



Complexes of 1, 8-naphthyridines with elements of the first transition series
by Ahmad Emad

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
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Abstract:

Twenty-three new complexes of 1,8-naphthyridine (NN) and 2,7-dimethyl-1,8-naphthyridine (dmNN) with transition metals have been prepared and characterized. These complexes have been classified according to the anion for purposes of discussion.

Five halide complexes, four with copper(II) and one cobalt(II) complex with NN or dmNN were synthesized. Among these, two magnetically anomalous complexes, $\text{Cu}(\text{NN})\text{Cl}_2$ and $\text{Cu}(\text{NN})\text{Br}_2$, were discovered. The possible structural geometries have been discussed.

Transition metal complexes of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and silver(I) perchlorates with NN were isolated. Chelation of NN with the divalent metal ions and monodentate coordination with silver(I) ion has been suggested.

Eight nitrate complexes of NN with the same transition elements have been prepared. Coordination of the naphthyridine molecule was found to be similar to that of the perchlorate compounds. In several of these complexes, coordination of the nitrate ions or water molecules is indicated by the infrared spectra.

The chemistry of complexes of this ligand with copper(I) ion was also studied. Four copper(I) complexes containing chloride and perchlorate anions with NN and dmNN were prepared. The possible coordination of the ligands and complexes is discussed and tentative structures proposed.

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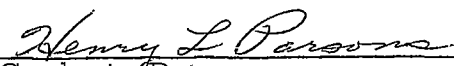
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ABSTRACT

Twenty-three new complexes of 1,8-naphthyridine (NN) and 2,7-dimethyl-1,8-naphthyridine (dmNN) with transition metals have been prepared and characterized. These complexes have been classified according to the anion for purposes of discussion.

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INTRODUCTION

REVIEW OF LITERATURE:

In recent years, there has been some interest in transition metal complexes of heterocyclic molecules, containing two nitrogen atoms, forming four-membered ring chelates (1,2,3). Most of the common chelating agents form five- or six-membered rings and little is known about the chelating powers of agents forming four-membered rings. The nitrogen heterocycles able to form five-membered ring chelates have long been studied (4,5,6). The examples of these are: 2,2'-bipyridine, 1,10-phenanthroline, and their derivatives. These molecules are good π -bonding ligands and their strong crystal field properties are partially due to their ability to participate in π -bonding with the metal atoms (7). The compound 1,8-naphthyridine and its derivatives by comparison form four-membered ring chelates rather than five. Ionic ligands which form four-membered chelate rings have been known for a long time, and their complexes are stabilized by ionic charges. Examples of these are: perchlorates (8,9), nitrates (10), carbonates (11), and carboxylates (12). The similarity of chelated 1,8-naphthyridine complexes to chelate complexes of acetate ions suggests that naphthyridines might form polynuclear complexes with copper or other transition metals, as acetate does in a few cases.

Among these anionic ligands, the carboxylate ions have been most thoroughly studied. They may coordinate through one or both

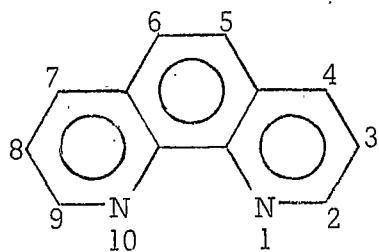
oxygens and they also form a class of polynuclear molecules with metal-metal interactions where the carboxylate group coordinates as a bidentate ligand to two metal atoms. A large number of these complexes have been investigated and characterized with copper(II) ions (12).

Dimeric copper(II) carboxylates show unusual magnetic properties. They exhibit a magnetic moment less than 1.7 B.M. compared with the value of 1.8-2.2 B.M. for normal copper(II) compounds. The magnetic susceptibility of these complexes does not obey the Curie-Weiss law. It passes through a maximum at or near room temperature and decreases rapidly as the temperature is lowered. Some of these compounds have anomalous magnetic properties at low temperature, but appear to be normal at or near room temperature. The interaction between d orbitals of copper(II) ions and the nature of the ligands are responsible for the magnitude of this subnormal behavior. The large overlap of the 3d orbitals between the copper(II) ions in the complex as well as the high tendency of the ligand for coordination will stabilize the dimeric structure of the complex. Similarly the formation of the dimeric compound in organic solvents such as alcohol, ether, etc. is more favorable than in aqueous solution. The dimeric structure is destroyed in water, resulting in monomeric hydrated ions. This is due to the stronger coordination ability of water compared with that of organic molecules.

