Studies on Selective Synthesis and Coordination Abilities of Unsymmetrical Azines with Pyridyl, Imidazolyl, and Oxazolyl Substituents and Structures and Properties of Their Iron(II) and Nickel(II) Complexes

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DECLARATION

I, Kennedy Mawunya Hayibor, declare that the work in this thesis was undertaken solely by me under my supervision and has neither wholly nor partially been presented elsewhere for another degree.

ABSTRACT

Chapter One provides a comprehensive overview and review of the chemistry of azine molecules containing the functional unit C=N-N=C. It offers a concise description of azines and thoroughly discusses the existing literature regarding these compounds' synthesis, properties, applications, and reactivity. As a class of organic molecules, Azines have gained recognition for their diverse properties encompassing biological, chemical, stereochemical, and material characteristics. Consequently, they find applications in various fields, including inorganic chemistry, photochemistry, material science, and Metallo-supramolecular chemistry. Notably, this chapter also highlights the coordinating capabilities exhibited by azines.



LIST OF ABBREVIATIONS

DCM	Dichloromethane
EtOAc	Ethyl acetate
MeOH	Methanol
MeCN	Acetonitrile
NMR	Nuclear Magnetic Resonance Spectroscopy
IR	Infra-Red
UV	Ultra-Violet
PAA	Pyridine aldazine
IAA/H2ICA ^R	Imidazole aldazines
PIA/HL ^R	(Pyridine)(imidazole)azines
CV	Cyclic voltammetry
CD	Circular Dichroism
SC-XRD	Single Crystal X-Ray Diffraction
Et ₂ O	Diethyl ether

DEDICATION

This thesis is dedicated to my stepmother, **Gertrude Dogbey** for her support of my education all these years.

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CHAPTER 1

1.1 GENERAL INTRODUCTION

Azine is a term used in chemistry to describe two distinct sets of organic molecules based on their structures. In heterocyclic chemistry, azines refer to aromatic sixmembered rings containing at least one nitrogen atom. In alicyclic chemistry, azines are molecules obtained from the reaction between hydrazine and either two molecules of a carbonyl or an excess of carbonyl. Symmetrical azine is formed when two identical carbonyl molecules react, resulting in a molecule with a symmetric structure. In contrast, an unsymmetrical azine is produced when two different carbonyl compounds are involved in the reaction, leading to a molecule with an asymmetric arrangement of functional groups (Figure 1.1).¹ The molecules are named based on the carbonyl moieties. If the carbonyl compound used is an aldehyde, the resulting molecule is called an aldazine, whereas if a ketone is used, the resulting molecule is called a ketazine.² B³ R R B²



Figure 1.1. The general structure of azine (a), symmetrical (b), and unsymmetrical (c) aldazines.

The alicyclic azines feature diimine functionality with a conjugated double bond and an N–N bond, forming a 2,3-diaza analog of 1,3-butadiene. This structural resemblance endows these compounds with interesting physical, stereochemical, biological, and chemical properties, making them widely useful in diverse fields. The alicyclic azines represent a well-known category of compounds that find applications in various areas.³



Figure 1.2. Azine (d) and 1,3-butadiene (e)

As shown in Figure 1.2, both azine functionality (C=N–N=C) and 1,3-butadiene (C=C–C=C) are similar and the only difference is that azine possesses an N–N bond between the conjugated double bonds. It is therefore expected that electronic delocalization will occur. In the late 20th and early 21st centuries, Glaser et al., and many other researchers, examined the bond lengths to find evidence of electronic delocalization within the azines structure.

Resonance structures of acetophenone azines (Figure 1.3) have been studied⁴ and through crystallographic data,⁵ NMR spectroscopic studies,⁶ and theoretical calculations,⁷ no or little evidence of electronic conjugation within the azine backbone has been found. It has been concluded that the azine linkage, acts as a "conjugation stopper"⁴, and prevents delocalization in the solid state. However, theoretically, the C=N–N=C spacer could have the necessary structural elements to function as a good conjugation bridge.^{7,8} Electrochemical studies⁹ and Cambridge Crystallographic Data also revealed a lack of delocalization.^{10,11}



Figure 1.3. Demonstration of azine acting as conjugation stopper.

