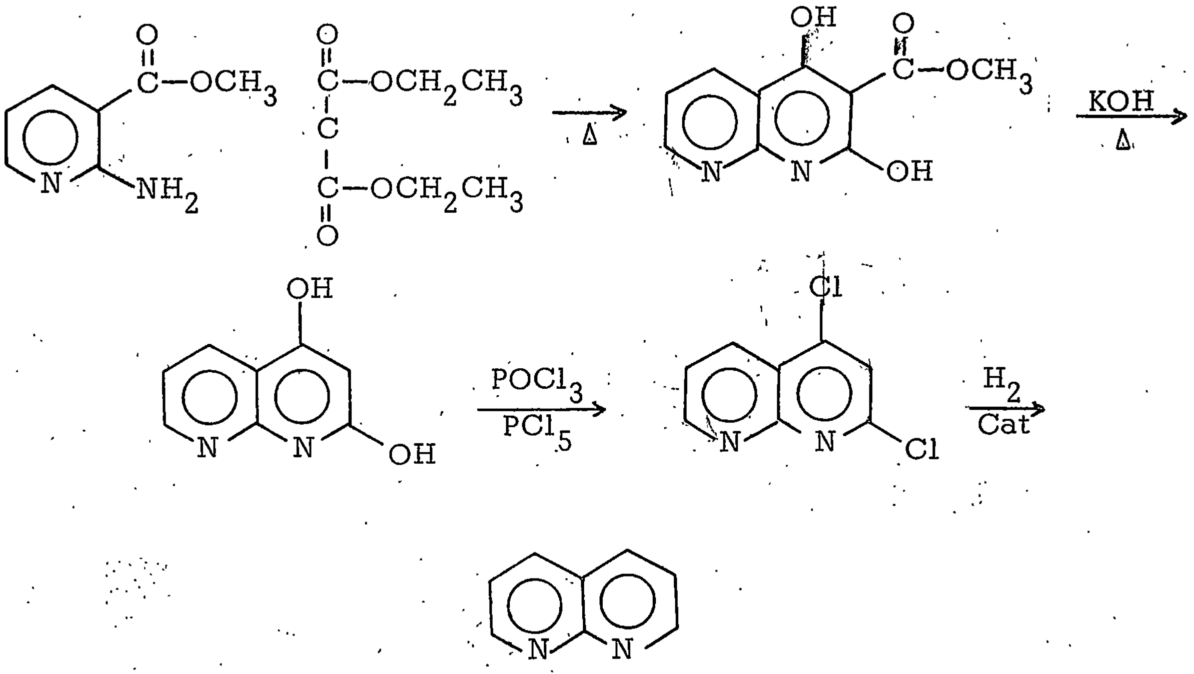
Figure 5

The two nitrogen atoms in 1,8-naphthyridine which could act as coordination sites would be estimated to be 2.4 Å, the separation of the corresponding carbon atoms in naphthalene, apart. If the binuclear structure were obtained in a copper 1,8-naphthyridine compound, the copper-copper distance might also be shorter than 2.64 Å and the copper-copper bond order increased if such a bond exists. An increased bond order would result in an even lower magnetic moment than that found in copper acetate monohydrate.

Since 1,8-naphthyridine-copper(II) complexes might have a binuclear structure similar to the structure of copper acetate monohydrate, it was decided to prepare and determine the structure of copper(II) compounds using 1,8-naphthyridine and 4-methyl-1,8-naphthyridine as ligands.

II. HISTORY

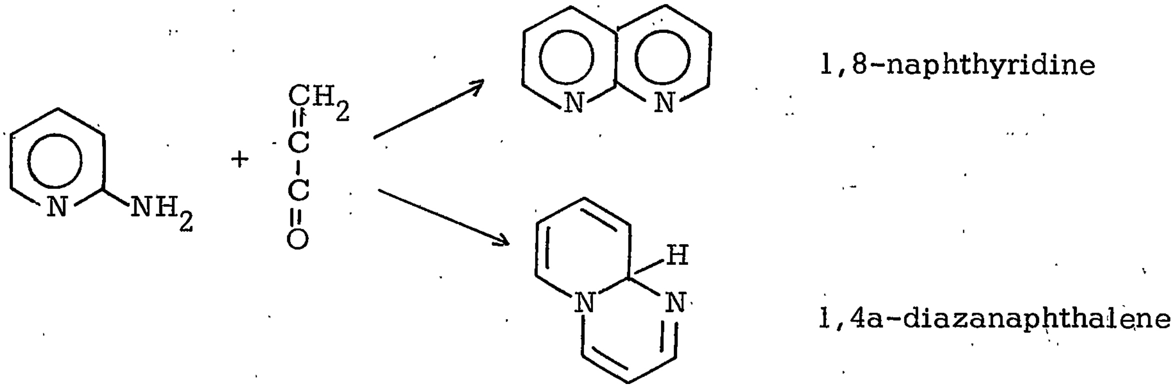
The first synthesis and isolation of a fully aromatic 1,8-naphthyridine derivative was reported by Koller (12) in 1924. He obtained the parent base by the reaction sequence given in Fig. 6.



Synthesis of 1,8-Naphthyridine (Koller)

Figure 6

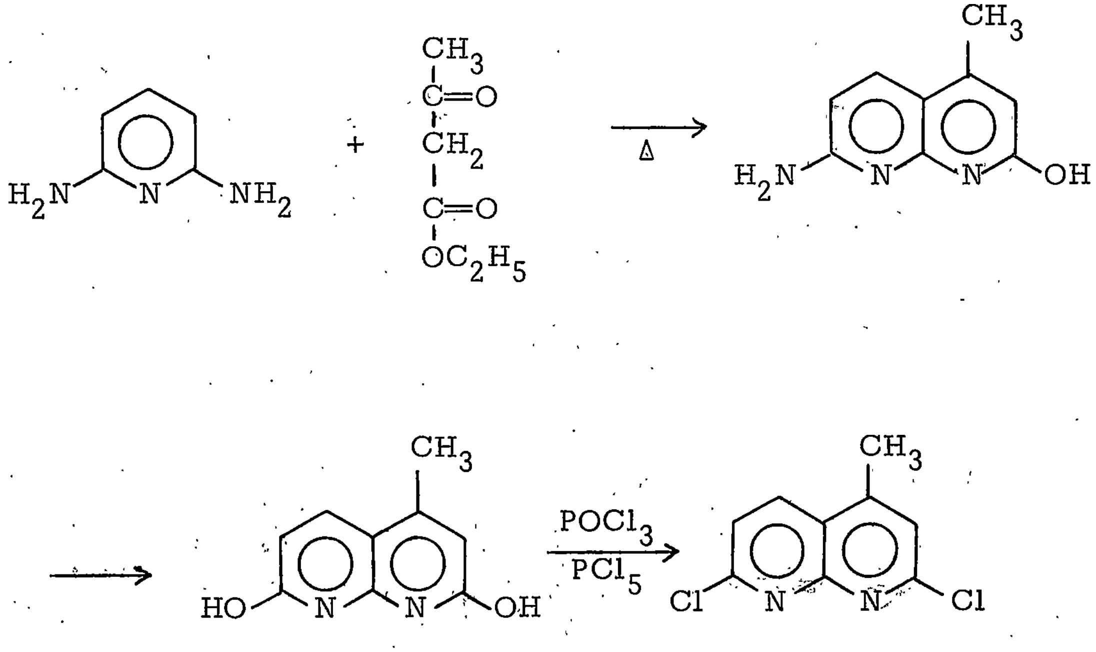
Earlier, other authors had reported synthesis of 1,8-naphthyridine derivatives (13). Most of these syntheses were Skraup or Dobner-von Miller syntheses using 2-aminopyridine and have been shown (13) to be syntheses of 1,4a-diazanaphthalenes via the alternate ring closure (Fig. 7).



Alternate Ring Closures

Figure 7

Siede (14) reported the syntheses of 4-methyl-1,8-naphthyridine derivatives by the sequence given in Fig. 8.



4-Methyl-1,8-Naphthyridine Derivatives (Seide)

Figure 8

In this case, the steric hindrance to cyclization at the ring nitrogen was sufficient to give preference to the 1,8-naphthyridine product. Brown (15) has also reported this same synthetic sequence with a few modifications. The conversion of 2,7-dichloro-4-methyl-1,8-naphthyridine to 4-methyl-1,8-naphthyridine by catalytic hydrogenation was reported by Ochiai and Miyaki (16).

In 1966, Carboni, Settimo, and Pirisino (17) reported the synthesis of 2-amino-7-hydroxy-1,8-naphthyridine from 2,6-diaminopyridine and malic acid. Paudler and Kress (18) reported in 1967, the isolation of 1,8-naphthyridine from a Skraup reaction on 2-aminopyridine in which they used meta-nitrobenzene sulfonic acid as the oxidizing agent. They proved the 1,8-naphthyridine structure by proton magnetic resonance spectroscopy. Paudler and Kress (19) also prepared 4-methyl-1,8-naphthyridine and characterized it in the same manner.

Except for the gold salt of 1,8-naphthyridine used by Koller (12) to characterize 1,8-naphthyridine, no other compounds using 1,8-naphthyridine or 1,8-naphthyridine derivatives have been reported.

EXPERIMENTAL

I. PREPARATION OF ORGANIC BASES

A. Preparation of 1,8-Naphthyridine

2-Amino-7-Hydroxy-1,8-Naphthyridine

The preparation 2-hydroxy-7-amino-1,8-naphthyridine was essentially that of Carboni, Pirisino and Settimo (17). To a mixture of 22 g. of 2,6-diaminopyridine and 30 g. of malic acid was added 100 ml. of sulfuric acid. The acid was added slowly at first with stirring until the solid was wet. The remainder of the sulfuric acid was added and the mixture slowly heated until the copious production of gas subsided and then heated strongly for thirty minutes. The solution was poured onto ice and neutralized with concentrated ammonium hydroxide to the litmus end point. The product was collected by suction filtration and dried in the air. The estimated yield of impure product was 90%. The compound was purified by recrystallization from dimethylformamide. Spectral data are given in Appendix A, Fig. 30, 31.

2,7-Dihydroxy-1,8-Naphthyridine

A solution of 10 g. of 2-hydroxy-7-amino-1,8-naphthyridine in 200 ml. of 10% sulfuric acid was cooled below 4°C. and a saturated solution of sodium nitrite was added dropwise until the solution gave a positive potassium iodide-starch test two minutes after the last addition of sodium nitrite. More concentrated acid solutions reduced the yield. The slurry was added carefully but quickly to 400 ml. of boiling water and the yellow precipitate collected by suction filtration. An estimated yield of 75% of crude product was obtained. The solid was dried in the air and purified for spectral data by crystallization from glacial acetic acid. Spectral data are given in Appendix A, Fig. 32, 33.

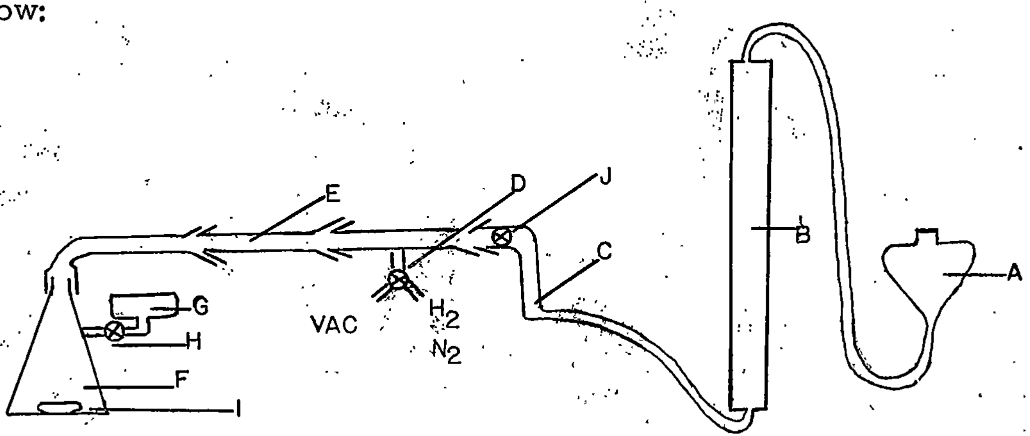
2,7-Dichloro-1,8-Naphthyridine

A 10 g. portion of 2,7-dihydroxy-1,8-naphthyridine was mixed with 10 g. of phosphorus pentachloride and covered with phosphorus oxychloride. The mixture was heated slowly until the initial reaction subsided and then refluxed for thirty minutes. The slurry was then poured onto ice and neutralized with concentrated ammonium hydroxide to the litmus end point. An estimated yield of 90% of impure product was obtained. The tan solid was recrystallized from benzene. The purified 2,7-dichloro-1,8-naphthyridine was a mass of silvery plates which sublimed above 175°C. Spectral data are given in Appendix A, Fig. 34, 35.

1,8-Naphthyridine

The catalytic reduction of 2,7-dichloro-1,8-naphthyridine was done in the atmospheric pressure hydrogenator described below. A mixture of 2.0 g. of impure 2,7-dichloro-1,8-naphthyridine and 1.0 g. of 5% palladium on calcium carbonate was placed in the hydrogenator and the apparatus purged with hydrogen. A 20 ml. portion of 5% potassium hydroxide in methanol was slowly added to the hydrogenator and the slurry vigorously stirred until the uptake of hydrogen ceased. The slurry was suction filtered taking care to keep the cake wet to prevent the catalyst from igniting. The solvent was then removed by slow evaporation and the residue extracted with ethyl acetate. The impure 1,8-naphthyridine was crystallized from the ethyl acetate by slow evaporation of the solvent and purified by sublimation under vacuum. The yield of impure 1,8-naphthyridine was estimated to be 90%. The 1,8-naphthyridine was not hygroscopic and was stored in air. Spectral data are given in Appendix A, Fig. 36, 37.

An atmospheric pressure hydrogenator was built for the catalytic reduction of dichloronaphthyridines; a drawing of the apparatus is shown below:



A. leveling bulb
B. gas buret
C. bubble trap
D. three way stopcock
E. drying tube (calcium chloride)
F. reduction flask
G. liquid reservoir
H. stopcock
I. magnetic spinbar
J. stopcock

Atmospheric Pressure Hydrogenator

Figure 9

The material to be reduced (a solid) and the catalyst (a solid) were placed in the flask F with a spinbar and the apparatus assembled. The stopcock D was opened to vacuum to remove all air from the system and then opened to the hydrogen supply. A slight pressure of hydrogen was produced at the gas inlet and the stopcock J opened to fill the buret B (previously filled with degassed water) with hydrogen. The stopcock D was closed and the solvent poured into the liquid reservoir G. The liquid level in the leveling bulb was adjusted to equal the level in the buret and the stopcock H carefully opened. Adjustment of the leveling bulb allowed the liquid to enter the flask F and all stopcocks were closed. The stirrer was started and reduction continued until gas uptake ceased. To quench the reaction, stopcock J was closed, stopcock D was opened to vacuum and the hydrogen removed. Stopcock D was opened to nitrogen and the flask removed.

B. Preparation of 4-Methyl-1,8-Naphthyridine

2-Hydroxy-4-Methyl-7-Amino-1,8-Naphthyridine

The preparation of 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine was essentially that of Brown (15). To 25 g. of 2,6-diaminopyridine and 30 g. of ethyl acetate was added 100 ml. of ortho phosphoric acid; the mixture was heated for one hour. The resulting solution was poured onto ice and neutralized with concentrated ammonium hydroxide to the litmus end point. The precipitate was collected by suction filtration and dried in air to give a tan solid. The yield of impure product was estimated to be 80%. The compound was purified for spectral analysis by the method of Seide (14); a slurry of the impure compound in boiling water was acidified with dropwise addition of concentrated hydrochloric acid until most of the solid had dissolved. The solution was filtered with suction and cooled. The 2-hydroxyl-4-methyl-7-amino-1,8-naphthyridine precipitated and was collected by suction filtration and dried in air. Spectral data are given in Appendix A, Fig. 20, 21.

2,7-Dihydroxyl-4-Methyl-1,8-Naphthyridine

The preparation of 2,7-dihydroxy-4-methyl-1,8-naphthyridine was essentially that of Seide (14). A 25% or 30% sulfuric acid solution was used to dissolve 10 g. of crude 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine. The solution was cooled to less than 4°C. and a saturated solution of sodium nitrite was added dropwise until the solution reacted positively to potassium iodide-starch two minutes after the last sodium nitrite addition. The slurry was then added carefully but quickly to 400 ml. of boiling water. The resulting solid was collected by suction filtration and dried in air. The yield of impure product was estimated to be 60%. The compound was purified for spectral analysis by recrystallization from glacial acetic acid. Spectral data are given in Appendix A, Fig. 22, 23.

2,7-Dichloro-4-Methyl-1,8-Naphthyridine

The preparation of 2,7-dichloro-4-methyl-1,8-naphthyridine was essentially that of Seide (14); a mixture of 10 g. of 2,7-dihydroxy-4-methyl-1,8-naphthyridine and 10 g. of phosphorus pentachloride was covered with phosphorus oxychloride and refluxed for 30 minutes. The solution was poured onto ice and kept cool while neutralized to the litmus end point with concentrated ammonium hydroxide. The resulting white solid was collected by suction filtration and dried in air. The yield of impure product was estimated to be 90%. One recrystallization from benzene afforded silvery crystals, m.p. 192.5 to 194.0°C. The literature melting point is 193°C. Spectral data are given in Appendix A, Fig. 24, 25.

2,7-Dihydrazino-4-Methyl-1,8-Naphthyridine

A mixture of 2.0 g. of 2,7-dichloro-4-methyl-1,8-naphthyridine and enough hydrazine hydrate to cover the naphthyridine was heated until the solid dissolved, and allowed to stand at room temperature for two days. The resulting red crystals were collected by filtration, washed with a minimum of cold water and dried in air. No purification was attempted. Spectral data are given in Appendix A, Fig. 26, 27.

4-Methyl-1,8-Naphthyridine

The preparation of 4-methyl-1,8-naphthyridine was similar to the preparation of 1,6-naphthyridine by Albert (20). A boiling solution of 7 g. of copper sulfate penthydrate in 30 ml. of water was added, dropwise at first and then more rapidly as the initial reaction subsided, to a solution of 1 g. of 2,7-hydrazino-4-methyl-1,8-naphthyridine in 25 ml. of boiling water. The solution was neutralized to the litmus end point with 5N sodium hydroxide while hot and refluxed in a beaker for 15 minutes. The slurry was quickly filtered with suction and washed with 10 ml. of hot water. The combined filtrates were cooled and extracted several times with chloroform. The combined chloroform extracts were dried over sodium sulfate and the solution filtered. Evaporation of the chloroform gave a brown oil which was dissolved in hexane. The yield of impure product was estimated to be 80%. Removal of the hexane with a stream of dry nitrogen caused crystallization of 4-methyl-1,8-naphthyridine as white feathery crystals, m.p. 55.0 to

56.5°C.; the crystals were very hygroscopic. Ochiai (26) reports 4-methyl-1,8-naphthyridine as an oil. Spectral data are given in Appendix A, Fig. 28, 29.