1,8-NAPHTHYRIDINES AND THEIR COMPLEXES:— The compound 1,8-naphthyridine is an aromatic molecule (Fig. 1) having one unshared pair of electrons on each nitrogen and is symbolized throughout this thesis as "NN" for simplicity. In naphthyridine molecules the pairs of electrons in the nonbonding atomic orbitals of the nitrogens are responsible for their basic properties, since overlap of this orbital, as a Lewis base, with an orbital of a Lewis acid will result in a bond. Substitution of two methyl groups in 1,8-naphthyridine "dmNN" would be expected to increase the basicity of the substituted molecule as is observed in 1,10-phenanthroline. The basicity of the parent phenanthroline molecule is lower compared to the 2,9-dimethyl substituted derivative. The pK_a values for some of the nitrogen heterocycles are listed in Table I, but the value of pK_a for 1,8-naphthyridine has not been reported in the literature. In Table I, the pK_a values of different aromatic amines are compared in which the K_a values are the dissociation constants of protonated ammonium ions at 25°C in water.

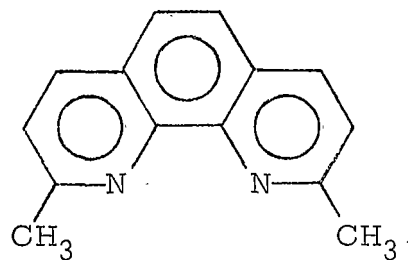
Table I

Compound	pK_a	Ref.
1,10-phenanthroline	4.86	(13)
2,9-dimethyl-1,10-phenanthroline	6.17	(13)
2,7-dimethyl-1,8-naphthyridine	4.50	(13)
Pyridine	5.18	(14)



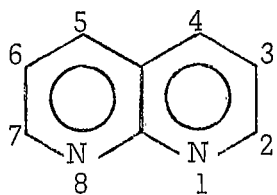
1,10-Phenanthroline

"phen"



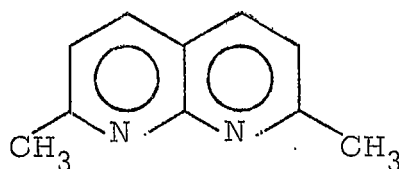
2,9-Dimethyl-1,10-phenanthroline

"dmp"



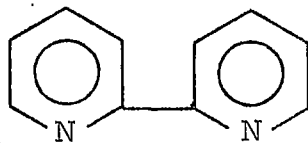
1,8-Naphthyridine

"NN"



2,7-Dimethyl-1,8-naphthyridine

"dmNN"



2,2'-Bipyridine

"bipy"

Heterocyclic molecules containing two nitrogen atoms.

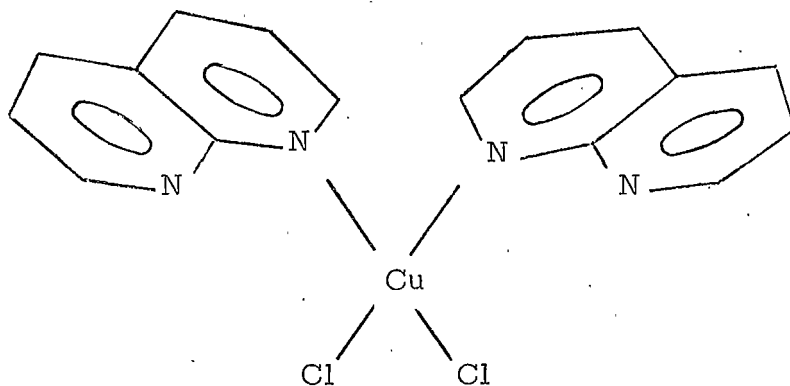
Figure 1

The compound 1,8-naphthyridine was prepared by Koller (15) and by Albert (16) by a multi-step sequence starting with methyl-2-aminonicotinate. Allen (17) reported the synthesis of 1,8-naphthyridine using 2-aminopyridine as the starting material. The synthesis of 2,7-dichloro-4-methyl-1,8-naphthyridine from 2,5-diaminopyridine was reported by Siede (18) in 1926. Ochiai and Miyaki (19) reported a catalytic hydrogenation scheme for conversion of 2,7-dichloro-4-methyl-1,8-naphthyridine to 4-methyl-1,8-naphthyridine. In 1964 the synthesis of 2-amino-7-hydroxy-1,8-naphthyridine from 2,6-diaminopyridine was reported (20). Enwall (21) synthesized 1,8-naphthyridine and its 4-methyl derivative by a four-step synthesis using 2,6-diaminopyridine.