Azines are often referred to as diimine Schiff-base molecules. In 1864 a German-born, Italian chemist, Hugo (Ugo) Schiff serendipitously discovered a new class of organic molecules; $R_1R_2C=NR'$ ($R' \neq H$), by studying the reaction of aniline with aldehydes, viz acetaldehyde, valeraldehyde, benzaldehyde, and cinnamaldehyde. He termed the product imines,^{12,13} and subsequently discovered many other imines, dubbed "*Schiff* *bases*^{''} which he researched extensively, leading to his development of the Schiff test.^{13,14} A year later, some metal complexes of the Schiff bases were synthesized and characterized.¹⁵ However, it took a quarter of a century to synthesize and characterize the first-ever diimine molecule, and in 1891 Curtius and Thun reported on the first azine, dimethylketazine from the reaction of two molecules of acetone with hydrazine.^{3,16} They also studied the effect of hydrazine hydrate on monoketones and orthodiketones.¹⁶ In the mid-20th century, Stratton et al., reported on the azine molecule, 2-pyridyl methyl ketazine, its irons, nickel, and cobalt complexes, and their spectroscopic properties.^{15,17–19} During the same era, Neureiter et al.²⁰ prepared and characterized formaldehyde azine, the simplest azine. Azines are typically synthesized directly or indirectly, by the reaction of hydrazine to carbonyl compounds can be more challenging than expected because of the bifunctionality of hydrazine. Hydrazine can behave both as a nucleophile and as a base so that it can exist in three forms: unprotonated, monoprotonated, and di-protonated.

The di-protonated form of hydrazine possesses nitrogen atoms with no free electron pair and is therefore unable to react with the carbonyl group. The mono-protonated and unprotonated forms of hydrazine can behave as nucleophiles. While both of them can form the hydrazone by reacting with one molecule of the carbonyl compound, only the unprotonated hydrazine can react with another molecule of the carbonyl compound to obtain the final azine of the type R(R')C=N-N=CR(R') (Scheme 1.1).



Scheme 1.1. Reaction scheme of the different mechanisms of addition of hydrazine to carbonyl

The reactivity of hydrazine towards various carbonyl molecules can greatly be affected by the type of carbonyl compound. Specifically, the reaction rate of hydrazine decreases with increasing steric hindrance, following the order: aldehyde > dialkyl ketone > alkaryl ketone > diaryl ketone. In brief, aldazines form more quickly than ketazines. As a result, the reaction of aldehyde hydrazones with a second molecule of aldehyde is faster than the reaction with hydrazine itself, resulting in aldazine being the normal final product. However, for more hindered ketazines, the presence of excess ketone, along with a catalyst such as acetic or formic acid is required.^{22,23}

Azines are structurally diverse molecules and thus display several forms of isomerism. Due to the C=N imine link and rotation across the N-N single bond, azines display two types of isomerism: (i) geometrical isomerism, and (ii) conformational isomerism. The four-atom chain C=N-N=C regulates the conformation of azines. Almost all studies on aromatic azines revealed that they exist in the preferred (E, E) configuration, even though aldazines and ketazines typically occur as three configurational isomers: (E, E), (E, Z), and (Z, Z) (Figure 1.4).^{24–29}

Nonetheless, the stability of the E and Z forms also depends on the substituents attached to the azine ligand. Substituents can affect the electronic properties of the molecule and alter its stability. For instance, electron-withdrawing groups tend to stabilize the Z form, while electron-donating groups tend to stabilize the E form.



Figure 1.4. Types of configurations azine ligands exhibit.

In the past few years, azine molecules received less attention due to (i) the predominance of the chemistry of hydrazones, which are tautomers of azines, and (ii) the fact that azine is highly basic and easily forms salts. In the protonated state azines and hydrazones become equivalent.³⁰ However, recently, azines have attracted much attention because of their versatility in different fields of application, ease of isolation, and identification due to their symmetrical and colorful structures and high melting points.^{8,31} Unsymmetrical azines are particularly interesting because of their functionality, which allows them to link two dissimilar groups. Some unsymmetrical azines are used as organic luminophores, and others are used to synthesize unsymmetrical diarylethene. Additionally, azines have played a significant role in supramolecular chemistry.^{32,33} They constitute an important class of significant nitrogen donor ligands in organometallic complexes, and their ability to act as binding molecules or modulators of biological receptors makes them suitable candidates for drug development.³⁴ Recently, their antibacterial activities against several germs³⁵, as well as their antifungal activities, were evaluated. Azines have also been studied for their use as antimalarial,³⁶ opioid antagonists,³⁷ anticonvulsants, antidepressants, antiinflammatory, antiviral,³⁸ and antitumor agents.³⁹