Catalytic Reduction of 2,7-Dichloro-4-Methyl-1,8-Naphthyridine

Two procedures were used to reduce the dichloro compound. The first procedure was similar to that of Ochiai (16). A mixture of 2.0 g. of 2,7-dichloro-4-methyl-1,8-naphthyridine, 1.0 g. of a prepared 5% palladium on calcium carbonate catalyst and 20 ml. of a 10% solution of potassium hydroxide in methanol were put in a Parr hydrogenation apparatus and hydrogenated at 2 atm. until hydrogen uptake ceased. The slurry was filtered with suction and the solvent removed by evaporation. A brown oil resulted which was distilled in vacuum to give a colorless oil. The second procedure used the atmospheric hydrogenation apparatus described above (page 13). A dry mixture of 2.0 g. of 2,7-dichloro-4-methyl-1,8-naphthyridine and 1.0 g. of the prepared catalyst were placed in the apparatus and the system purged with hydrogen. Slowly, 29 ml. of 5% potassium hydroxide in methanol was allowed to enter the reduction flask and the slurry stirred vigorously until hydrogen uptake stopped. The slurry was filtered and the filtrate treated as above. The same colorless oil resulted. This oil was shown by thin layer chromatography to be a mixture of several components with two predominant fractions.

II. PREPARATION OF COORDINATION COMPOUNDS

A. Bis-1,8-Naphthyridine)-Copper (II) Chloride

A solution of 100 mg. of 1,8-naphthyridine and 0.2 g. of copper chloride in 25 ml. of water was allowed to stand for several days in a closed container. The green prismatic crystals which separated were removed by decantation and washed with a minimum of water. Single crystals of the compound were mounted for X-ray determination of the structure. The crystal density was 1.68 g./cc.

B. Bis-(1,8-Naphthyridine)-Copper (II) Bromide

A solution of 76 mg. of 1,8-naphthyridine and 0.2 g. of copper bromide in 50 ml. of water was allowed to stand for two days in the open. The red-brown crystals which formed were removed by decantation and washed with a minimum of water. The product was analyzed for bromide and preliminary crystallographic data obtained. The crystal density was 2.00 g./cc.

C. Bis-(2,7-Dichloro-4-Methyl-1,8-Naphthyridine)-Copper (II) Chloride

Ethanol solutions of anhydrous copper chloride and 2,7-dichloro-4-methyl-1,8-naphthyridine were mixed and heated gently. The blue powder which precipitated was collected by suction filtration and dried in a vacuum dessicator. Copper analysis indicated two moles of ethanol of solvation.

D. Copper (I) Complex of 2,7-Dichloro-4-Methyl-1,8-Naphthyridine

An attempt was made to use copper (I) chloride in the same manner as C above. An orange product resulted, but no consistent analysis could be obtained. It is possible that no true copper(I) complex was formed but that ring coupling occurred to produce the orange color.

E. Methyl Naphthyridine Copper Complex

A green crystalline complex was obtained in a small yield from an ethanol solution of the catalytic reduction product of 2,7-dichloro-4-methyl-1,8-naphthyridine. The green compound co-crystallizes with a yellow powder and was separated from it manually. Only enough material was collected to obtain crystallographic data and a single gravimetric halide analysis.

III. ANALYTICAL TECHNIQUES

A. Thin Layer Chromatography

All thin layer chromatography reported here was done on silica gel plates prepared in the laboratory by standard methods. Analytical plates had a layer of silica gel 0.1 mm. thick; the silica gel was activated by baking for one hour in a 120°C. oven. Determination of spot position was made by the fluorescence of the materials under ultraviolet light and the absorption of iodine vapor on the spots. Preparative plates were marked with a stylus under UV light and scraped into extraction flasks. All analytical plates were run for purposes of purity control and no attempts were made to identify compounds according to R_f values. The solvent system used was butanol-acetic acid-water (12:3:5; V/V).

B. Gas Chromatography

All gas chromatography was done on columns packed with Gas Chrom C as solid support; the liquid phase was 30% by weight SE-30. All runs were made in the F&M (Model 400) gas chromatograph at 230°C. with helium as carrier gas and detection by flame ionization. The samples were injected in chloroform and retention times measured from the time of injection. No quantitative data were taken from the gas chromatographic data other than retention times.

C. Nuclear Magnetic Resonance

Nuclear magnetic resonance data were obtained in a Varian A-60 Spectrograph. Samples were run in microcells in deuterated chloroform with tetramethylsilane as an internal reference.

D. Ultraviolet-Visible Spectra

All UV-visible spectra were determined on the DK-2 Spectrophotometer in 1 cm. quartz cells with pure solvent as reference.

E. Infrared Spectra

All infrared spectra were determined on the Beckman IR-4 Spectrophotometer with a programmed slit and double beam. Spectra were run in micro-potassium bromide pellets and in chloroform solution with a balancing wedge cell filled with chloroform.

F. Copper Analyses

Copper analyses were determined by iodometric titration with sodium thiosulfate by the method outlined by Koltoff and Sandell (21). In all cases severe difficulty was encountered in determining end points; the end point would be achieved, but would fade out. The naphthyridine seemed to interfere with the end point. Estimation of accuracy for copper determination is given with the analytical data.

G. Halide Analyses

The Fajans titration was attempted on samples containing 1,8-naphthyridine as a ligand, but was unsuccessful. When the dichlorofluoroscein indicator was added, the solution immediately turned orange; the orange color masked the titration end point. Halide analyses were determined by a simple silver halide gravimetric determination using a very small filtering crucible and determining weights on the Mettler microbalance. The gravimetric procedure used is outlined by Walton (22).

H. Crystal Density

Crystal densities were determined by the flotation method. A crystal was placed in a beaker partially filled with a solvent in which the crystal did not dissolve and in which it sank. A heavier miscible solvent was added until the crystal seemed to remain suspended in the solution. The solution density was determined by weighing aliquots of the solution withdrawn with a class A pipet. The densities were estimated to be in error by no more than 0.05 g./cc. These accuracies are sufficient to determine the number of molecules per unit cell in the crystal.

I. Magnetic Susceptibilities Measurements

Magnetic moments were determined by the Gouy method on a Gouy balance built at Montana State University and previously described by Houk (10). All measurements described here were made at room temperature. Measurements were made in triplicate and the average value of the balance deflections used to calculate the mass susceptibilities according to the equation:

$$\chi_g = \frac{(2g)\ (\Delta w)\ (l)}{(H^2)\ (m)}$$

where l = sample length

m = sample weight

g = acceleration of gravity

Δw = weight change

H = magnetic field

The magnetic field was determined by the Gouy method using a standard of known susceptibility. The standard used was freshly prepared cobalt mercury thiocyanate which obeys the Curie Weiss law (1):

$$\chi_g = C/T + \theta$$

$$\theta = 10$$

$$\chi_g(20^{\circ}\text{C.}) = 16.44 \times 10^{-6} \text{ e.s.u.}$$

Measurements were made at several values of magnetic field to prevent errors due to ferromagnetic impurities.

IV. X-RAY ANALYTICAL TECHNIQUES

A. Powder Diffraction

Two different techniques were used to obtain powder diffraction data. The first technique used standard photographic techniques with a Phillips powder camera of radius 57.3 mm. No attempt was made to correct for film shrinkage in any measurements reported. All measurements of 2θ angles were made on a vernier scale film measuring light box, and were made from arc to arc across the center of the diffraction cone. The second technique used the General Electric Goniostat (belonging to Montana State University Chemistry Department). In this technique, 2θ diffraction angles were read directly from the position of peak centers on a strip chart recorder. These peaks were generated as the scintillation counter moved in a normal 2θ scan mode, and a powder sample of the material was left stationary at the focus of the beam. In all cases where only positive values were taken they were judged in error by as much as 0.2 degrees due to mechanical misalignment. Error in determining the center of peaks on the chart paper was less than 0.01 degrees.

B. Single Crystal Diffraction

All crystals were initially examined under the polarizing microscope for signs of twinning. If the crystal appeared to be single, it was optically aligned and mounted for oscillation line-up photographs on a Weissenberg camera. Oscillation and rotation photographs were taken to align the crystal; first and second level Weissenberg photographs were taken if no indication of twinning had appeared. If the crystal was found to be single, a second layer photograph was taken to determine the crystallographic space group. If the crystal was very thin in one dimension, precession photographs were used to determine the space group. For all Weissenberg investigations, copper K_α radiation was used; for precession photographs, molybdenum K_α radiation was used.

Cell dimensions were determined by the methods outlined by Buerger (23) from film measurements made on a vernier measuring light box capable of an accuracy of ±.01 cm. Calculation of the β angle for monoclinic crystals mounted on the a or c axes was done by the method of angular lag. Precession photographs were also used to measure the β angle directly.

C. Single Crystal Diffraction Studies on Bis-(1,8-Naphthyridine)-Copper(II) Chloride

All preliminary work was done by standard Weissenberg and precession techniques using cameras and equipment available at Montana State University. Preliminary examination of a crystal of Bis-(1,8-naphthyridine)-copper(II) chloride showed systematic absences consistent with either of the space groups C/2c or Cc. The crystal was mounted along the a axis. The goniometer head and crystal were transferred from the Weissenberg camera to a General Electric X-RD-5 Goniostat with a copper tube and nickel filter. The crystal was aligned by the "basal plane" (Appendix C) alignment technique. Accurate cell constants were determined by averaging the values determined from high angle axial reflections.

The cell constants obtained from the goniostat were used as input data for the computer program DIFFSET which calculated machine settings for the collection of intensity data. Goniostat geometry and all programs used are discussed in Appendices C and B respectively. One reflection was chosen as a standard to prevent any accidental loss of alignment; the intensity of this reflection was taken at the beginning and end of each data collection shift. All intensity data were taken by technicians employed for the purpose. The data were taken by the standard $\theta - 2\theta$ scan technique. Background intensity was counted on both the upper and lower sides of the peak. The peak was scanned for 100 seconds at a 2θ scan rate of 2 degrees per minute and backgrounds counted for 50 seconds without scanning. The intensity of a peak was considered to be the difference between the count for the peak scan and the sum of the background counts. All intensities with a net count of less than 30 were considered unobserved. Intensity data for all unique reflections with a value less than 120 degrees were collected.

Because of the nature of the program DIFFSET, intensity data were collected on all reflections h,k,l and then on reflections -h,k,l. When almost all of the intensity data for reflection h,k,l had been collected, the intensity for the standard reflection suddenly dropped almost to zero. Optical examination of the alignment showed that the crystal had moved translationally out of the X-ray beam. The crystal was moved laterally back into the beam and the intensity of the standard returned to normal. It was assumed that the crystal was still in alignment and data collection resumed. When all the data were collected structure factors were calculated from the intensities by the program LI. The structure factors were used in a

Patterson synthesis (program FOURIER) in which the space group ambiguity is not important since a Patterson map is necessarily centric.

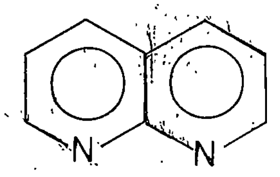
The crystal density indicated that there were four copper atoms in the unit cell which meant that the copper atoms were in special positions if the space group were C2/c. The two-fold axis seemed the most promising position and the remaining co-ordinate of the position was determined from the Patterson map. Using the computer program MAIR the structure factors for this position were calculated and refined. The R for the copper only was 52%. A Fourier synthesis was then calculated with the programs ICR6 and ICR1 using the observed structure factors and the signs of the structure factors from the calculated position for the copper atom. The Fourier map indicated a position for the chlorine atom which was then used in a structure factor calculation and refinement. The copper and chlorine positions were refined to an R of 29%. The calculation of a new Fourier synthesis indicated the positions of some of the light atoms. Successive structure factor calculations and Fourier syntheses gave positions for all the atoms expected in the structure. Refinement of these positions would not proceed below a R of 16% by either block diagonal or full matrix (program ORFLS) technique. Choice of Cc as the space group would not improve the refinement. It was evident that the data were in some way grossly in error.

Since the crystal had moved suddenly at about the end of the h,k,1 data collection, separate refinements were made. The h,k,1 data refined in five cycles of block diagonal refinement to a R of 6%. The -h,k,1 data would not refine below 14%. The data were recollected.

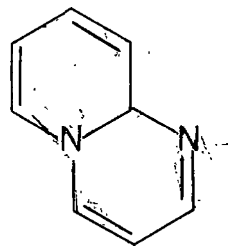
The second data collection used zirconium filtered molybdenum radiation to minimize the effects of absorption in the crystal. The same crystal was used for the second data collection except that a small fragment was lost in remounting. The computer program DSET was written to calculate machine settings for a "chi ninety" alignment procedure. The crystal was aligned on the Weissenberg camera and transferred to the goniostat. Calculations determined that the reflection -2,0,4 was very nearly perpendicular to the b* - c* plane; this reflection was chosen as the alignment reflection. Judicious movement of the goniometer arcs and constant following with the detector allowed the alignment reflection to be moved to "chi ninety". The crystal was then aligned by a procedure obtained from Watenpaugh (24) and very similar to that outlined by Jensen (25). When the crystal was aligned, new cell constants were determined by charting the diffraction intensity for a number of reflections for both positive and negative values of 2θ. The true value of the 2θ angle was considered to be the average of the positive and negative values. The 2θ values for 12 reflections were entered into the program PARAM which gave the best cell parameters by a least square refinement. These cell parameters and the "Goniostat space" co-ordinates of the "chi ninety" and one other reflection were entered into the program DSET to obtain machine settings for data collection. Three widely spaced reflections were chosen to use as standards for scaling data and to prevent accidental loss of alignment. The crystal alignment was checked each day and the standard reflection intensities were taken every four hours and at the beginning and end of each data collecting day. A graphical display of the scales obtained from the standard reflections was used to determine the diffractometer stability and is given in Appendix C, Fig. 40. The raw intensity data were collected in a similar manner to that used before except that 60-second scans were used and backgrounds counted for 30 seconds. All data for 2θ less than 60 degrees were obtained for h,k,l reflections and all data for 2θ less than 45 degrees for -h,k,l. These data were reduced with program RDN to structure factors. Refinement of all data for 2θ less than 45 degrees with the program DLS reduced the R to 6.8% for isotropic temperature factors. Anisotropic refinement reduced the R to 6.1%. Bond angles, distances and estimated standard deviations were calculated with the program BAD and are given together with tables of structure factors in Appendix C.

DISCUSSION

Although both 1,8-naphthyridine and 4-methyl-1,8-naphthyridine were reported in the literature (12,16), it was necessary to develop a new synthesis for each of these compounds. Skraup syntheses of 1,8-naphthyridines from 2-aminopyridine have been reported to yield 1,4a-diazanaphthalenes (Fig. 10) rather than 1,8-naphthyridines (13). In pyridine, the most electronegative position is the nitrogen atom (Fig. 11).



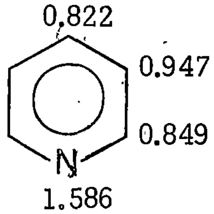
1,8-naphthyridine



1,4a-diazanaphthalene

Alternate Ring Closure Products

Figure 10

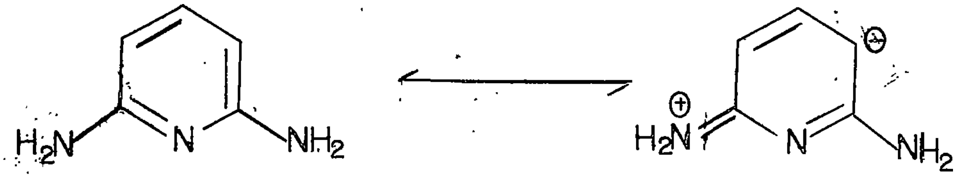


π-Electron Densities in Pyridine (26)

Figure 11

Ring condensation, such as occurs in the Skraup reaction, would therefore be likely to occur at the ring nitrogen as well as at the 3-position in the ring and possibly preferentially at the ring nitrogen. A recent report of the synthesis of 1,8-naphthyridine via the Skraup synthesis indicates that some ring closure can occur in the 3-position. The 1,4a-diazanaphthalenes are easily cleaved to regenerate 2-aminopyridines (13); the 1,8-naphthyridines are not easily cleaved. Proper choice of reaction conditions could produce 1,8-naphthyridine. Attempts to reproduce the synthesis of Paudler and Kress (19) have shown that the yields are in general low so that the reaction may not be of great synthetic utility.

Substituents in the 6-position of 2-aminopyridine can improve the yield of 1,8-naphthyridines (13). When the 6-substituent is an amino group, the yields are greatly enhanced. Figure 12 shows that the 6-amino group can contribute electron density to the 3-position.

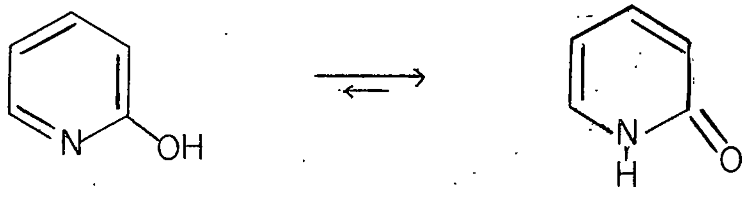


Resonance Structures for 2-6-diamino Pyridine

Figure 12

Steric hindrance to ring closure at the nitrogen is surely involved as well, since a methyl group in the 6-position will increase the yield. The 6-methyl group does not promote the formation of 1,8-naphthyridines to the extent that the 6-amino group does, but this effect may be accounted for in two ways; the ability of the 6-amino-1,8-naphthyridines to form intramolecular hydrogen bonds to the nitrogen would mean greater steric hindrance by the amino group and the activation of the 3-position to electrophilic substitution could increase the rate of ring closure in the 3-position.