All these previous syntheses which require a multi-step synthesis proceed in a low yield. Paudler and Kress (22, 23) reported in 1967 a one-step synthesis of 1,8-naphthyridine. They applied the Skraup reaction to 2-aminopyridine using meta-nitrobenzene sulfonic acid (sulfo-mix) as the oxidizing agent. The condensation of 2-aminopyridine employing sulfo-mix and glycerol gave 1,8-naphthyridine in 30% yield whereas the 2-amino-6-methylnaphthyridine reaction with crotonaldehyde and sulfo-mix produced 2,7-dimethyl-1,8-naphthyridine in 17% yield.

The first transition metal complex with 1,8-naphthyridine was synthesized and its structure determined by X-ray diffraction by Enwall (24) in this laboratory. Enwall (21) isolated $\text{Cu}(\text{NN})_2\text{Cl}_2$ and

$\text{Cu}(\text{NN})_2\text{Br}_2$. The former was a green crystalline substance and the latter an orange compound with a disordered crystal structure. Both compounds were crystallized out of aqueous solution and the chloride complex was shown to have a cis square planar structure. Naphthyridine is coordinated through one of its nitrogens; the uncoordinated nitrogens lie below and above the plane of the complex.



Bis(1,8-naphthyridine)copper(II)chloride

Figure 2

The copper-chloride distance is 2.25 \AA , the copper-nitrogen distance is 2.02 \AA , and the copper-uncoordinated nitrogen distance is 2.76 \AA . The magnetic susceptibility measurement of the complex at room temperature showed that it had a normal magnetic moment of 1.90 B. M.

Hendricker and Reed (13) in 1969 reported the preparation and characterization of Group VIb metal carbonyl complexes with

2,7-dimethyl-1,8-naphthyridine. From the infrared spectra, carbonyl stretching frequencies, and their force constants compared with the five-membered ring nitrogen chelates they concluded that naphthyridine is a slightly better π -bonding ligand.

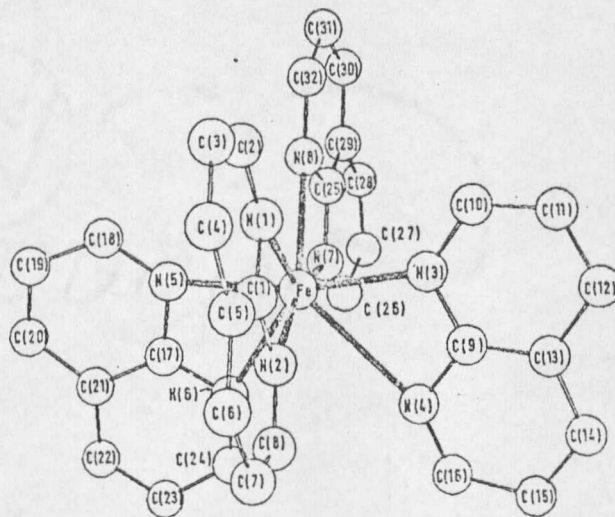
Hendricker (25) reported the dialkyltin dichloride adducts of this same ligand and from their infrared and pmr spectra he decided that the ligand forms a four-membered ring chelate with the central metal.

Hendricker and Bodner (26) isolated magnesium(II), calcium(II), strontium(II), and barium(II) perchlorate complexes of 1,8-naphthyridine and its 2,7-dimethyl derivative from anhydrous organic solutions. Complexes of 1,8-naphthyridine were hydrated, but complexes of 2,7-dimethyl-1,8-naphthyridine were anhydrous except for the magnesium(II) complex. The source of the water in hydrated compounds was not explained. From infrared and proton magnetic resonance spectra they concluded that all were chelated with naphthyridine through both nitrogens and the perchlorates were all coordinated to the central metal except in $\text{Mg}(\text{dmNN})_2(\text{ClO}_4)_2 \cdot 3.5 \text{H}_2\text{O}$ where water molecules were coordinated to the metal instead of perchlorates.