In synthetic organic chemistry, azines serve as synthons to yield a series of other azo and heterocyclic compounds via reduction-oxidation, cyclo-additions, and named reactions. Gillis et al reported the oxidation of some groups of aldazines and ketazines with lead tetraacetate, which produced substituted 1,3,4-oxadiazoles⁴⁰ (Scheme 1.2).



Scheme 1.2. Oxidation of aldazines and ketazines with lead tetraacetate.

Almeida et al reported synthesizing azo compounds after respective reductionoxidation of azines using hydrogen molecules and palladium or platinum as catalyst followed by cupric salts, oxygen, or hydrogen peroxide⁴¹ (Scheme 1.3).



Scheme 1.3. Reduction of azines with subsequent oxidation

Similarly, in the presence of dienophiles, azines undergo an unusual 1,3- dipolar cycloaddition reaction, providing a convenient route to five-membered rings and leading to the formation of some notable compounds such as pyrazoles, purines, and pyrimidines. The first example of this kind of chemistry was given by Hartzler et al in 1969, who suggested that acetone azine underwent 1,3-dipolar cycloaddition by diazomethane extrusion.⁴² However, years later, Satsumabayashi et al in 1976, reported a cycloaddition reaction of 2,2-diphenylethenone with aldehyde azines to afford the substituted and derivative product of 4,5-dihydro-*6H*-1,3-ozazin-6one,⁴³ where azines participated as ene fragments in (3+2) cycloaddition reactions. This is in Scheme 1.4 and Scheme 1.5 respectively.



Scheme 1.4. Hartzler reaction.



Scheme 1.5. Satsumabavashi reaction.

Another interesting reaction of azine reported by Hashidzume et al. in 2006, was the formation of a polymer. In this work, alkyl aldehyde azines (e.g. acetaldehyde azine (AcAz)) underwent crisscross addition with a 1,4-phenylene diisocyanate (Ph(IC)₂) under mild conditions to obtain a polymeric product⁴⁴ (Scheme 1.6).



Scheme 1.6. Crisscross addition of acetaldehyde azine with 1,4-phenylene It is important to emphasize that azines exhibit some fascinating reactivity with transition metals and as ligands, they present several possibilities as mono- and dinucleating coordination modes due to the flexibility of the ligands around the N–N single bond, the two N lone pairs as well as the C=N π -systems.⁴⁵ However, despite this extraordinary potential, finding more than a few examples of azine complexes in literature is challenging. Combined with other donors, azine ligands can form several types of complexes, including mono-^{25,46–48}, di-^{49–51}, tri-⁵², and tetranuclear metal complexes.^{53,54}

A notable example is 2-pyridineazine, (2-PAA), which is a tetrafunctional molecule that has long been used as a ligand and analytical reagent.^{55,56} Due to its four N donors, 2-PAA can act as a bidentate, double bidentate, and tridentate molecule with different geometries and configurations. Cationic complexes of 2-PAA with a different mode of coordination, configurations (E-E, Z-E, and Z-Z), and stoichiometries [M(2-PAA)₂]²⁺ (M = Fe, or Ni),^{17,57} $[M_2(2-PAA)_3]^{4+}$ (M = Fe, Ni or Co),¹⁹ and $[M(2-PAA) 2]^{2+}$ $(M = Mn)^{58}$ as well as $[M_2(2-PAA)]^{2+}$ $(M = Ir, Mo, Cu \text{ or } Mn)^{59}$ have been isolated (Figure 1.5). Likewise, salicylaldehyde or its derivatives-based azine ligands with -N₂O₂- donor groups formed complexes analogous to those of 2-PAA (Figure 1.6).⁶⁰



Figure 1.5. Configuration and coordination modes of 2-PAA



Figure 1.6. Coordination modes of salicylaldehyde

In 1971 Stapfer et al reported and described novel complexes of cobalt(II) halides with azine and some of their chemical properties. One such example is a benzophenone azino complex of cobalt(II) bromide which was obtained by refluxing a suspension of bis-hydrazine in 2 equivalent of benzophenone. It is interesting to know that the authors underline that this compound could not be obtained by direct reaction of benzophenone azine with cobalt(II) bromide (Scheme 1.7).