The increased yield of 1,8-naphthyridines from 2,6-diaminopyridines gives an excellent route to substituted 1,8-naphthyridines which in turn provides an excellent route to the parent compound. Carboni, Settimo, and Pirisino (17) reported the synthesis of 2-amino-7-hydroxy-1,8-naphthyridine from which removal of the amino and hydroxy groups would yield the parent base. The amino group on a benzene ring can be removed by diazotization and treatment with hypophosphorus acid. The hydroxy group could be removed by distillation from zinc, a very destructive process. In pyridine chemistry, it is difficult to replace the 2-amino group with hydrogen by diazotization in hypophosphorus acid since it is difficult to obtain stable diazonium salts from 2-amino-pyridines even in strong acids. In weakly acidic solution the diazonium salt decomposes immediately to give the phenol. The compound resulting from the treatment of 2-amino-7-hydroxy-1,8-naphthyridine with nitrous acid is then a dihydroxy-1,8-naphthyridine. The problem is to remove two 2-hydroxy groups from the pyridine rings. The application of benzene chemistry is once more misleading because the compound which may be called 2-hydroxy-pyridine does not exist in the phenolic form, but rather in the keto form as shown in Fig. 13.



$\frac{[B]}{[A]} = 2 \times 10^5$

A B

2-Hydroxypyridine 2-Pyridone

Tautomerism in 2-Hydroxypyridine (27)

Figure 13

The 2-pyridone type of compound may, however, be converted to a 2-chloropyridine by the reaction with a mixture of phosphorous pentachloride and phosphorous oxytrichloride. The 2,7-dichloro-1,8-naphthyridine obtained in this sequence may be hydrogenated to give 1,8-naphthyridine. Hydrogenation of 2,7-dichloro-4-methyl-1,8-naphthyridine obtained in this same manner does not give 4-methyl-1,8-naphthyridine. The product mixture contains two predominant components. It was first believed that one of these components was the 4-methyl-1,8-naphthyridine and that the second component was a dihydro or tetrahydro-4-methyl-1,8-naphthyridine. Gas chromatography with an SE-30 liquid phase resolved the two components. Since the SE-30 separates compounds primarily on a molecular weight basis, 4-methyl-1,8-naphthyridine and a dihydro or tetrahydro-4-methyl-1,8-naphthyridine should have similar retention times. The retention times differed by about ten percent, which is reasonable for the difference postulated. Thin layer chromatography of the reduction product on silica gel plates again showed two predominant compounds with widely different R_f values. For the products postulated, a material which separates on base strength (such as silica gel) should give very different R_f values (compare the base strength of pyridine and piperidine in Table I).

Table I

BASE STRENGTHS OF PYRIDINES (10)

Compound	pKa
pyridine	1.7×10^{-6}
piperidine	1.6×10^{-3}

Although the two predominant reduction products could be separated on a glass analytical gas chromatography column, no separation was achieved with the metal preparative columns used. Severe decomposition occurred and no product was recovered. Decomposition of the partially hydrogenated 1,8-naphthyridine would not be unusual, but the fully aromatic base should be stable. Preparative thin layer chromatography was also attempted to separate the two predominant fractions, but was only successful in enriching the different fractions. The PMR spectra of the enriched fractions did not indicate that either fraction was clearly the desired 4-methyl-1,8-naphthyridine.

Catalytic hydrogenation is not the only method of removing a 2-chloro group from a pyridine ring. Thielepappe (28) reported that metal ion oxidation of 2-hydrazinopyridines gives the free pyridine. Albert (20) has used this technique in the preparation of 1,6-naphthyridines. The 2,7-dichloro-4-methyl-1,8-naphthyridine was converted to the

2,7-dihydrazino-4-methyl-1,8-naphthyridine which was then oxidized with copper sulfate. The initial two attempts to produce 4-methyl-1,8-naphthyridine by this method gave no product at all and the starting material was not recovered. The product may have complexed with the excess copper ion in solution and not have been extracted in the procedure used. The third attempt to prepare the compound by this technique produced an estimated 90% yield of crystalline 1,8-naphthyridine which was characterized by its PMR spectrum and showed to be pure by gas chromatography. The product was first obtained as an oil which is the reported physical form for 4-methyl,1,8-naphthyridine. Examination of Table II would indicate that 4-methyl-1,8-naphthyridine should be a solid at room temperature.

Table II

MELTING POINTS OF 1,8-NAPHTHYRIDINE (13)

Compound	Lit. m.p.	Obs. m.p.
1,8-naphthyridine	99	98-99
4-methyl-1,8-naphthyridine	(oil)	56
2,4-dimethyl-1,8-naphthyridine	63	—

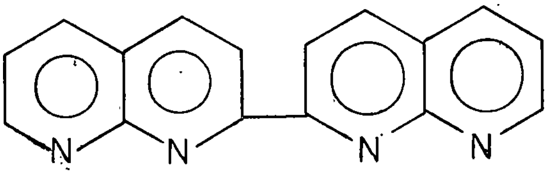
On considerations of molecular weight alone, 4-methyl and 2,4-dimethyl-1,8-naphthyridine would be expected to melt at a higher temperature than 1,8-naphthyridine. However, the higher symmetry of 1,8-naphthyridine probably allows better packing in the crystal and this consideration could easily over-ride the effects of molecule weight. It is, however, difficult to see how 2,4-dimethyl-1,8-naphthyridine could pack much better than 4-methyl-1,8-naphthyridine. If the packing characteristics are similar, or if 4-methyl-1,8-naphthyridine has the better packing characteristics of the two compounds, it should surely be a solid at room temperature. The melting point might be low enough to make crystallization difficult. Rapid evaporation of the hexane (with a stream of dry nitrogen) from a solution of 4-methyl-1,8-naphthyridine in hexane caused precipitation of white crysttals. These crystals proved to be 4-methyl-1,8-naphthyridine. Comparison of the gas chromatographic characteristics of the pure 4-methyl-1,8-naphthyridine with those of the oil obtained from catalytic reduction of 2,7-dichloro-4-methyl-1,8-naphthyridine (Table III) clearly shows that neither of the predominant fractions in the oil is 4-methyl-1,8-naphthyridine. The compounds remain unidentified; they both may be hydrogenated derivatives of 4-methyl-1,8-naphthyridine.

Table III

GAS CHROMATOGRAPHIC RETENTION TIMES

Material	Retention time (min.)
1,8-naphthyridine	2.0
4-methyl-1,8-naphthyridine	2.08
Catalytic Reduction Product (oil)	3.45, 4.0

The first copper-naphthyridine complex prepared was Bis-(2,7-dichloro-4-methyl-1,8-naphthyridine)-copper(II) chloride ethanolate. This compound was obtained as a blue powder which did not dissolve as a coordination compound in any of the ordinary solvents. Treatment with hot water destroys the complex, dissolving copper chloride and leaving the insoluble naphthyridine. The naphthyridine is not a very strong complexing agent. Long exposure to the air apparently causes a loss of solvent or a solvent exchange; the compound turns pink. The pink material has not been investigated. Attempts to prepare a similar compound with copper (I) chloride failed to give any copper (I) complex. An orange material was produced which seemed to be a mixture of the light blue Bis-(2,7-dichloro-4-methyl-1,8-naphthyridine)-copper (II) chloride and bright orange organic product. What has apparently occurred is a reaction analogous to the Ullmann coupling of aryl halides (29). The product would be a binaphthyridine (Fig. 14) which could be highly colored. The orange organic product is slightly soluble in ethanol but has not been further investigated.



Binaphthyridine

Figure 14

The small amount (about 150 mg.) of 4-methyl-1,8-naphthyridine prepared has prevented the preparation of any copper complexes with this ligand, but two copper containing products were prepared from fractions of the oil obtained by catalytic reduction of 2,7-dichloro-4-methyl-1,8-naphthyridine. The two products precipitated together from ethanol solutions. One compound is a yellow powder which probably is a mixture. The other is a dark green crystalline compound for which X-ray data are given (Table XIII). Samples of both compounds were dissolved in aqueous ammonia and the solutions extracted and chromatographed. The green crystals gave a pure material which is one of the two organic components of the oil, but too little was available to clearly assign the structure of the ligand other than that it is clearly not 4-methyl-1,8-naphthyridine. The extract from the yellow powder was not much different from the oil used to give both the green and yellow products.

A copper(II) chloride complex of 1,8-naphthyridine was prepared by precipitation from a water solution of the two reactants. No water of hydration is found in the complex, indicating the strong coordination strength of the compound. Analysis of naphthyridine complexes was difficult due to the interference of naphthyridines in copper and chloride volumetric titrations. A study of the solution spectra by Job's method indicated that the complex formed in solution contained two moles of 1,8-naphthyridine per mole of copper(II) chloride.

The single crystal of Bis-(1,8-naphthyridine)-copper(II) chloride was mounted for single crystal studies. The experimental procedure followed in data collection has been described on page 25. The first set of data were in error, but they were sufficient for the general solution of the crystal and molecular structure. Crystallographic data for this compound are given in Table XI. The general position in space group C2/c is eight fold but the molecular formula indicated for the complex in solution would give only four molecules in the unit cell. Other possible molecular formulae would not give as good agreement with the experimental density. This molecular formula was assumed to be the true formula for the initial stages of the structure determination and was confirmed by the final results. If only four copper atoms are to be located in a space group which has an eight fold general position, the copper atoms must lie on special positions. The special positions for the space group C2/c are given in Table IV.

Table IV

COORDINATES OF EQUIVALENT POSITIONS FOR THE SPACE GROUP C2/c (30)

No. of Positions	Coordinates
8 (f)	(0,0,0; ½,½,0) + x,y,z; x,y,z; x,y,½-z; x,y,½+z
4 (e)	(0,0,0; ½,½,0) + 0,y,¼,0;y,¾
4 (d)	(0,0,0; ½,½,0) + ¼,¼,½; ¾,¼,0
4 (c)	(0,0,0; ½,½,0) + ¼,¼,0; ¾,¼,½
4 (b)	(0,0,0; ½,½,0) + 0,½,0,0,½,½
4 (a)	(0,0,0; ½,½,0) + 0,0,0; 0,0,½

The space group is not uniquely determined by the systematic absences. The space group could also be Cc. In Cc, the general position is four fold (Table V).

Table V

COORDINATES OF EQUIVALENT POSITIONS IN THE SPACE GROUP Cc (30)

No. of Positions	Coordinates
4 (a)	(0,0,0; ½,½,0) + x,y,z; x,y,½+z

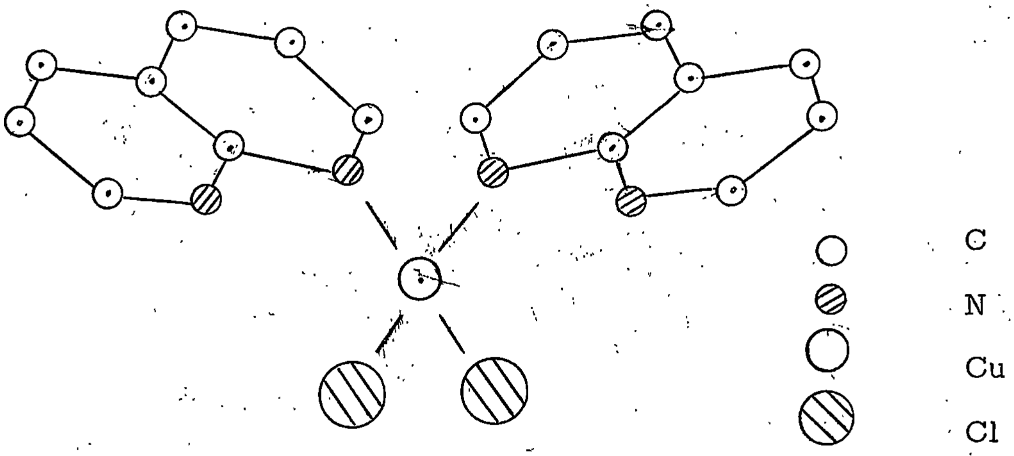
Analysis of the Patterson map generated from the experimental data indicated that the copper atoms lay on the two fold axes or that the space group was in fact Cc. (Locating the copper atoms in the space group Cc is no different from locating the copper atoms in the space group C2/c if the atoms lie on the two fold axes.) The general features of the Patterson map were also taken as indicative that the crystal was centrosymetric. The copper atom was given the position 0, y, 1/4. The value of y was determined from the Patterson map. This position was refined and a Fourier synthesis calculated to determine the positions of chlorine atoms. The Fourier map indicated several possible locations for the chlorine atoms. The chlorine is a large atom and would normally be expected to be clearly located; the poor quality of the Fourier map may be due to the errors known to be present in the data collection. One possible location of the chlorine was chosen and refined. The refinement was considered adequate for the initial stages ($R \sim 40\%$). Several Fourier syntheses were calculated with no success in locating the atoms.

Analysis of the Patterson map indicated that an incorrect position was chosen for the chlorine atom; a position for the chlorine indicated by the Patterson map was then refined along with the copper position. This position refined to a lower value ($R \sim 29\%$). Successive cycles of Fourier synthesis and refinement revealed the gross crystal structure.

The gross structure did not refine to the degree expected, and the possibility that the crystal was not centrosymmetric was investigated. Refinement of the structure using the space group Cc gave a small improvement in R but did not improve the estimated standard deviations in the bond lengths. A non-centric calculation of structure factors can improve the R for a proposed structure by masking some of the disagreement in structure factors since the phase angle can absorb some of the disagreement. No alternative remained except that the data were somehow in error.

The data were recollected with more care than had been used in the first case. These data immediately allowed refinement of the structure to a reasonable value of R (6%). The final crystallographic data are given in Tables XIV, XV, XVI. The data for the initial collection procedure are given in Table VII and it is clear that there is little difference between the two sets. This agreement points out how nearly correct structures can be with poor data, but at the same time how valuable good data is in the determination of exact crystallographic structures.

A projection of the Bis-1,8-naphthyridine)-copper (II) chloride molecule is given in Fig. 15.

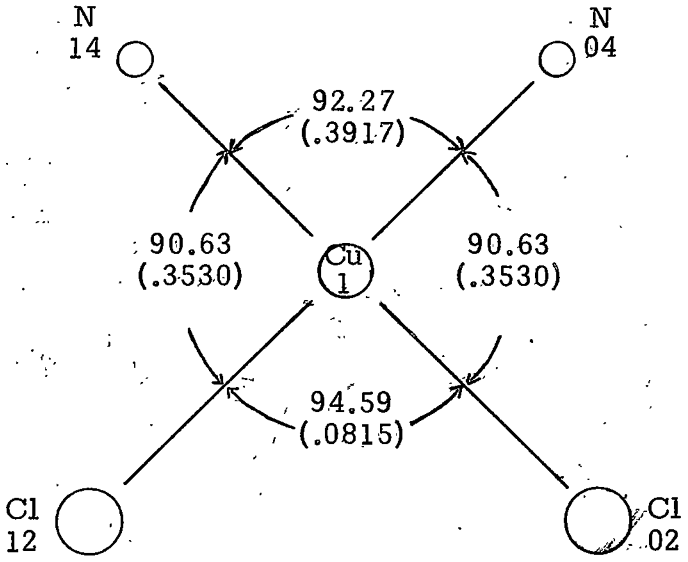


One Molecule of Bis-(1,8-naphthyridine)-copper (II) chloride

Projected on the b-c Plane

Figure 15

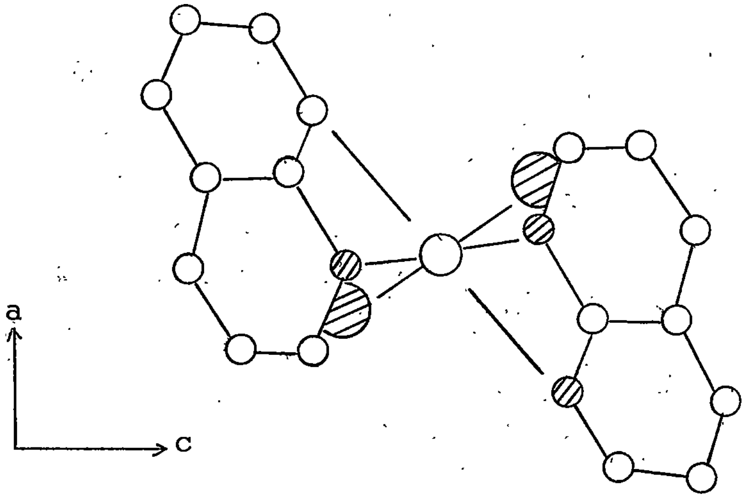
This projection does not clearly show the square planar coordination of the copper atom. The close approximation to true square planar coordination is better shown by Fig. 16 and Table VI.



Geometry of Copper Coordination

Figure 16

The coordination around the copper must also be viewed from another projection, given in Fig. 17.