These same authors (7,27) reported transition metal complexes of iron(II) to zinc(II) as well as cadmium, mercury, and silver with dmNN. Their anhydrous complexes had stoichiometry $\text{M}(\text{dmNN})_3(\text{ClO}_4)_2$ except for mercury and silver, which were reported as bis (dmNN) complexes. From the infrared, ultraviolet, and visible spectra they assigned

octahedral geometry to all their tris compounds except $\text{Cu}(\text{dmNN})_3^{2+}$. They did not observe any d-d transition for the copper(II) complex.

The above authors (1,2) also reported eight-coordinate transition metal complexes of NN with metal ions manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II), palladium(II), and cadmium(II). All complexes reported were anhydrous with stoichiometry $\text{M}(\text{NN})_4(\text{ClO}_4)_2$. Their powder photograph data showed that complexes of manganese(II) to copper(II) were all isomorphous and that the cadmium and zinc compounds were similar. The structure of the $\text{Fe}(\text{NN})_4(\text{ClO}_4)_2$ complex has been determined (3) by X-ray diffraction methods. The complex has a distorted dodecahedral geometry. The structure is shown in Figure 3.



Structure of tetrakis(1,8-naphthyridine)iron(II)perchlorate (3).

Figure 3

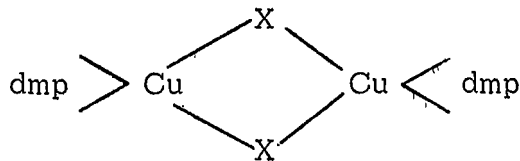
The iron-nitrogen distance varies from 2.18 to 2.75 Å. Four nitrogens, one from each naphthyridine molecule, are 2.18 to 2.25 Å distant from the iron atom; the other four nitrogens are all at significantly greater distances, 2.35 to 2.75 Å, indicating very unsymmetrical coordination of the naphthyridines. Coordination of the naphthyridine molecules through both nitrogens is in contrast to the monodentately coordinated ligand in $\text{Cu}(\text{NN})_2\text{Cl}_2$ reported by Enwall (21). This raises a number of important and interesting questions about how the coordination should be described in these two types of complexes. These questions will require further study and have not been dealt with in this thesis.

NITROGEN COMPLEXES OF COPPER(I):— In the course of this investigation a number of copper(I) compounds were discovered which proved to have unusual properties; the literature on related compounds is summarized here.

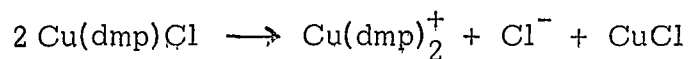
Copper(I) complexes with various ligands, such as 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp), 2,2'-bipyridine (bipy), diazoaminobenzene, diazene and substituted diazenes have been studied (6,28,29). These complexes have been prepared either by reduction of copper(II) salts or by direct reaction of copper(I) salts and an appropriate base. Preparation and characterization of several copper(I) complexes of monosubstituted diazenes ($\text{RN}=\text{NH}$) have been reported (29). The crystal structures of $(\text{CH}_3\text{N}=\text{NCH}_3)_2\text{Cu}_2\text{Cl}_2$ and $(\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{N}-\text{C}_6\text{H}_5)_2\text{Cu}_2$ have been

determined by X-ray diffraction methods (30,31). The $(\text{CH}_3\text{N}=\text{NCH}_3)\text{Cu}_2\text{Cl}_2$ molecule consists of infinite chains of copper and chlorine atoms with copper roughly tetrahedrally coordinated by three chlorine atoms in the chain and by a nitrogen lone pair from a diazene molecule (30). The $(\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{N}-\text{C}_6\text{H}_5)_2\text{Cu}_2$ molecule exists in a dimeric form in which the diazoaminobenzene molecules are linked by nearly linear nitrogen-copper-nitrogen coordination to form an eight-membered ring with a copper-copper distance of 2.45 \AA (31).