Scheme 1.7. Formation of benzophenone azino complex of cobalt(ii).

Singh *et al.* in 1996 unraveled a novel unsymmetrical tetradentate azine, 2acetylpyridinesalicylaldazine (Haps), by condensing salicyl hydrazone with 2acetylpyridine. The ligand was made to react with a few first transition metal salts viz; Mn, Co, Ni, Cu, and Zn acetates to afford deprotonated M(aps)₂(H₂O)₂ complexes as shown in Figure 1.7.⁶¹



Figure 1.7. Mononuclear, homobinuclear, and heterobinuclear azine-bridged complexes

Nickel(II) complexes of azine diphosphine ligands were prepared by Almeida *et al.* for the first time in 2002 by reactions with anhydrous NiX₂ (X = Cl, Br, I). The azine is coordinated as a tetradentate ligand in E, Z configuration and forms a bicyclic ligand frame (Scheme 1.8).⁴¹



Scheme 1.8. Tetradentate coordination of an azine diphosphine to nickel(II).

According to Dönnecke *et al.*, two common reactions occur when azine ligands with halogen substituents in the ortho position are treated with Fe₂(CO)₉. The first is the symmetrical breakage of the azine's N-N bond, which results in either binuclear or trinuclear iron carbonyl compounds. The other is the development of a molecule with a trinuclear iron carbonyl cluster and a tetrahedral Fe₃N cluster core. The molecule with the fluoro in the ortho position was the most effective among all the other halogens the authors studied. Fe₂(CO)₉ treatment made the material significantly more reactive, but only five distinct clusters could be isolated and identified (Scheme 1.9).⁶²



Scheme 1.9. Identified products of the reaction between $Fe_2(CO)_9$ and azine ligands bearing

Azine and its derivatives are well known to form supramolecules. However, there have been fewer reports on metal-azine supramolecules, as such the design of metalzine coordination polymers of supramolecular architecture has been an important area of focus for azine chemistry. In 2008 Hwang reported his studies on the extended structure of silver complexes with azine ligands. The choice to use silver as the metal centers is because, as a soft acid, the Ag(I) ion helps a lot in forming supramolecular assemblies, and it favors stable coordination with soft bases like unsaturated nitrogen. As it is known, the development of supramolecules is also largely affected by the nature of the counter ions. Hwang observed that with a di-2-pyridyl ketone azine, the coordination environment and the packing of the crystals were different using different anions. Three coordination complexes built up by self-assembly of the azine and Ag ions have been structurally characterized: nitrate and trifluoroacetate complexes are tetranuclear but with dissimilar coordination structures to the Ag(I) centers, whereas the perchlorate complex has a polynuclear chain structure (Scheme 1.10).⁶³ Such variation in the environment of a complex molecule is termed "Chemical Frustration."



Scheme 1.10. Azine complexes of silver

In the past two decades, Sunatsuki et al. reported a series of mono- and di-nuclear iron (II) complexes with imidazole-4-carbaldehyde azine and other imidazole groups as azine ligands showcasing different modes of coordination towards the iron(II) in the various complexes. These complexes exhibited unique spin cross-over and promising electrochemical properties.^{64,65} A notable and distinguished among them all is an iron(II) complex bearing an unsymmetrical azine ligand of (2-pyridyl)(2-methyl-4-imidazolyl)azine which crystallized out as kryptoracemate.⁶⁶ Though there has been progress in the chemistry of the alicyclic azine molecules as ligands, in recent times, their chemistry is under-explored compared to other Schiff-based molecules, especially unsymmetrical types of azine bearing two different heteroaromatic or

heterocyclics substituents. Also, a glance through the literature suggests that azine complexes of iron triads (Fe, Co, and Ni) are very rare: apart from some studies on the iron cluster, no example of azine complex has been reported for these metals.