One Molecule of Bis-(1,8-naphthyridine)-copper(II) chloride

Projected on the a-c Plane

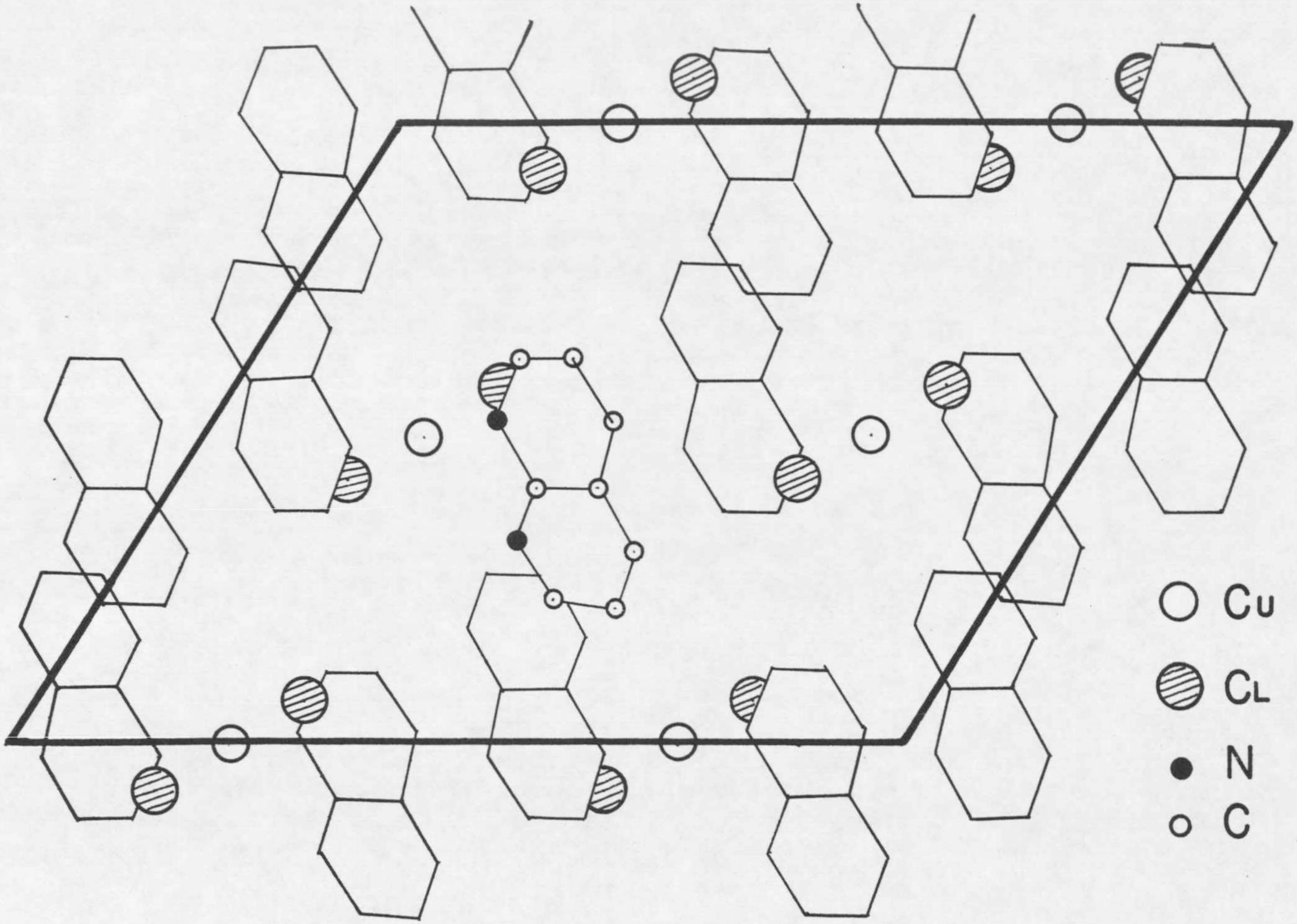
Figure 17

Table VI

DEVIATIONS FROM THE LEAST SQUARES PLANE FOR COPPER COORDINATION

Atom	Deviation (Å)
Cl 02	-0.4174
Cl 12	0.4174
N 04	0.3343
N 14	-0.3343

The second nitrogen atom in the molecule is located in a position near the copper atom and could be considered to be weakly coordinated. The geometry then would be that of a distorted octahedron. This copper-nitrogen distance is long but must be considered. The crystal field surrounding the copper is definitely that of a distorted octahedron. Such a symmetry should destroy any orbital contribution to the magnetic moment of the molecule, and a value of 1.9 Bohr magnetons would be expected if the orbital contribution is completely quenched. The spin only value of the magnetic moment would by 1.73 Bohr magnetons, but the spin-orbit coupling in copper compounds (as estimated from values measured for the free ion) increases the expected value to 1.9 Bohr magnetons. A value of the magnetic moment less than 1.9 Bohr magnetons would imply some sort of exchange interaction in the crystal; but no exchange should be possible. Fig. 18 gives a projection of the crystal structure onto the a-c plane of the unit cell. The copper atoms are much to far apart for any direct interaction and are not bridged in any way by other atoms. A value greater than 1.9 Bohr magnetons for the magnetic moment is possible if the orbital contribution is



Packing Diagram for Bis-(1,8-naphthyridine)-copper(II) chloride

Figure 18

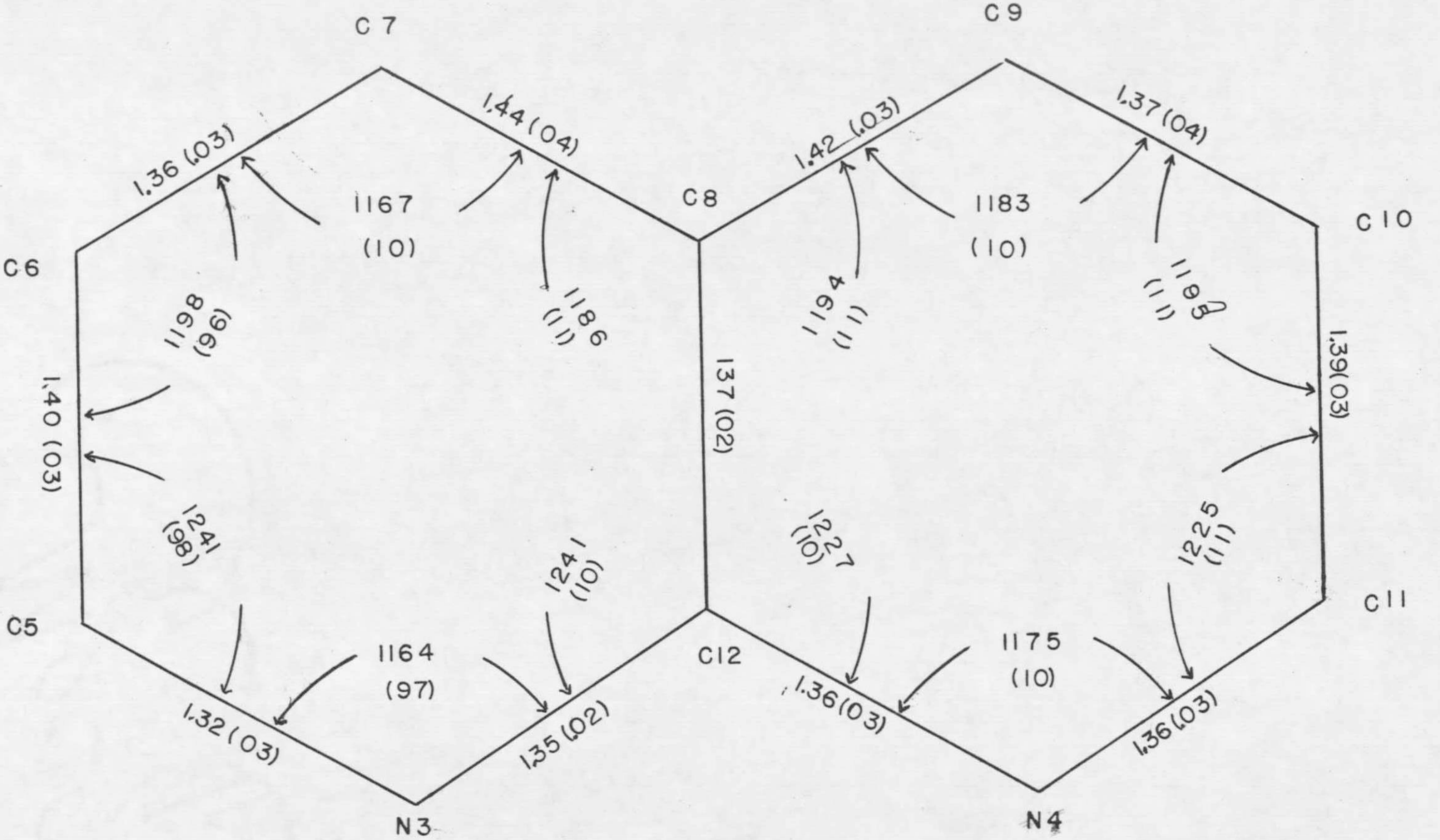
not quenched. Octahedral geometry should quench the orbital contribution (1) and geometries of less symmetry (such as the square plane or distorted octahedron) should also quench the orbital contribution.

The structure of the 1,8-naphthyridine (Fig. 19) molecule is also available from the total structure although it may be distorted slightly by the coordination. The accuracy of the bond lengths is affected by the presence of the heavy atoms in the structure.

The final refinement of the structure was done giving all the atoms anisotropic thermal parameters. Two of the cross terms in the anisotropic thermal parameters for the copper atom were not varied. These two terms are invariant under the space group operations and must therefore be held constant (31). No large parameter shifts were observed and the structure may be considered to show little anisotropy.

The cis-square planar coordination at the copper atom is unusual. The structure of Bis-pyridine-copper (II) chloride (32) is typical of the geometry expected in nitrogen coordinating copper (II) halides. This structure has a trans square planar geometry with long interactions to two chlorine atoms to form an elongated octahedron. These longer interactions are not unusual and may constitute a bridging pathway for exchange and spin correlation. The isolation of the copper atoms in Bis-(1,8-naphthyridine)-copper (II) chloride provides an excellent test case for measurement of interaction between molecules in the crystal.

Single crystal studies were also begun on Bis-(1,8-naphthyridine)-copper (II) bromide. The preliminary photographs show that an unusual form of disorder must exist in the crystal. Rotation photographs with Cu K_α



1,8-Naphthyridine Bond Lengths and Bond Angles (Standard Deviations)

Figure 19

radiation show five layer lines. The Weissenberg photograph of the first is extremely weak and the spots are severely elongated along the trace of the festoons. The zero, second and fourth levels are normal and the third so weak that it was only dark enough the show the same streaking. Reindexing the photograph to make the normal layers zero, one and two gives the crystallographic data given in Table XII. The cell resulting from this indexing requires that the copper atoms be disordered. The nature of the streaking indicates that the disorder is one dimensional but no further work has been done to determine the exact nature of the disorder.

SUMMARY

Since it was believed that 1,8-naphthyridine might form binuclear complexes with copper(II) halides, and since such binuclear complexes could provide information about the nature of the copper-copper interactions in copper(II) compounds with subnormal magnetic moments, it was decided to prepare and determine the crystal and molecular structure of some copper(II) halide complexes with 1,8-naphthyridines. Attempts were made to prepare both 4-methyl-1,8-naphthyridine and 1,8-naphthyridine for use as ligands since no suppliers of 1,8-naphthyridines exist.

The preparations of 1,8-naphthyridine and 4-methyl-1,8-naphthyridine given in the literature are not satisfactory for the preparation of these compounds in the amounts necessary for use as a ligand in the preparation of inorganic coordination compounds. The preparation of 4-methyl-1,8-naphthyridine does not yield the fully aromatic base in any quantity. The major products are not the reported 4-methyl-1,8-naphthyridine but probably hydrogenated derivatives. A new preparation of 4-methyl-1,8-naphthyridine has been developed which gives 4-methyl-1,8-naphthyridine as a crystalline product for the first time. The structure of 4-methyl-1,8-naphthyridine is clearly shown by PMR spectroscopy. A new preparation of 1,8-naphthyridine from readily available starting materials has been developed. This preparation gives yields of 1,8-naphthyridine in adequate quantities for use as a ligand in the preparation of coordination compounds.

Several copper(II) complexes of 1,8-naphthyridine have been prepared and characterised. The crystal and molecular structure of one of these

complexes, Bis-(1,8-naphthyridine)-copper(II) chloride, has been determined. The compound does not have the hoped for binuclear structure, but the structure is very unusual and provides a compound with isolated square planar coordination which may prove useful as a test in studies of ligand field theory. The square planar coordination is also unusual in that it forms a cis-square plane in contrast to the trans-square plane usually found in copper(II) compounds.

APPENDIX A

Spectroscopic and Magnetic Data

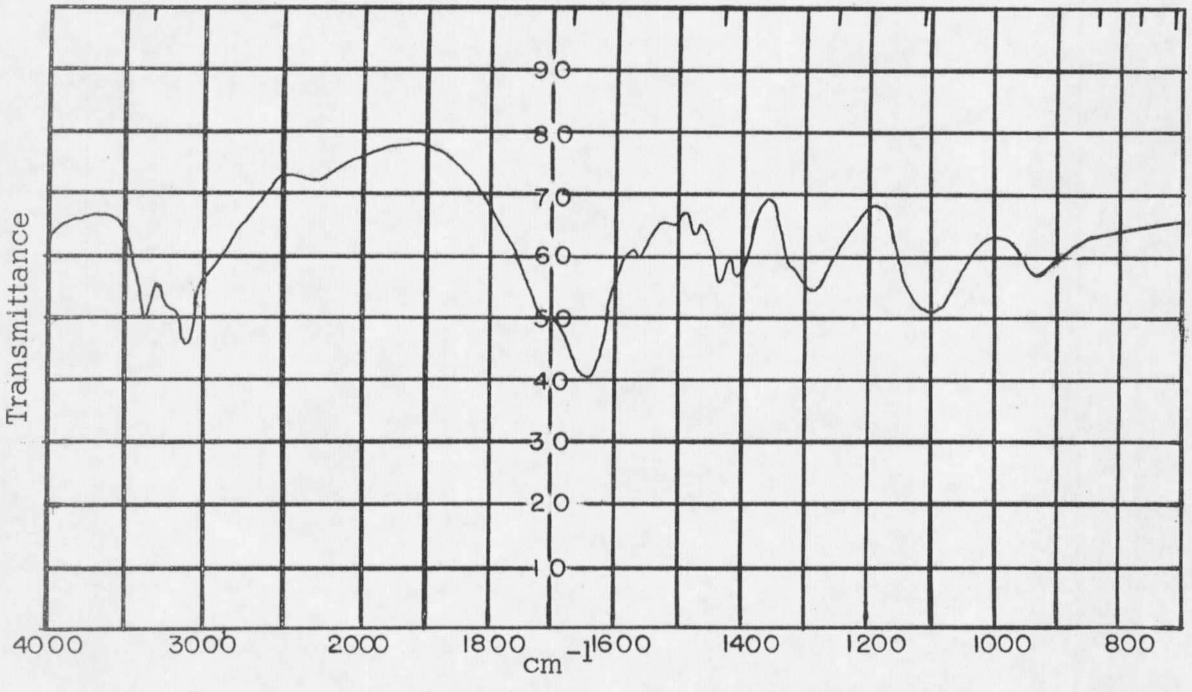


Figure 20. IR Spectrum of 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine

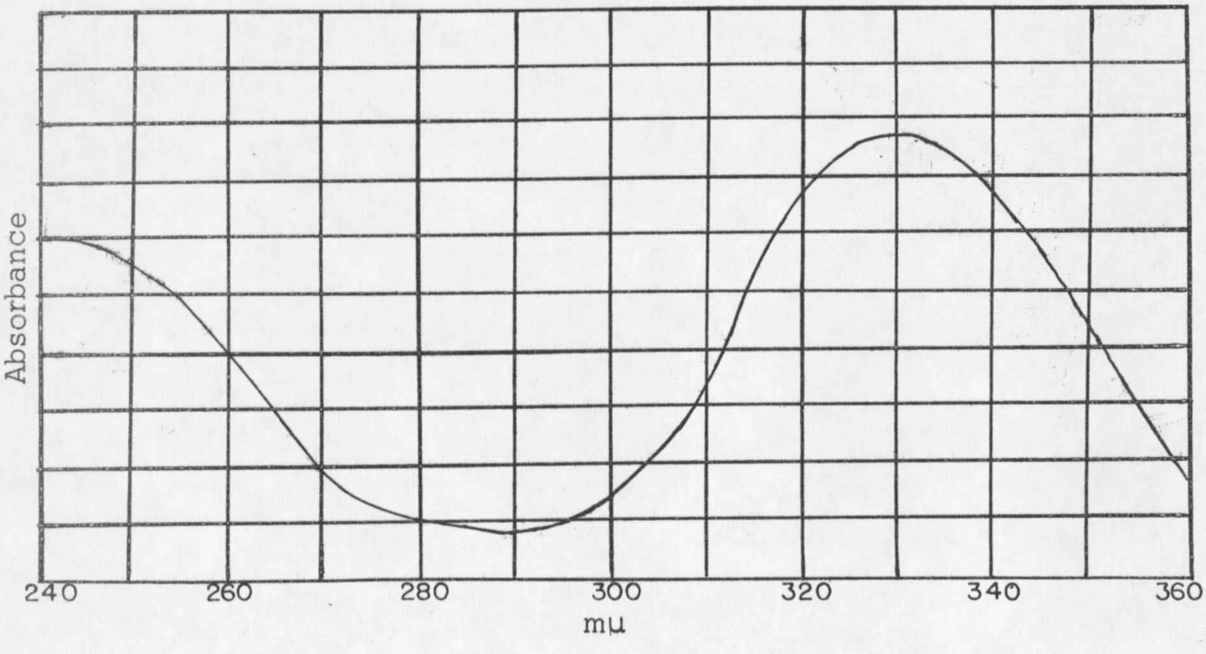


Figure 21. UV Spectrum of 2-hydroxy-4-methyl-7-amino-1,8-naphthyridine

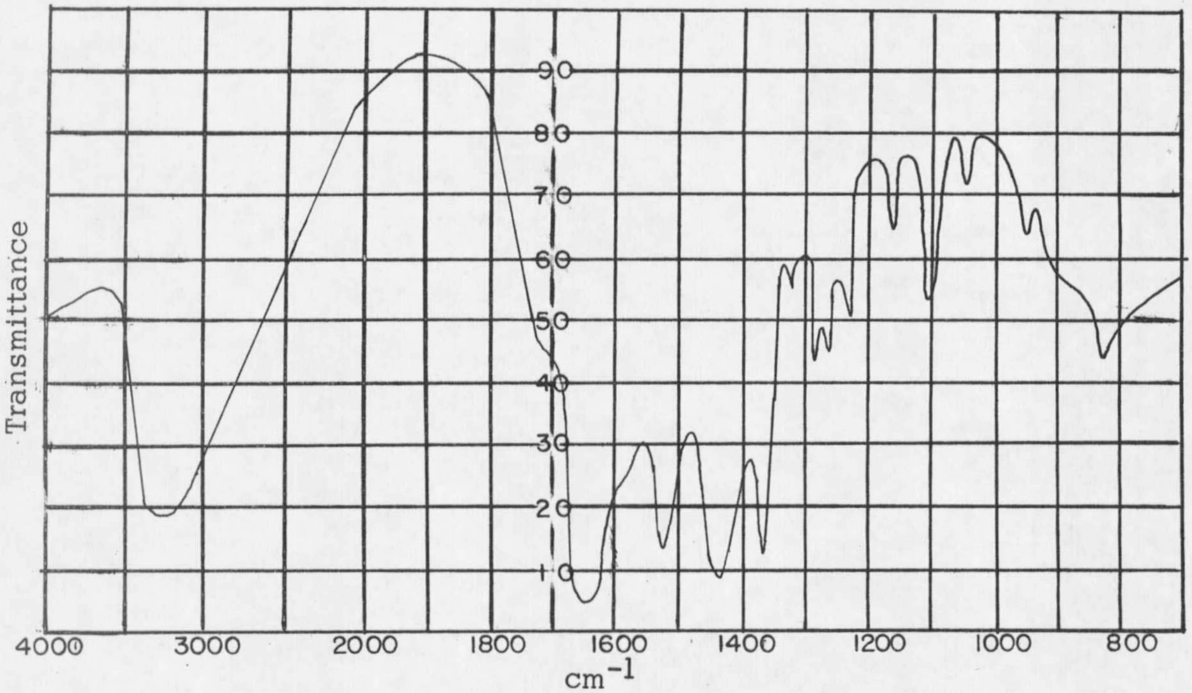


Figure 22. IR Spectrum of 2,7-dihydroxy-4-methyl-1,8-naphthyridine (KBr)