Reduction of 1,10-phenanthroline, or 2,2'-bipyridine complexes of copper(II) salts in ammoniacal solution with hydrazine, sodium bisulfite, or hydroxylamine has been reported by Tartarini (6). In some cases the copper(I) complexes were prepared directly from a mixture of copper(I) salt and the ligand. The preparation of $\text{Cu}(\text{phen})_2\text{I}$, $\text{Cu}(\text{bipy})\text{I}$, $\text{Cu}(\text{phen})_2\text{ClO}_4$ and $\text{Cu}(\text{bipy})_2\text{ClO}_4$ have been reported (6). These complexes were conductors in nitrobenzene solution and their spectrophotometric measurements showed the presence of the common ion CuL_2^+ (L=phen or bipy). There was also some evidence for a small amount of the bridged dimer of 2,9-dimethyl-1,10-phenanthroline (dmp) in equilibrium:



The following reaction has been proposed for the presence of ionic species in the solution of this complex:



The solution spectra showed absorption maxima at 21700 cm^{-1} , indicative of Cu(dmp)_2^+ ion (6). Petredis *et al.* (29) have also observed similar ionic species with copper(I) complexes in the solution and have isolated the Cu(bipy)_2^+ ion as its tetraphenylborate salt.

AIMS OF THIS RESEARCH:

All previous studies on transition metal complexes of 1,10-phenanthroline and 2,2'-bipyridine (Figure 1) have shown that these ligands coordinate through their two nitrogen atoms to the central metal. The $[\text{Cu(phen)}_2\text{X}]\text{X}$ and $[\text{Cu(bipy)}_2\text{X}]\text{X}$ compound ($\text{X} = \text{Cl}$ or Br) were shown to contain five-coordinated copper(II) ion, where the metal has a trigonal pyramid geometry. When salts of anions other than halides were used, perchlorate and nitrate for instance, the ligands were still found to chelate in the same manner. By contrast, the report of the structure determination of $\text{Cu(NN)}_2\text{Cl}_2$ by X-ray diffraction methods showed that the naphthyridine molecule behaves differently (21). Both halogens are coordinated to the metal and the naphthyridines are coordinated through only one of the nitrogens. This was the only transition metal complex with 1,8-naphthyridine reported until 1968. This unexpected property of 1,8-naphthyridine compared with

1,10-phenanthroline and 2,2'-bipyridine stimulated interest in studies on transition metal complexes containing various anions. It has been pointed out (7) that in 1,8-naphthyridine and its 2,7-dimethyl derivative the electron pairs are extended in a parallel manner and separated by approximately 2.2 \AA , whereas in phenanthroline the lone nitrogen pairs are not parallel but subtend an angle of about 85° at 2.00 \AA from the metal center. This characteristic of the naphthyridine molecule, which is similar to that of carboxylate ion, results in the formation of polynuclear complexes with subnormal magnetic susceptibilities. Two such complexes have indeed been prepared during this work. Complexes of 2,7-dimethyl-1,8-naphthyridine were obtained to study the effect of the two methyl groups on coordination characteristics compared with the unsubstituted ligand. Isolation of metal perchlorate complexes with 1,8-naphthyridine from aqueous solutions was carried out to determine the effect of water of hydration on coordination characteristics of the ligand compared with anhydrous compounds reported in the literature (1,2,3). Complexes of metal salts of nitrate, sulfate, and acetate ions were also prepared to determine the effect of these anions on its coordinating powers. Finally, four copper(I) complexes of 1,8-naphthyridine and its 2,7-dimethyl-1,8-naphthyridine were isolated in order to investigate the nature of an incorrectly reported complex in the literature (7).

EXPERIMENTAL

ANALYTICAL TECHNIQUES

The ligand 1,8-naphthyridine and its 2,7-dimethyl derivative were prepared by using the Paudler and Kress procedures (21,22).

Reagent grade chemicals were used for all syntheses without further purification.

The copper(II) concentrations were determined by a titrimetric method using EDTA standard solution (0.01-0.02 M) and fast Sulphone Black F as end-point indicator (32). In some cases where the end-point was not sharp the iodometric method (33), using standard sodium thio-sulfate solution (0.1 N), was applied.

Copper(I) concentrations were determined by iodometric titration (33) of an aqueous solution of the complex which had been previously air oxidized.

Manganese(II) and zinc(II) concentrations were estimated with standard EDTA solution using Eriochrome Black T as the end-point indicator (32).

Cobalt(II) concentrations were determined by EDTA titration which was previously used in this laboratory (34).

Nickel(II) was determined by gravimetric method using dimethyl-glyoxime as precipitant (32).

Silver(I) concentrations were determined by gravimetric procedure and precipitates were weighed out as silver(I) chloride (33).