1.2 PROBLEM STATEMENT

Azines are unique and versatile Schiff-base molecules that possess an immense wealth of structural, stereochemical, biological, and electronic properties. These molecules exhibit a vast range of properties and possess a unique coordinating prowess that sets them apart from other Schiff-base molecules such as hydrazones and other azo compounds. However, the chemistry of these molecules compared to other Schiff-base molecules remains unexplored or underexplored. Therefore, a thorough investigation of the complexes of these azine ligands, particularly the unsymmetrical types, could potentially uncover some intriguing abilities.

1.3 AIM

This project aims to synthesize and characterize complexes of unsymmetrical azine ligands that coordinate to the first transition metal series in excellent yield. Our research group has a long-standing interest in transition metal chemistry and has previously reported on the synthesis and reactivity of Schiff-based complexes of transition metals and Lanthanide series metals with various π -acceptor ligands, including hydrazone, hydrazine, arylhydrazone, and azine complexes of Manganese, iron, nickel, and cobalt.

We are now extending our research to investigate unsymmetrical azines such as (2pyridyl)(2-methyl-4-imidazolyl)/(2-methyl-4-oxazolyl)azine of various metals. Our goal is to deepen our understanding of the coordination chemistry of these ligands, which is still not well explored in the literature. Additionally, we aim to explore how the nature of the metal fragment could alter the properties of the organic "azine" group. To complete this work, we will comprehensively characterize all the compounds we prepare through spectroscopic and crystallographic analysis. This research will form the basis of my thesis.

1.4 SPECIFIC OBJECTIVES

- 1) To synthesize (2-pyridyl)(4-imidazolyl)- or (2-methyl-4-imidazolyl)/ (2-methyl-4oxazolyl) azine, Fe and Ni complexes
- 2) To purify the complexes via the recrystallization technique
- 3) To obtain crystals of the various metal complexes
- 4) To determine the structures of the complexes using FT-IR, UV, and SC-XRD
- 5) To determine the complexes' percentage compositions of carbon, hydrogen, and nitrogen.

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CHAPTER 2

Selective Formation of Unsymmetric Multidentate Azine-Based Ligands in Nickel(II) Complexes

ABSTRACT

A mixture of 2-pyridine carboxaldehyde, 4-formylimidazole (or 2-methyl-4formylimidazole), and NiCl2·6H2O in a molar ratio of 2:2:1 was reacted with two equivalents of hydrazine monohydrate in methanol, followed by the addition of aqueous NH₄PF₆ solution, afforded a Ni^{II} complex with two unsymmetric azine-based ligands, [Ni(HL^H)₂](PF₆)₂ (1) or [Ni(HL^{Me})₂](PF₆)₂ (2), in a high yield, where HL^H denotes 2-pyridylmethylidenehydrazono-(4-imidazolyl)methane and HL^{Me} is its 2methyl-4-imidazolyl derivative. The spectroscopic measurements and elemental analysis confirmed the phase purity of the bulk products, and the single-crystal X-ray analysis revealed the molecular and crystal structures of the Ni^{II} complexes bearing an unsymmetric HL^H or HL^{Me} azines in a tridentate $\kappa^3 N$, N', N'' coordination mode. The HL^H complex with a methanol solvent, 1·MeOH, crystallizes in the orthorhombic non-centrosymmetric space group $P_{2_12_12_1}$ with Z = 4, affording conglomerate crystals, while the HL^{Me} complex, $2 \cdot H_2 O \cdot Et_2 O$, crystallizes in the monoclinic and centrosymmetric space group $P2_1/n$ with Z = 4. In the crystal of $2 \cdot H_2O \cdot Et_2O$, there is intermolecular hydrogen-bonding interaction between the imidazole N-H and the neighboring uncoordinated azine-N atom, forming a one-dimensional polymeric structure, but there is no obvious magnetic interaction among the intra- and interchain paramagnetic Ni^{II} ions.

2.1 INTRODUCTION

Nickel azine ligand complexes have a fascinating history and have been extensively studied due to their unique properties and potential applications in various fields such as catalysis, materials science, and medicinal chemistry.^{1,2} However, a cursory review of the literature reveals that there are only a few reported instances of nickel complexes bearing azine ligands of the diimine type (-C=N-N=C-), making them rare and valuable.