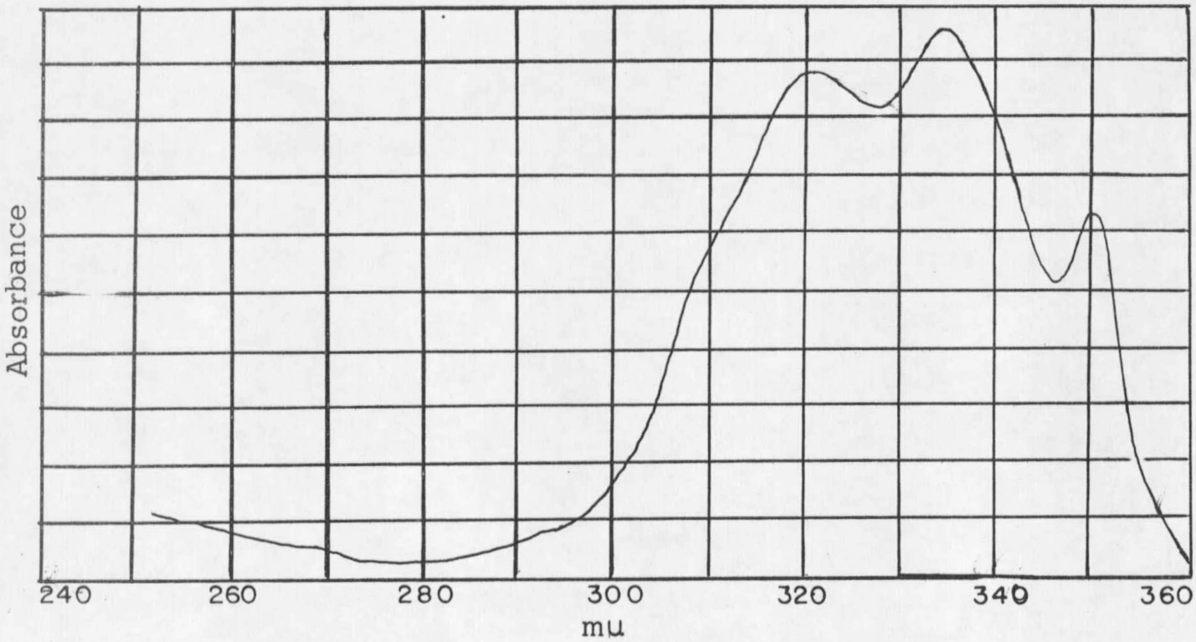


Figure 23. UV Spectrum of 2,7-dihydroxy-4-methyl-1,8-naphthyridine

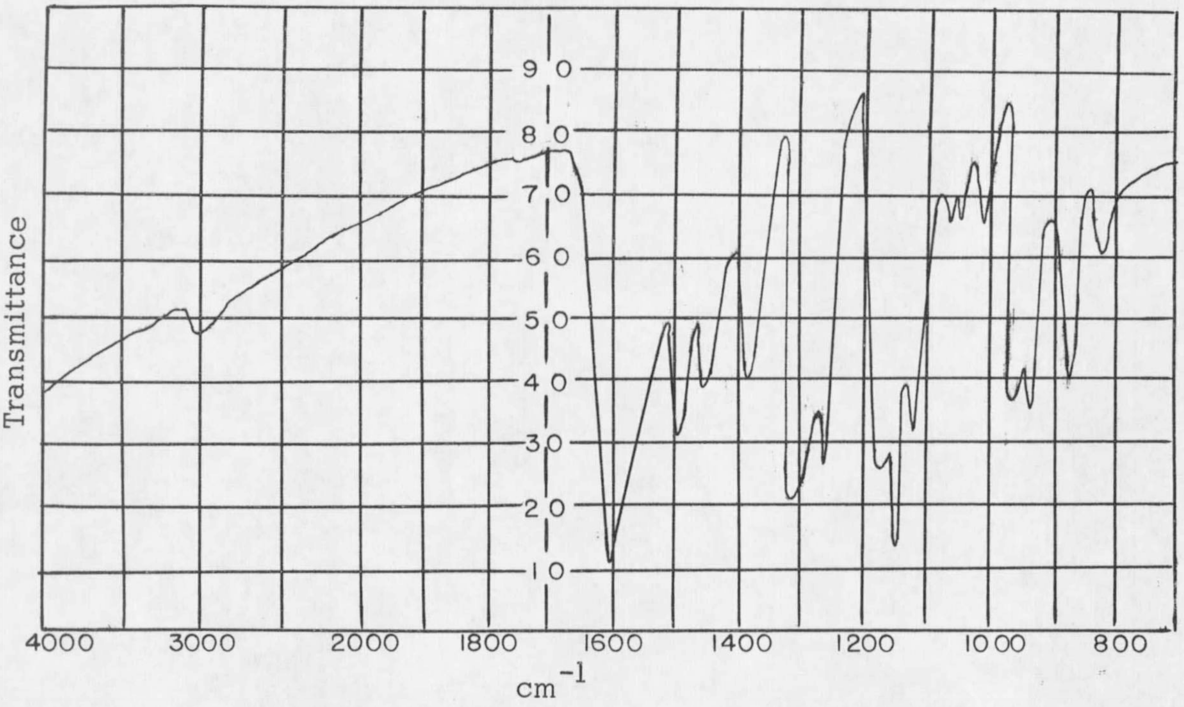


Figure 24. IR Spectrum of 2,7-dichloro-4-methyl-1,8-naphthyridine (KBr)

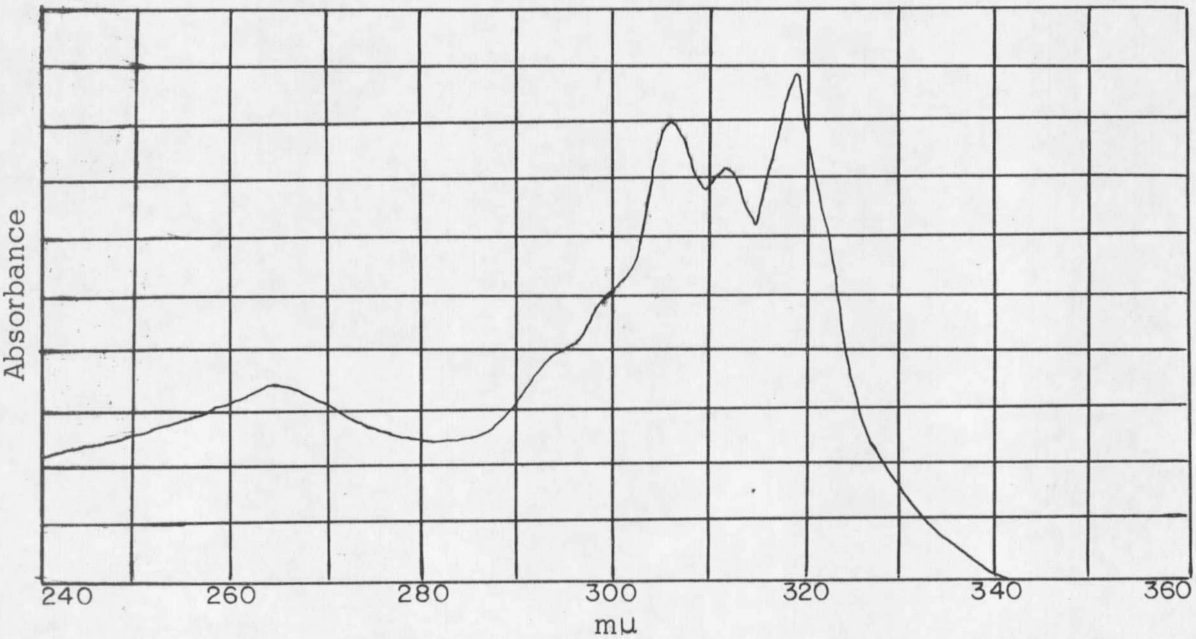


Figure 25. UV Spectrum of 2,7-dichloro-4-methyl-1,8-naphthyridine

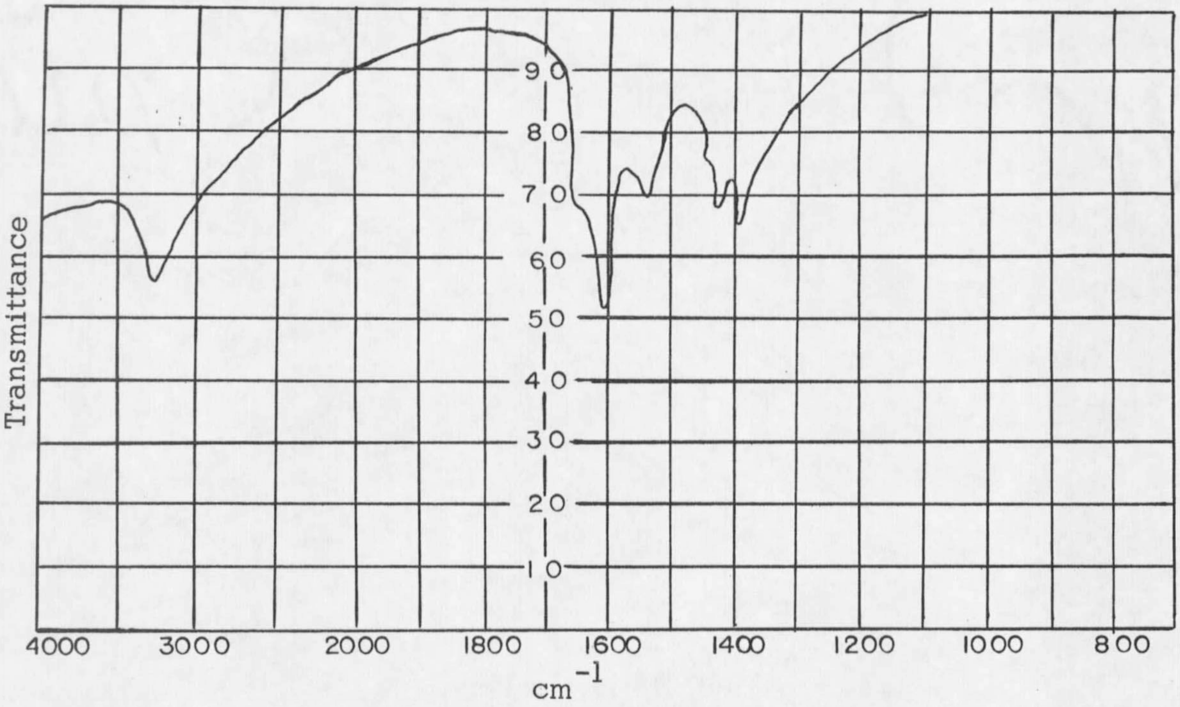


Figure 26. IR Spectrum of 2,7-dihydrazino-4-methyl-1,8-naphthyridine (KBr)

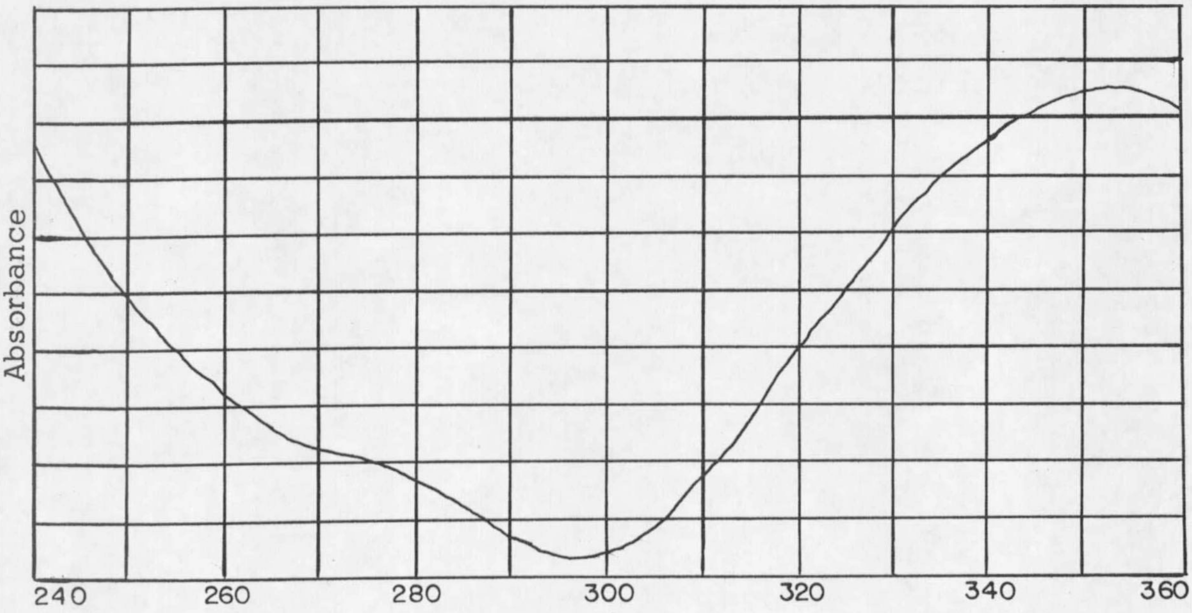


Figure 27. UV Spectrum of 2,7-dihydrazino-4-methyl-1,8-naphthyridine

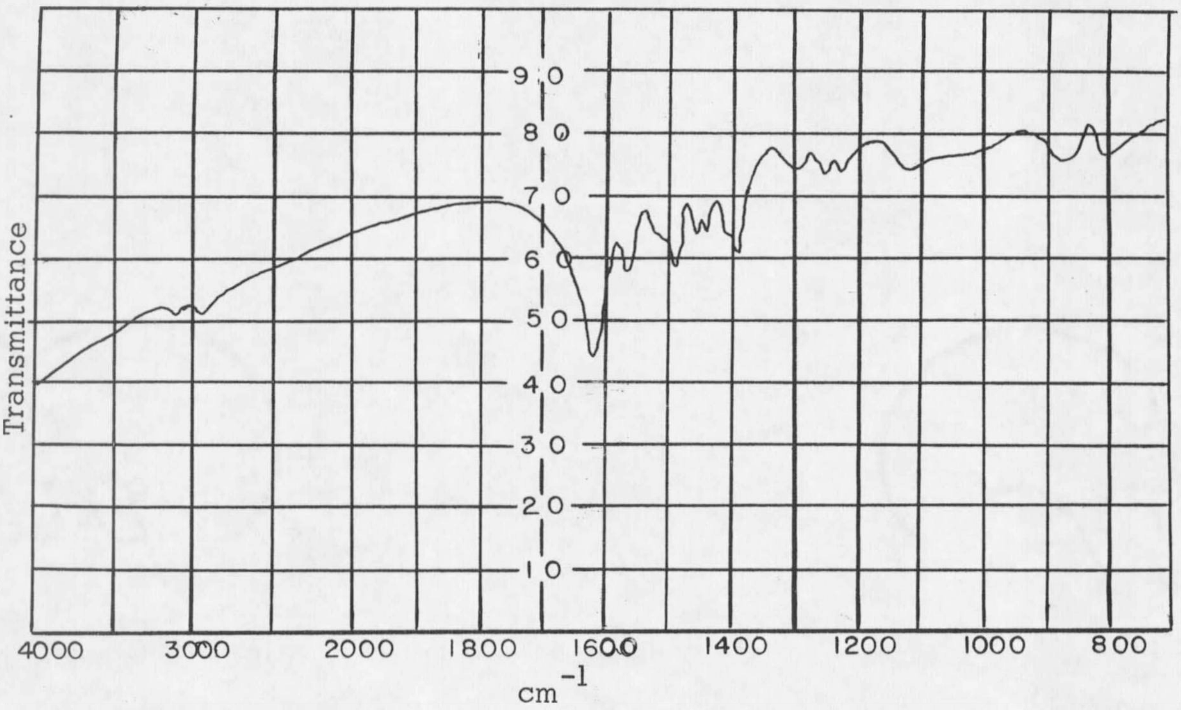


Figure 28. IR Spectrum of 4-methyl-1,8-naphthyridine

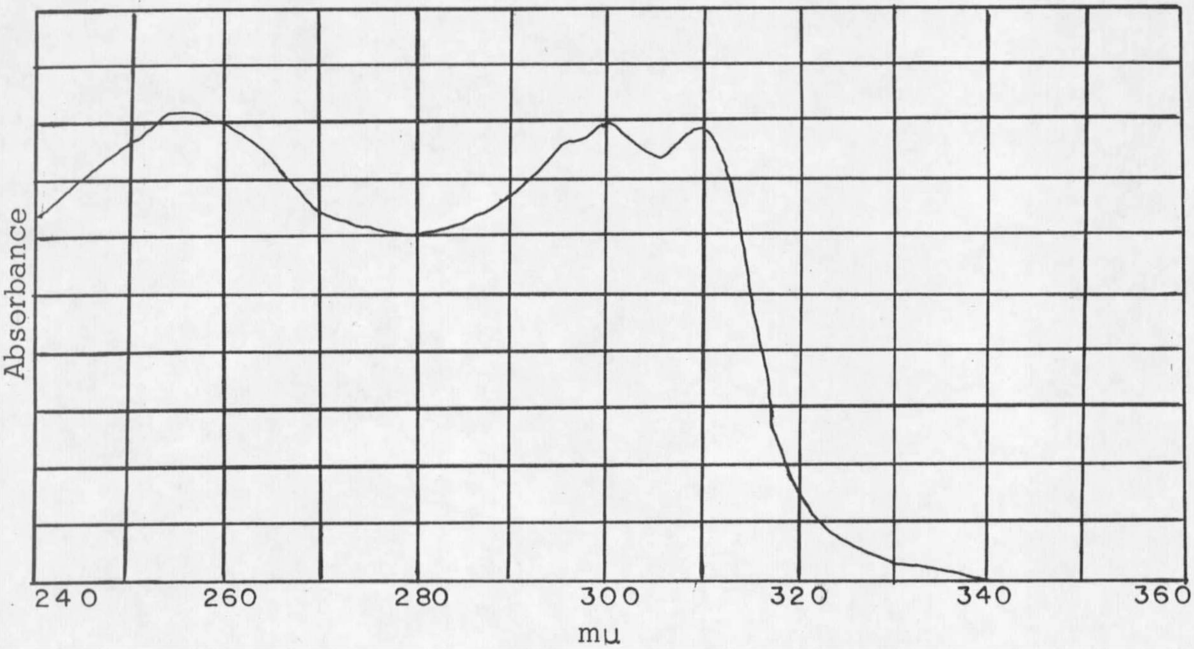


Figure 29. UV Spectrum of 4-methyl-1,8-naphthyridine

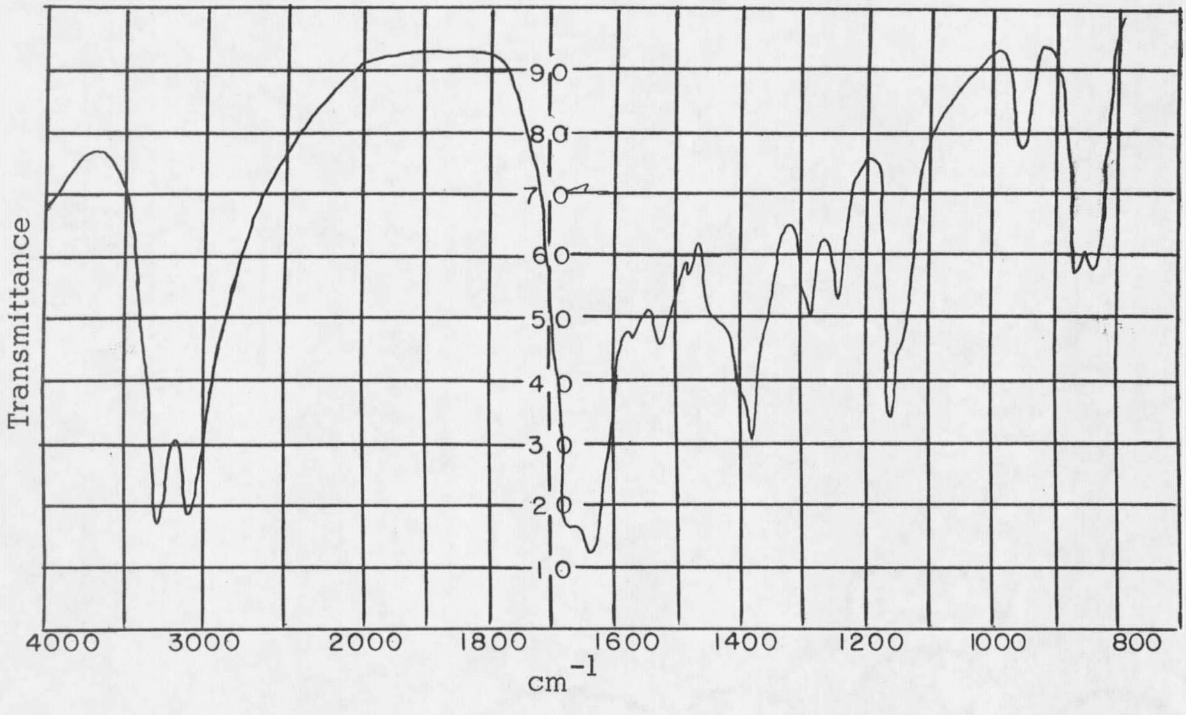


Figure 30. IR Spectrum of 2-amino-7-hydroxy-1,8-naphthyridine (KBr)