Two of the few complexes reported are 2-pyridinecarbaldazine and 2-pyridyl methyl ketazine of nickel(II), which were thoroughly characterized and found to possess excellent magnetic and analytical properties.^{3–5} Another notable report by Almeida et al. in 2002 described the synthesis of Nickel(II) complexes of azine diphosphine ligands, which were assessed for their redox processes via cyclic voltammetry. The study results showed that the redox processes were significantly affected by the type of halides used and the presence of alkyl substituents.⁶ Moreover, a nickel complex of a novel ligand N-(2-acetyl-2-thiazoline)-N'-(2-thiazolidin-2-one) azine (ATHTd) has been characterized by various spectroscopic techniques. The complex was found to show some pharmacological and therapeutic properties, along with rare magnetic properties.⁷

Given their adaptability, coordinating ability, and ease of synthesis, our laboratory has investigated various azine metal complexes in the past few years. We previously studied and reported on a series of mono- and dinuclear iron(II) complexes with imidazole-4-carbaldehyde azine and other imidazole groups as azine ligands, showcasing different modes of coordination towards iron(II) in various complexes.⁴⁰

My laboratory a few years back investigated the chemistry of pyridyl and imidazolyl azine-based ligands, where an unprecedented selective synthesis of the unsymmetric (2-pyridyl)(2-methyl-4-imidazolyl)azine is obtained in an excellent yield with an interesting bonding mode.¹⁰ Pursuing our interest in the unsymmetric azine-based

ligand, we attempted to synthesize the corresponding nickel(II) complexes bearing 2pyridylmethylidenehydrazono-(4- imidazolyl)methane (HL^H) and 2pyridylmethylidenehydrazono-(2-methyl-4-imidazolyl) methane (HL^{Me}).

2.2 MATERIALS AND METHODS

2.2.1 Chemicals and Physical Methods

All chemicals and solvents used to synthesize azine compounds and Ni complexes reagent grade and used without further purification. First, 2were pyridinecarboxaldehyde, 1H-imidazole-4-carboxaldehyde, 2-methyl-1H-imidazole-4carboxaldehyde, nickel(II) chloride hexahydrate, and ammonium hexafluorophosphate were purchased from FUJIFILM (Tokyo, Japan). All reactions were carried out under aerobic conditions. Infrared spectra (KBr pellets; 4000-400 cm⁻¹) were recorded on a JASCO FT-001 Fourier transform infrared spectrometer (JASCO, Tokyo, Japan). Absorption spectra were recorded on a Shimadzu UV/Vis-1650 spectrophotometer (Kyoto, Japan) in the range of 200-600 nm at room temperature in acetonitrile. The ¹H NMR spectra were acquired on a Varian 400-MR spectrometer (Los Angeles, CA, USA); the chemical shifts were referenced to residual ¹H NMR signals of solvents and were reported versus TMS. Elemental analyses were conducted at the Advanced Science Research Center, Okayama University. Magnetic susceptibilities were measured on a Quantum Design MPMS XL5 SQUID magnetometer (Tokyo, Japan) in a 1.9-300 K temperature range under an applied magnetic field of 0.1 T at the Okayama University of Science. Corrections for diamagnetism were applied using Pascal's constants.¹⁵

2.2.2 Syntheses of the symmetrical and unsymmetrical azine compounds 2.2.2.1 Pyridine-2-carboxaldehyde azine (PAA)

A methanol solution (30 mL) of pyridine-2-carboxaldehyde (5.36 g, 50.0 mmol) was added to a methanol solution (30 mL) of hydrazine monohydrate (1.26 g, 25.0 mmol),

and the mixture was refluxed with stirring at *ca* 60 °C for 5 h. The resulting precipitate was collected by filtration, and the filtrate was concentrated under a vacuum to obtain an extra precipitate. The combined precipitate was sequentially washed several times with acetonitrile, ethanol, and methanol, and dried in a vacuum. Yield: 5.24 g (99.7%). ¹H NMR (DMSO-*d*₆), δ : 8.00 (ddd, *J* = 4.8, 1.8 and 1.0 Hz, 1H), 7.84 (s, –CH=N, 1H), 7.40 (dt, *J* = 7.9 and 1.1 Hz, 1H), 7.26–7.21 (m, 1H), 6.81 (ddd, *J* = 7.6, 4.8 and 1.2 Hz, 1H): FT-IR (KBr pellets; cm⁻¹): 1630 (C=N diimine, stretching), 1580 (C=N pyridine ring) and 1460 (C=C stretching).

2.2.2.2 Imidazole-4-carboxaldehyde azine (H₂ICA^H)

A methanol solution (30 mL) of 1*H*-imidazole-4-carbaldehyde (0.961 g, 10.0 mmol) was added to a methanol solution (30 mL) of hydrazine monohydrate (0.258 g, 5.00 mmol). The mixture was refluxed with stirring for 5 h and concentrated under reduced pressure, giving an amorphous pale-yellow residue. The residue was washed with methanol and ethanol several times and dried over P₂O₅ in a desiccator. Yield: 0.922 g (98.0%). ¹H NMR (DMSO-*d*₆), δ : 12.68 (d, *J* = 14.3 Hz, 1H), 8.53–8.40 (m, –CH=N, 1H), 7.75 (dd, *J* = 33.2 and 10.5 Hz, 1H), 7.46 (d, *J* = 14.3 Hz, 1H): FTIR (KBr pellets; cm⁻¹): 3200–2600 (N–H, stretching), 1635 (C=N diimine, stretching), 1540 (C=N imidazole ring) and 1380 (C=C stretching).

2.2.2.3 2-Methylimidazole-4-carboxaldehyde azine (H₂ICA^{Me})

A methanol solution (30 mL) of 2-methyl-1*H*-imidazole-4-carbaldehyde (0.159 g, 1.44 mmol) was transferred to a methanol solution (30 mL) of hydrazine monohydrate (0.038 g, 0.72 mmol). The mixture was refluxed with stirring for 5 h and concentrated under reduced pressure, giving a yellowish powder. The powder was washed with methanol and ethanol several times and dried over P_2O_5 in a desiccator. Yield: 0.154 g (98.9%). ¹H NMR (DMSO-*d*₆), δ : 12.34 (d, *J* = 19.8 Hz, 1H), 8.39 (m, –CH=N, 1H), 7.71–
7.17 (m, 1H), 3.37 (s, 1H): FTIR (KBr pellets; cm⁻¹): 3400–2800 (N–H, stretching), 1632 (C=N diimine, stretching), 1580 (C=N imidazole ring) and 1420 (C=C stretching).

2.2.2.4 Attempt to prepare 2-pyridylmethylidenehydrazono-(4-imidazolyl or 2methyl-4-imidazolyl)methane (HL^H or HL^{Me})

To a mixture of equivalent amounts of pyridine-2-carboxaldehyde and imidazole-4carboxaldehyde or 2-methylimidazole-4-carboxaldehyde in 60 mL methanol was added a slightly excess (1.2 equiv.) amount of hydrazine monohydrate. The mixture was refluxed with stirring for 5 h and concentrated under reduced pressure, giving a yellowish residue. The residue was sequentially washed with methanol, acetonitrile, and ethanol and dried over P₂O₅ in a desiccator. ¹H NMR analyses of the products from imidazole-4-carboxaldehyde in several attempts gave two spectra (Appendix 1 (d)), this further ascertains the fact that the direct method results in a mixture of compounds. The upper spectrum is likened to the PAA spectrum (Appendix 1 (a)), this was confirmed by crystal structures (not reported) from some crystals obtained from the above experiment. The ¹H NMR spectra in Appendix 1 (d) and (e) confirmed the complicated nature of the products: a mixture of PAA, H₂ICA^H (or H₂ICA^{Me}), and HL^H (or HL^{Me}) which was found to be difficult to separate into the respective azine compounds.