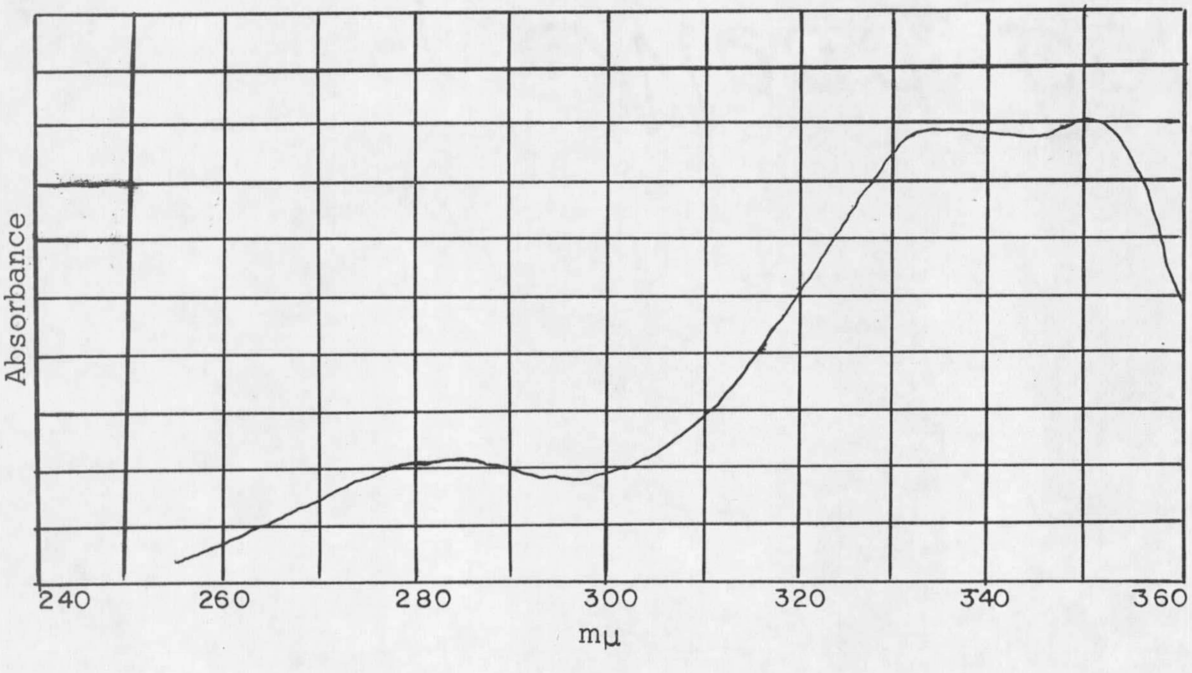


Figure 31. UV Spectrum of 2-amino-7-hydroxy-1,8-naphthyridine

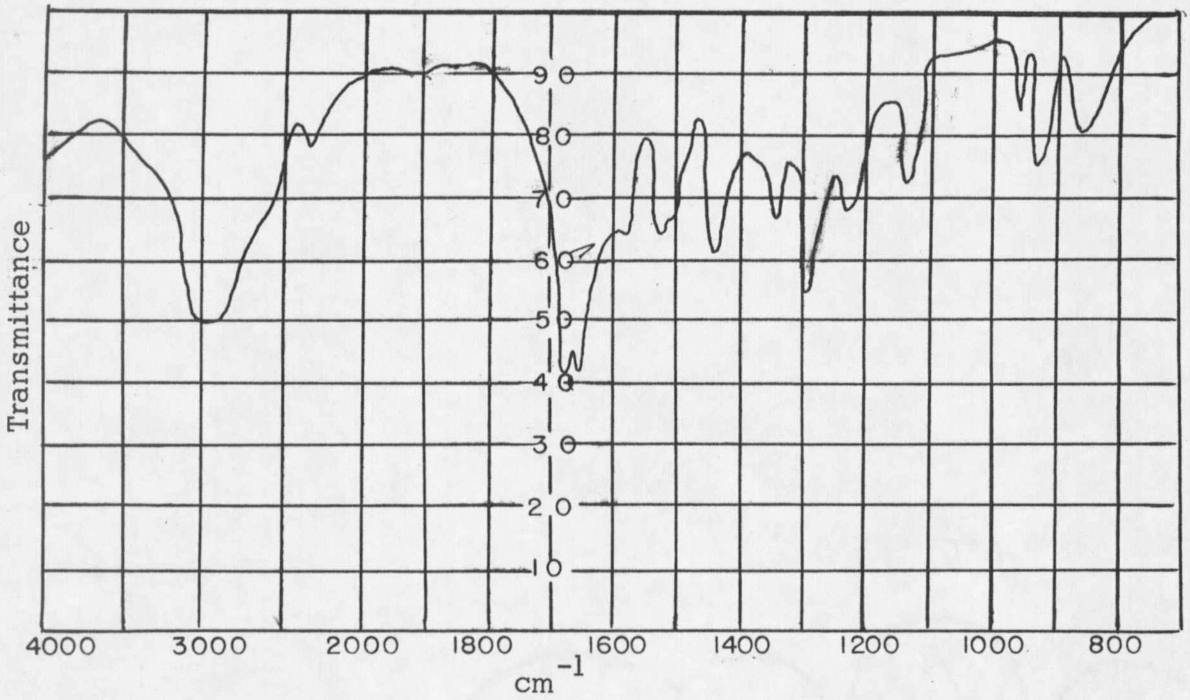


Figure 32. IR Spectrum of 2,7-dihydroxy-1,8-naphthyridine (KBr)

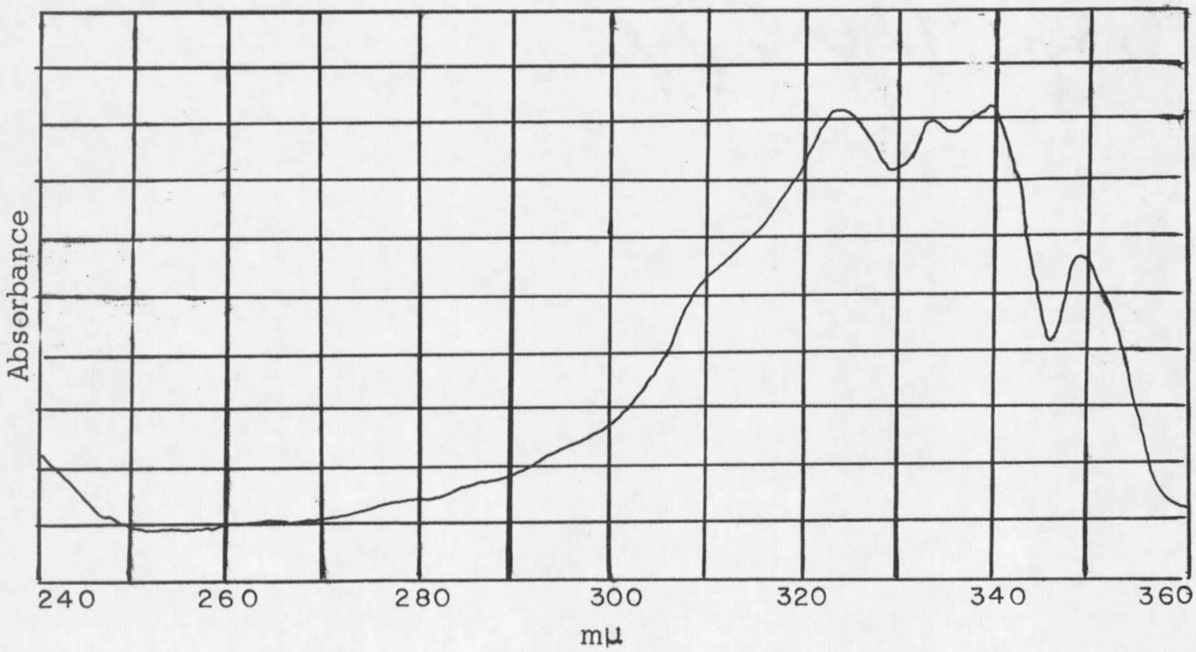


Figure 33. UV Spectrum of 2,7-dihydroxy-1,8-naphthyridine

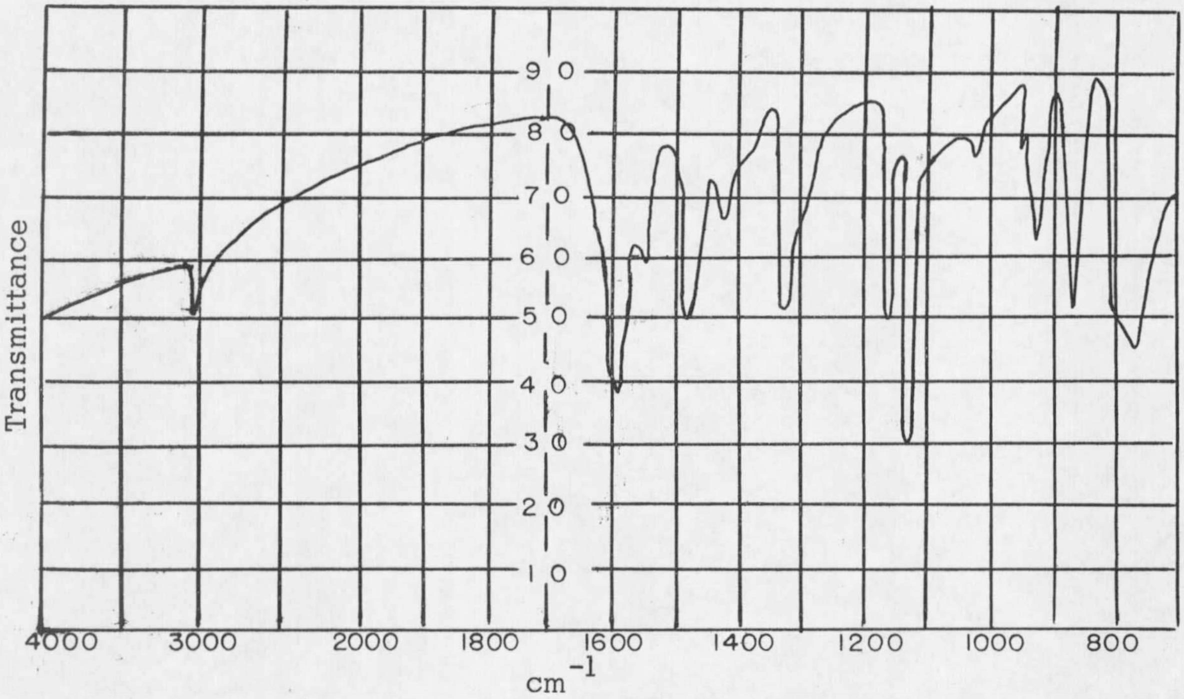


Figure 34. IR Spectrum of 2,7-dichloro-1,8-naphthyridine (KBr)

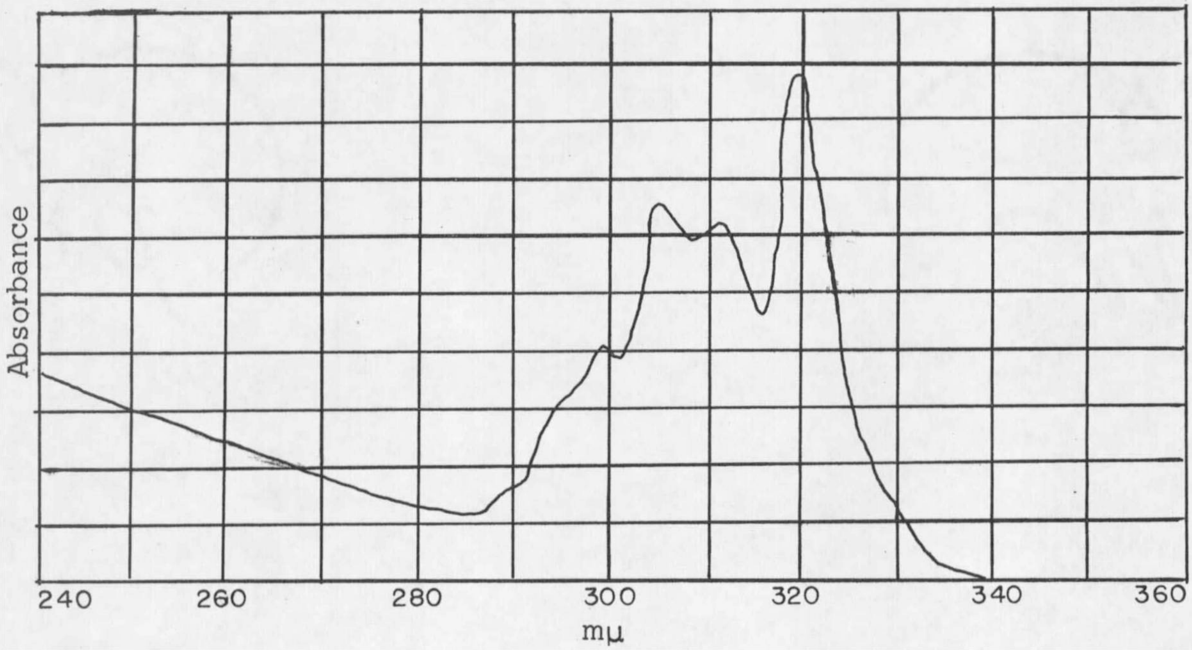


Figure 35. UV Spectrum of 2,7-dichloro-1,8-naphthyridine

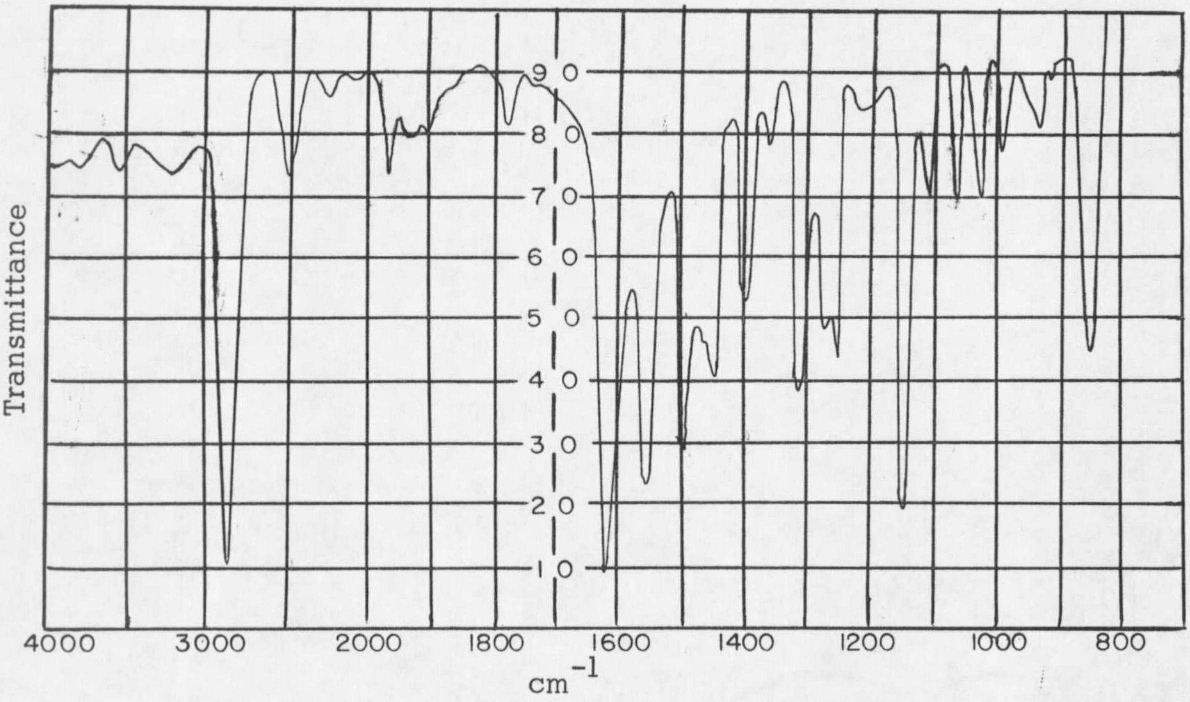


Figure 36. IR Spectrum of 1,8-naphthyridine ($CHCl_3$)

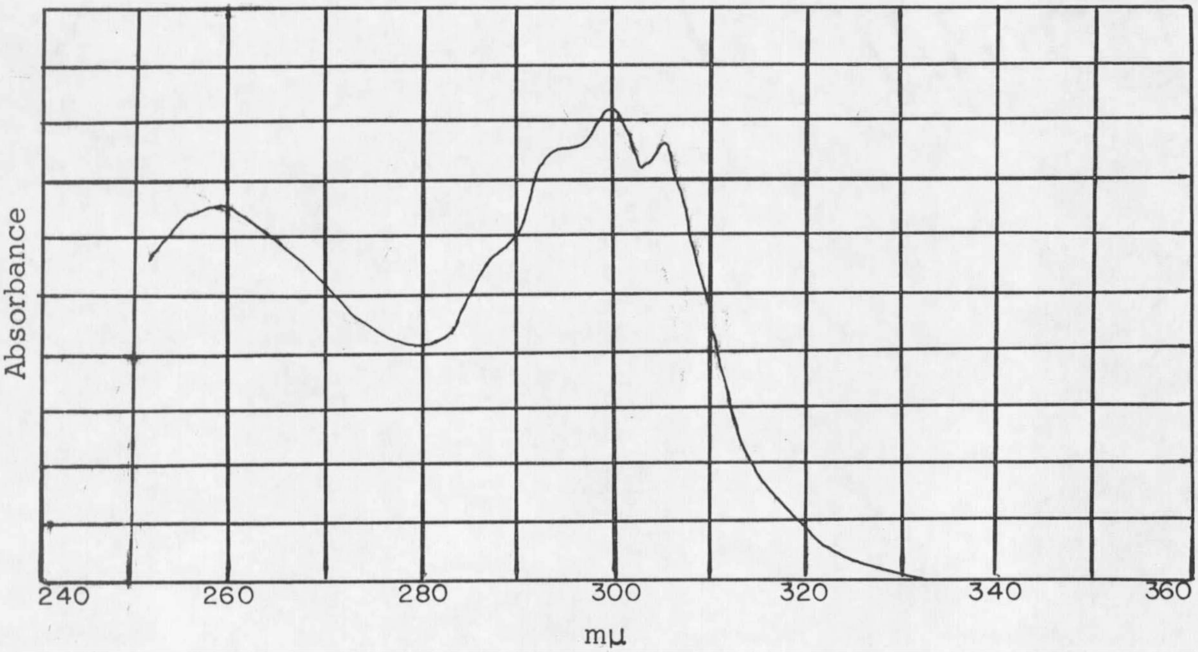


Figure 37. UV Spectrum of 1,8-naphthyridine

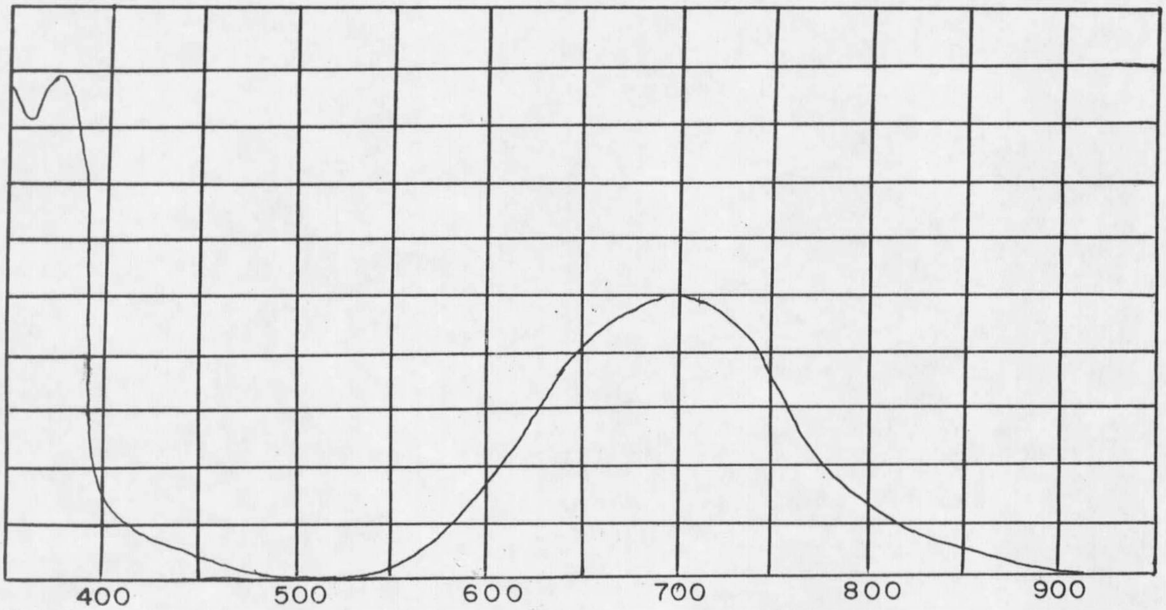


Figure 38. Visible Spectrum of Bis-(1,8-naphthyridine)-copper(II) chloride in water.

Table VII

EXTINCTION COEFFICIENTS OF

BIS-(1,8-NAPHTHYRIDINE)-COPPER(II) CHLORIDE IN WATER

Δ_{max}(mμ)	ε
368	26 (±1)
700	15 (±1)

Table VIII

THE MOST INTENSE BANDS

IN THE ULTRAVIOLET SPECTRA OF NAPHTHYRIDINES

(all spectra in 95% ethanol) (a)

Compound	λmax	(ε)
2-hydroxy-4-methyl-7-amino-1,8-naphthyridine	333	$(\quad \times 10^{6})$
2,7-dihydroxy-4-methyl-1,8-naphthridine	339	$(>10^{6})$
2,7-dichloro-4-methyl-1,8-naphthyridine	311	$(>10^{6})$
2,7-dihydrazino-4-methyl-1,8-naphthyridine	356	$(>10^{6})$
4-methyl-1,8-naphthyridine	255	
2-amino-7-hydroxy-1,8-naphthyridine	353	$(>10^{6})$
2,7-dihydrazino-1,8-naphthyridine	325	$(>10^{6})$
2,7-dichloro-1,8-naphthyridine	378	$(1.3 \times 10^{6} \pm .1)$
1,8-naphthyridine	307	$(5.7 \times 10^{6} \pm .1)$

(a) In all cases, ultraviolet spectra were determined by weighing 2 mg. samples of the compound in 100 ml. of 95% ethanol. Where extinction coefficients are reported as greater than 10^{6}, the sample was incompletely dissolved and if it had dissolved completely, the extinction coefficient would have been greater than 10^{6}.

Table IX

PROTON MAGNETIC RESONANCE SHIFTS AND COUPLING CONSTANTS OF 1,8-NAPHTHYRIDINES

	Proton	Shift (ppm)	Coupling	cps
1,8-Naphthyridine				
	α	.9	α-β	4.5±.5
	β	2.6	β-γ	8.5±.5
	γ	1.9	α-γ	2.2±.5
2,7-Dichloro-4-Methyl-1,8-Naphthyridine				
	CH_3	6.70	β-CH_3	.9±.1
	γ	1.4		
	β	2.32	β-γ	9.0±1.0
4-Methyl-1,8-Naphthyridine				
	CH_3	6.70		
	α	1.00		
	γ	1.40	β-γ	9.0±1.0
	β	2.33	α-γ	2.0±.5

Table X

ROOM TEMPERATURE MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS (a)

Compound	χ_M (e.s.u.)	μeff (Bohr magnetons)
2,7-dichloro-4-methyl-1,8-naphthyridine (b)	$150\ (\pm 100) \times 10^{-6}$	
Bis-(2,7-dichloro-4-methyl-1,8-naphthyridine)-copper (II) chloride ethanolate (c)	$1505\ (\pm 50) \times 10^{-6}$	2.12

(a) Ligand corrections in the calculation of μeff were obtained from reference 1.

(b) The extremely small deflections produced by this compound in the Gouy balance caused large estimated errors.

(c) The value of χ_g for 2,8-dichloro-4-methyl-1,8-naphthyridine calculated from Pascals constants was used in the calculation of μeff for this compound.

APPENDIX B

Computer Programs

COMPUTER PROGRAMS

DIFFSET

This program was written in FORTRAN by Dr. Robert Witters at Harvey Mudd College. This program is designed to calculate Goniostat settings for the "basal plane" alignment of a crystal. All settings for reflections above the basal plane are calculated for values of 2θ less than some input value. The program will not omit reflections absent due to extinction.

LI

A data reduction program written in SPS for the 1620 computer, by Drs. Charles Caughlan and Chi Tang Li, this program was designed for photographic Weissenberg data. The program calculates the Lorentz and polarization correction for data on the basis of equi-inclination angle (which is zero for all diffractometer data). Reflections with an intensity less than some input value are given an unobserved indicator. All other reflections are considered observed. The program has a provision for calculating the parameters for a Wilson plot for overall scale and temperature factor and a subroutine for making absorption corrections.

FOURIER

This Fourier synthesis program was written by Drs. Charles Caughlan and George Svetich in SPS for the 1620 computer. The program will accept observed structure factors for the calculation of a Patterson synthesis or observed and calculated structure factors for the calculation of a Fourier synthesis. The program will calculate both Fourier and Patterson syntheses for all space groups. The program is very fast, but it is limited in the available output formats.

MAIR

The program was written by Dr. G. A. Mair and revised at the University of Canterbury. Programs P4, P5, and P6 were obtained from Dr. Bruce Penfold. The program calculated the structure factors for all space groups and calculates shifts to refine the input parameters. The program minimizes the function

$$M = w\,(kF_o)^2 - (F_c)^2\,)^{1/2}$$

In all cases w - 1.

This program will refine positions and isotropic or anisotropic temperature factors as well as the overall scale.

ICR6

This program was written by Dr. R. van der Helm in SPS at the Institute for Cancer Research, and is part of a general Fourier synthesis program. The program prepares structure factor output for the summation portion of the Fourier synthesis program (ICR6). The program was revised at the University of Canterbury for card input and output.

ICR1

Also written by Dr. R. van der Helm in SPS, this is the summation portion of the Fourier synthesis. All space group specificity has been dealt with in ICR6 so this program is a general one. The program will calculate both Fourier and Patterson syntheses; output is on cards in alphanumeric format.

ORFLS

This program is a FORTRAN full matrix least squares refinement program for crystallographic data written by Drs. Busing, Levy and Martin at the Oak Ridge National Laboratories. This is a widely used refinement program; the version used here was obtained from Washington State University. All calculations were done by teletype control at the Western Data Processing Center at the University of California at Los Angeles.

DSET

This program was written by E. L. Enwall to calculate the Goniostat settings for the "chi ninety" alignment technique. Machine settings are calculated for indices in blocks according to the signs of the various indices and provision is made for the omission of systematically absent reflections. The program gives the machine settings for the Friedel's law related reflection if the value of the original reflection is negative.

PARAM

This program is a modification of the PARAM from the X-RAY-65 systems tape written by Dr. James Stewart. The program gives the best least squares cell parameters on the basis of measured values of 2θ for any set of reflections. The program refines only the parameters variable under the space group in question and will recycle to continue refining until the shifts in parameters are very small. The program was modified at Montana State University by E. L. Enwall.

RDN

This program and DLS were written by Dr. F. Ahmed and modified at Ohio University by Dr. G. D. Smith. RDN is a general data reduction program for all normally used data collection geometries. The portion of the program dealing with Goniostat geometry was modified by E. L. Enwall at Montana State University. The Goniostat portion has provision for Lorentz and polarization corrections and for the scaling of data before reduction. Estimated standard deviations are calculated for all reflections by the techniques suggested by Jensen (25). No absorption correction was applied.

DLS

Also written in FORTRAN by Dr. Ahmed and modified by Dr. Smith, this is a structure factor calculation and block diagonal least squares refinement program. This program minimizes the same function as does MAIR, but the value of w was determined from the expression;

$$w = 1/(\text{sig})^{1/2}$$

where sig is the estimated standard deviation in F_o.

BAD

A FORTRAN program written by Dr. K. Watenpaugh and modified by E. L. Enwall, this program calculates bond lengths and bond angles for atom positions entered as input data. Standard deviations may be calculated if the standard deviations in positions are also given as input data.

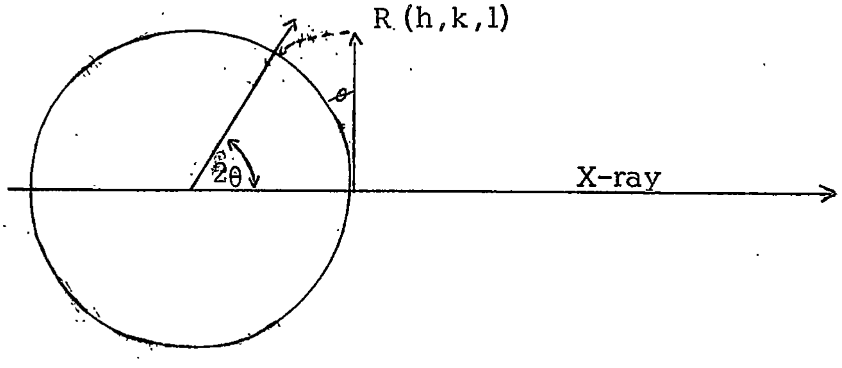
APPENDIX C

Crystallographic Data and Goniostat Geometry

Goniostat Geometry

The Goniostat geometry consists of four circles which define motions of the instrument. Two of these circles, the θ circle and the ω circle, lie in the basal plane of the instrument. The basal plane of the instrument is defined by the loci of the X-ray source, the center of the crystal and the position of the detector. This basal plane is approximately horizontal. All the circles of the Goniostat have their centers at the center of the crystal. The X circle has its axis in the basal plane and bisects the angle centered at the crystal center and defined by the X-ray source and detector. The θ circle axis lies in the X circle.

In practice, the ω circle of the Goniostat is used only to compensate for mechanical misalignment. Motion in the other three circles is used to bring the reciprocal lattice of the crystal into a position so that reflection occurs. The proper condition for reflection is best discussed in terms of the Ewald diagram, Fig. 39.



Ewald Diagram

Figure 39

If the reciprocal lattice vector R is in the plane of the circle of reflection and tangent to the circle a rotation of the crystal perpendicular to the circle of an amount θ will cause the reciprocal lattice vector R to intersect the circle of reflection. The construction of the Ewald diagram (Fig. 39) implies that a reflection will then occur at an angle 2θ to the X-ray beam and in the plane of the circles of reflection. In terms of Goniostat geometry, a reciprocal lattice vector must lie in the basal plane and perpendicular to the X-ray beam when the value of θ is zero. The rotation of θ will bring the vector into reflecting position and the detector, which moves at twice the angular rate, will be in position (2θ) to measure the intensity of the diffracted beam. The Φ and X modes of motion suffice to bring any reciprocal lattice point into the proper position. The Φ motion (all other settings zero) can bring any reflection into the plane of the X circle, and X motion can then bring the reflection into the basal plane.

The calculation of settings for the θ, X, and Φ circles for conditions of reflection demand that the exact real orientation of the crystal be known. The process of determining the exact orientation is easiest if the crystal is in one of two particular orientations. The name "alignment" is given to the process of bringing the crystal into one of these orientations. The first alignment position is the "basal" position. This position requires that two axial rows of the reciprocal lattice lie in the basal plane of the Goniostat. If this requirement is met and the Φ value for proper reflection of one axial row is known, the exact orientation of the crystal is determined. The second and preferred alignment (because it is easier to attain) is the "chi ninety" position. In this orientation, one reciprocal lattice vector is made coincident with the Φ axis and the proper reflection Φ is determined for some other reflection. This determines the exact crystal orientation. It is not necessary to "align" a crystal at all, but determination of the exact orientation becomes more difficult if no alignment is used. Most of the computer programs written for the calculation of machine settings for data collection assume one of the two alignment positions described although at least one program has been written for general positioning.

Once the position of any two non-co-linear reciprocal lattice vectors is exactly determined (alignment), all other positions can be calculated. This is done by calculating the positions of the known vectors in some artificial orientation and determining the transformation from the aritificial orientation to the real orientation. This transformation will then convert any vector in the artificial orientation to the vector in the real orientation. The real orientation of a vector allows the calculation of the Φ and X motions necessary to bring the vector into a position (at θ = zero) where it is tangent to the circle of diffraction. The 2θ value is calculated from the length of the reciprocal lattice vector so that a short scan may be used to obtain the diffracted intensity.

Table XI

SINGLE CRYSTAL DATA FOR
BIS-(1,8-NAPHTHYRIDINE)-COPPER(II) CHLORIDE

Crystal Dimension: .30mm x .17mm x .10mm

Crystal Density: found 1.68 g./cc. calc. 1.68 g./cc.

Unit Cell Constants:

a = 13.745 ± .029

b = 8.192 ± .010

c = 16.382 ± .013

β = 122.32 ± .09

Vol = 1558.6 Å^3

Conditions for Systematically Absent Reflections:

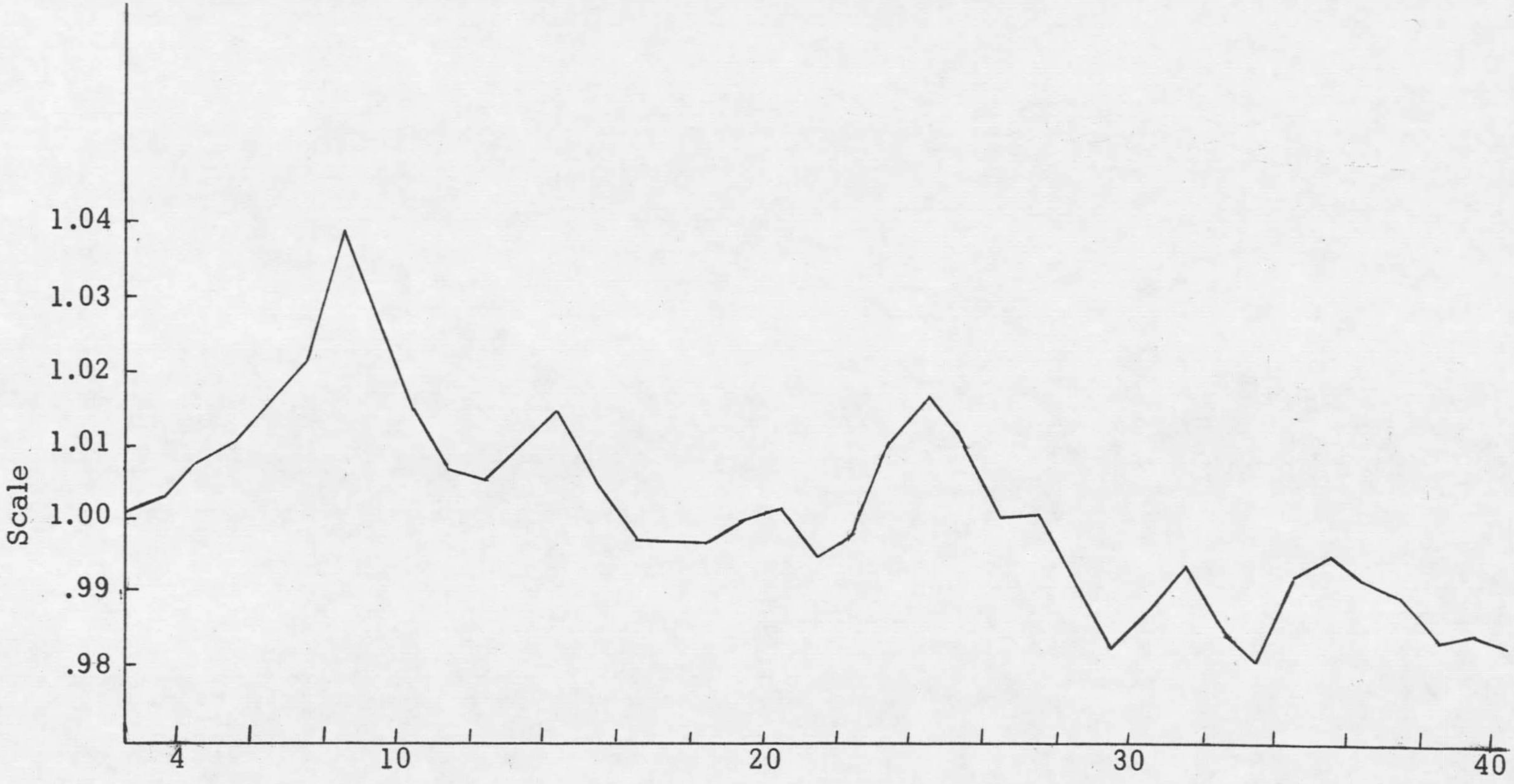
hkl; h + k = 2n

h0l; h + l = 2n

0k0; (k = 2n)

Space Group from Systematic Absences: C2/c or Cc

Molecules Calculated per Unit Cell: 4.003



Average Scale for Diffractometer Data Bis-(1,8-naphthyridine)-copper(II) chloride

Figure 40

Table XII

SINGLE CRYSTAL DATA FOR

BIS-(1,8-NAPHTHYRIDINE)-COPPER(II) BROMIDE

Crystal Dimensions:	.1mm x .1mm x .4mm	
Crystal Density	found 2.00 g./cc.	calc. 2.06 g./cc.

Unit Cell Constants: a = 4.28
b = 14.66
c = 13.30
β = 85.6°
Vol = 832.0 Å^3

Conditions for Systematically Absent Reflections:
khl; h + k = 2n
h0l; h + l = 2n
0k0; (k = 2n)

Space Group from Systematic Absences: C2/c or Cc

Molecules Calculated per Unit Cell: 2.065

Table XIII

SINGLE CRYSTAL DATA FOR

METHYL NAPHTHYRIDINE COPPER COMPLEX

Crystal Dimensions:

Crystal Density: found 1.72 g./cc.

Crystallographic System: orthorhombic

Unit Cell Constants: a = 14.7
b = 19.5
c = 20.4
Vol = 5840 Å^3

Molecules per unit cell on basis of molecular formula $Cu(C_9H_6N_2)Cl_2$: 14.5

Table XIV

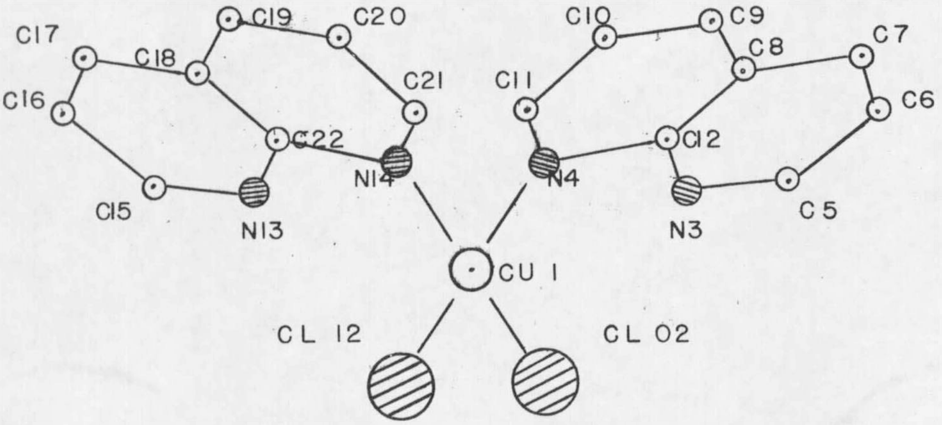
FINAL ATOM POSITIONS AND STANDARD DEVIATIONS

	x	y	z	σx	σy	σz
Cu 1	.5000	.31605	.25000	.00000	.00023	.00000
Cl 2	.43224	.12966	.30844	.00022	.00033	.00020
N 3	.66764	.44226	.42568	.00069	.00108	.00065
N 4	.47756	.49489	.32308	.00066	.00106	.00058
C 5	.76410	.46377	.51025	.00086	.00141	.00078
C 6	.77655	.57499	.58035	.00089	.00142	.00076
C 7	.68476	.66681	.56349	.00084	.00105	.00073
C 8	.57907	.64449	.47182	.00087	.00118	.00075
C 9	.47777	.73232	.44628	.00092	.00135	.00083
C 10	.37897	.69895	.35893	.00092	.00146	.00084
C 11	.38000	.57688	.30029	.00093	.00134	.00079
C 12	.57529	.52892	.40982	.00078	.00122	.00070

Table XV

FINAL ANISOTROPIC THERMAL PARAMETERS

	B11	B22	B33	B23	B13	B12
Cu 1	.00447	.01091	.00304	.00000	.00340	.00000
Cl 2	.00671	.01310	.00425	.00028	.00565	.00209
N 3	.00582	.01294	.00479	.00102	.00633	.00335
N 4	.00667	.01053	.00356	-.00028	.00474	.00111
C 5	.00553	.01501	.00377	.00253	.00364	.00127
C 6	.00621	.01537	.00404	.00289	.00515	-.00197
C 7	.00630	.01655	.00392	-.00104	.00578	-.00449
C 8	.00699	.00924	.00461	.00142	.00731	.00091
C 9	.00747	.01334	.00501	-.00137	.00712	-.00133
C 10	.00736	.01123	.00610	.00190	.00570	.00350
C 11	.00742	.01252	.00433	.00211	.00666	-.00081
C 12	.00530	.01026	.00330	.00160	.00438	.00026



Numbering Diagram for Bis-(1,8-naphthyridine)-copper(II) chloride

Figure 41

Table XVI

BOND DISTANCES AND BOND ANGLES FOR BIS-(1,8-NAPHTHYRIDINE)-COPPER(II) CHLORIDE

Bond	Length	Standard Deviation
Cu 1-Cl02	2.2514	.0047
Cu 1-N 03	2.7514	.0224
N 03-C 05	1.3207	.0346
C 05-C 06	1.4029	.0273
C 06-C 07	1.3643	.0284
C 07-C 08	1.4374	.0367
C 08-C 09	1.4172	.0300
C 09-C 10	1.3743	.0411
C 10-C 11	1.3920	.0249
C 11-N 04	1.3614	.0267
C 12-N 04	1.3639	.0321
C 12-N 03	1.3528	.0234

Center Atom at Vertex	Angle	Standard Deviation
Cl02-Cu-Cl12	94.54	.0815
Cl02-Cu-N04	90.63	.2759
N 04-Cu-N 14	92.27	.3917
N 04-Cu-N 03	54.17	.2818
C 12-N 03-C 05	116.37	.9716
N 03-C 05-C 06	124.06	.9798
C 05-C 06-C 07	119.83	.9657
C 06-C 07-C 08	116.75	1.0334
C 07-C 08-C 09	121.90	1.0486
C 08-C 09-C 10	118.32	1.0751
C 09-C 10-C 11	119.51	1.0677
C 10-C 11-N 04	122.49	1.0884
C 11-N 04-C 12	117.51	.9946
N 04-C 12-C 08	122.67	.9963
C 12-C 08-C 09	119.37	1.0747
C 12-C 08-C 07	118.64	1.0642
N 03-C 12-C 08	124.12	1.0139

Table XVII

ATOMIC POSITIONS FOR FIRST DATA COLLECTION

Atom	x	y	z	β
Cu	.5000	.3157	.2500	2.636
Cl	.4322	.1293	.3084	2.415
N 03	.6685	.4403	.4254	3.009
N 04	.4782	.4942	.3250	2.234
C 05	.7659	.4689	.5112	2.995
C 06	.7807	.5775	.5812	3.099
C 07	.6830	.6684	.5614	3.066
C 08	.5797	.6468	.4753	2.581
C 09	.4737	.7294	.4457	3.073
C 10	.3786	.6966	.3619	3.432
C 11	.3779	.5741	.2970	2.809
C 12	.5736	.5276	.4074	2.690

Table XVIII

MOST INTENSE DIFFRACTION LINES FOR BIS-(1,8-NAPHTHYRIDINE)-COPPER CHLORIDE

(photographic data)

d (Å)	Intensity Order
6.8	3
5.4	2
4.5	1
3.6	4
3.2	5

Table XIX

MOST INTENSE DIFFRACTION LINES FOR 1,8-NAPHTHYRIDINE COPPER(II) CHLORIDE

(photographic data)

d (Å)	Intensity Order
7.6	2
6.4	1
3.7	3
3.3	4
3.1	5

Table XX

MOST INTENSE DIFFRACTION LINES FOR 1,8-NAPHTHYRIDINE COPPER(II) CHLORIDE

(diffractometer data positive angles only)

d (Å)	Intensity Order
7.6	1
6.4	2
3.2	3
2.5	4
3.7	5

Table XXI

TABLE OF OBSERVED AND CALCULATED STRUCTURE FACTORS

```
K=  0 L=  0
  6  26  15
  2 168 192
 -2 226 192
  4  82  84
 -6  24  15
  8  17  17
 10  32  29
-10  32  29
 12  43  43
-12  45  43
K=  0 L=  2
  0  64  58
  2 237 269
 -2 159 152
  4  99 106
 -4  38  51
  6  50  50
 -6  42  46
  8  48  51
 -8  35  34
 10  31  34
-10  29  27
K=  0 L=  4
  0 100  90
  2 210 218
 -2 101 111
  4 154 161
  6  59  57
 -6  13  14
  8  20  21
 -8  97  93
-10  70  69
-12  84  81
K=  0 L=  6
  0  57  53
  2  49  57
 -2  53  49
  4  89  89
  6  86  91
 -6  86  86
  8  27  28
 -8  26  28
-10  75  74
-12  47  45
-14  23  26
K=  0 L=  8
  0  54  54
 -2  18  20
  4  50  52
 -4  49  51
  6  28  29
 -6  79  74
 -8 145 144
-10  74  69
-12  32  31
-14  21  22
K=  0 L= 10
  2  23  20
 -2  56  56
 -4 119 122
 -6 160 169
 -8  82  82
-10  46  56
K=  0 L= 12
  0  53  49
 -2  37  37
 -4 106 107
 -6  66  72
 -8  47  53
-14  17  15
K=  0 L= 14
  0  32  27
 -2 120 117
 -6  42  48
K=  0 L= 16
 -2  38  35
 -4  47  45
K=  1 L=  0
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 -3  11   7
  5  33  35
 -5  35  35
  7  84  82
 -7  81  82
  9  23  16
 -9  18  16
 11  37  34
-11  35  34
K=  1 L=  1
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 -1  99  96
  3 116 116
 -3 119  97
  5  81  89

 -5  46  42
  7  16  18
 -7  17  14
  9  22  21
 -9  43  43
-11  59  54
K=  1 L=  2
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 -3 112 123
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 -5 100  89
  7  38  40
 -7  82  77
  9  72  79
 -9  34  34
 11  20  24
-11  49  46
K=  1 L=  3
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 -1 174 174
  3 141 136
 -3 147 139
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 -5  28  23
  7  41  42
  9  25  29
 -9  60  61
-11  48  48
-13  39  40
K=  1 L=  4
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  3  56  53
 -3  13   5
 -5  92  89
  7  25  26
 -7  22  23
  9  28  28
K=  1 L=  5
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 -1  52  40
  3  70  73
 -3  99  89
  5  71  75
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  7  53  55
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  9  20  16
 -9  79  75
-11  70  68
-13  23  21
K=  1 L=  6
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 -1  64  57
  3  29  25
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 -5  39  34
 -9  59  54
-13  17  19
K=  1 L=  7
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  3  59  59
 -3  69  67
  5  51  55
 -5  70  63
  7  42  42
 -7 107 110
 -9  93  93
-11  52  52
-13  30  30
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  3  21  21
 -3  76  73
 -7  13   7
-13  34  34
K=  1 L=  9
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 -3  51  50
  5  41  44
 -5  85  86
 -7  76  84
 -9  59  62
K=  1 L= 10
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  3  27  26
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-11  39  44
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K=  1 L= 11
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 -3  62  56
 -5  76  85

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K=  1 L= 12
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K=  1 L= 16
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 -5  27  29
 -7  17  19
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 10  33  33
-10  34  33
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  6 103 102
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 10  25  27
-10  46  46
K=  2 L=  2
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  6  23  23
 -6  59  62
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 10  33  40
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  2  32  29
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-10  43  44
-12  41.  39
K=  2 L=  5
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 -8  20  22

K=  2 L=  6
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 -4 123 132
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K=  2 L=  7
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 -2 137 133
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K=  2 L=  8
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  4  25  22
  6  35  35
 -8  43  44
-10  55  53
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-14  30  29
K=  2 L= 10
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K=  2 L= 11
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-14  32  31
K=  2 L= 12
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K=  2 L= 13
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K=  2 L= 14
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K=  2 L= 15
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 -9  33  30

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  5  21  25
 -5 118 116
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-11  21  21
-13  38  36
K=  3 L=  5
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  7  23  23
 -7  30  30
-11  21  21
K=  3 L=  6
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 -1 117 115
  3  28  26
 -3 169 167
  5  22  23
 -5 144 138
  7  37  37
 -7  32  32
-11  16  15
K=  3 L=  7
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K=  3 L=  8
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  3  21  22
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  5  29  16
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K=  3 L= 10
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K=  3 L= 11
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K=  3 L= 12
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-13  24  21
K=  3 L= 13
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-11  42  42
K=  3 L= 14
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 -9  40  41
-11  53  50

K=  3 L= 15
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K=  3 L= 16
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 -9  43  39
K=  4 L=  0
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  2  14  11
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 -4  40  35
  6  44  41
 -6  42  41
  8  40  39
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K=  4 L=  1
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K=  4 L=  2
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 10  26  32
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K=  4 L=  3
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K=  4 L=  5
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  8  28  27
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K=  4 L=  6
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 -8  59  56
-10  32  30
K=  4 L=  7
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  2  90  89
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-10  21  23
K=  4 L=  8
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  2  27  25
 -2  22  21
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  6  29  30
 -6  43  43
 -8  41  40
-10  30  31

K=  4 L=  9
  0  43  38
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  4  52  53
 -4  54  55
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 -8  29  29
-12  31  32
K=  4 L= 10
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  2  33  33
 -4  27  29
 -6  19  19
-10  26  25
K=  4 L= 11
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  2  34  33
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 -4  31  29
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 -8  21  22
-10  46  53
-12  37  36
K=  4 L= 12
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 -6  30  29
K=  4 L= 13
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 -2  34  31
 -4  45  47
 -8  28  29
-10  21  31
K=  4 L= 14
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-10  24  23
K=  4 L= 15
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K=  5 L=  0
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  3  45  48
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 -7  25  22
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K=  5 L=  2
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  3  83  85
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  5  38  39
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  7  28  31
  9  18  18
-11  18  17
K=  5 L=  3
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  3  39  43
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-11  21  22
K=  5 L=  4
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 -3  25  27
  5  64  66
  7  30  30
 -7  32  33
 -9  21  25
K=  5 L=  5
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 -1  18   9
  3  57  57
  5  66  64
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K=  5 L=  6
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  3  32  30
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 -5  31  29
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 -9  52  50
-11  35  30
K=  5 L=  9
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 -3  21  25
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 -5  47  44
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 -5  37  35
 -9  23  24
K=  5 L= 12
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 -3  34  33
 -5  52  53
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 -9  27  27
K=  5 L= 13
 -3  41  42
 -5  31  32
K=  5 L= 14
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K=  6 L=  0
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  2  55  55
 -2  54  55
  4  33  33
 -4  35  33
  6  21  19
K=  6 L=  1
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  2  41  41
 -2  50  51
  4  39  43
K=  6 L=  2
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  2  52  52
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  4  30  32
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K=  6 L=  3
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  4  53  58
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K=  6 L=  4
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K=  6 L=  5
  0  23  24
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  6  32  33
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K=  6 L=  8
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  2  18  17
 -2  23  20

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K=  6 L=  9
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-10  22  22
K=  6 L= 10
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 -2  24  24
 -6  41  41
 -8  28  27
-10  18  19
K=  6 L= 11
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 -6  46  47
 -8  23  21
K=  6 L= 12
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 -4  31  29
 -6  28  31
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K=  7 L=  0
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 -1  29  29
K=  7 L=  1
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  5  38  41
 -5  47  46
  7  40  41
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K=  7 L=  2
  1  40  42
  3  22  23
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 -5  35  34
K=  7 L=  3
  1  23  24
 -1  31  30
  3  16  13
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K=  7 L=  4
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K=  7 L=  5
  1  29  29
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K=  7 L=  6
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K=  7 L=  7
  1  34  33
 -1  22  21
 -3  33  34
 -5  21  22
 -7  25  22
K=  7 L=  8
 -5  17  17
 -7  24  20
K=  7 L=  9
 -1  40  38
 -3  26  28
 -5  17  19
K=  7 L= 10
 -5  28  28
K=  8 L=  1
  2  18  18
K=  8 L=  2
 -2  29  30
 -4  29  30
K=  8 L=  4
 -2  34  35
 -4  60  61
 -6  40  41
K=  8 L=  5
 -6  18  20
K=  8 L=  6
  0  46  44
 -2  44  43
 -4  45  43
```

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