2.2.3 Preparation of Nickel(II) Complexes

2.2.3.1 [Ni(HL^H)₂](PF₆)₂ (1)

A methanol solution (30 mL) of NiCl₂·6H₂O (0.477 g, 2.00 mmol) was added to a methanol solution (60 mL) containing 2-pyridinecarboxaldehyde (0.432 g, 4.00 mmol) and 1*H*-imidazole-4-carboxaldehyde (0.387 g, 4.00 mmol), followed by additions of hydrazine monohydrate (0.207 g, 4.00 mmol) in methanol (30 mL) and NH₄PF₆ (0.652 g, 4.00 mmol) in water (20 mL). The mixture was stirred at ca. 60 °C for 3 h. The resulting solution was concentrated by a rotary vacuum evaporator to give a deep reddish-orange precipitate. The crude product was dissolved in methanol and

acetonitrile and recrystallized by slow evaporation to deposit deep reddish-orange microcrystals. Crystals suitable for the SC-XRD study were obtained from a mixture of acetonitrile and methanol. Yield: 1.72 g (80%). Anal. Found: C, 32.41; H, 2.36; N, 18.38%. Calcd for C_{20.5}H₂₀F₁₂NiN₁₀O_{0.5}P₂ (for 1·0.5MeOH: C, 32.27; H, 2.64; N, 18.36%. IR (KBr pellet): v_{C=N} (imine) 1619, 1603 cm⁻¹; v_{P-F} (PF₆⁻) 840 cm⁻¹.

2.2.3.2 [Ni(HL^{Me})₂](PF₆)₂ (2)

Complex **2** was obtained in a similar manner using 2-methyl-1*H*-imidazole-4-carboxaldehyde instead of 1*H*-imidazole-4-carboxaldehyde. Yield: 83%. Anal. Found: C, 35.45; H, 3.43; N, 17.95%. Calcd for C_{25.5}H₃₁F₁₂NiO_{1.5}P₂ (for **2**·CH₃CN·1.5CH₃OH: C, 35.44; H, 3.62; N, 17.83. IR (KBr pellet cm⁻¹): $v_{C=N}$ (imine) 1635, 1609 (fs) v_{P-F} (PF₆⁻) 845(s). Deep reddish-orange platelet crystals (**2**·H₂O·Et₂O) suitable for SC-XRD were obtained from a mixture of methanol and diethyl ether.

2.3 Structure determination by x-ray crystallography

The single-crystal X-ray diffraction data for compounds 1·MeOH and 2·H₂O·Et₂O were collected at 188(2) K using a Rigaku RAXIS RAPID II imaging plate area detector employing graphite monochromated Mo K α radiation (λ = 0.71073 Å). The structures were solved by the direct method, employing the SIR2014 software packages,¹⁶ and refined on F^2 by full-matrix least-squares techniques using the SHELXL2014 program package.¹⁷ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the calculations with riding models. All calculations were performed using the Crystal Structure software package.¹⁸ The crystal parameters, data collection procedure, and refinement results for the two compounds 1·MeOH and 2·H₂O·Et₂O are summarized in Table 2.1.

2.4 RESULTS AND DISCUSSION

2.4.1 Preparation of Unsymmetric (2-Pyridyl)(4-Imidazolyl)azines and Their Nickel(II) Complexes

The most intuitive and possibly simplest method for preparation of an unsymmetric (2-pyridyl)(4-imidazolyl)azine is a reaction of stoichiometric amounts of 1H-imidazole-4-carboxaldehyde 2-pyridinecarboxaldehyde, (or its 2-methyl derivative), and hydrazine (Scheme 2.1).^{11,12} However, as was expected, all attempts to prepare the compounds HL^R with this method failed to isolate the desired compounds, because the reaction gave a complicated mixture of the products (Appendix 1) which were hard to separate by any purification method. In a previous study¹⁰, we serendipitously found that the reaction in the presence of iron(II) salts gave selectively the crystals of a Fe^{II} complex bearing unsymmetric azine, [Fe(HL^{Me})₂](PF₆)₂·1.5H₂O. To clarify the role of transition-metal salts in the selective formation of a certain complex, we used a nickel(II) chloride for the preparation of (2-pyridyl)(4-imidazolyl)azine complexes.



Scheme 2.1. Preparation of (2-pyridyl and/or 4-imidazolyl)azine compounds.

A mixture of 2-pyridine carboxaldehyde, 4-formylimidazole (or 2-methyl-4formylimidazole), and NiCl₂·6H₂O in a 2:2:1 molar ratio in methanol was reacted with a stoichiometric amount of hydrazine monohydrate, followed by the addition of an aqueous solution of NH₄PF₆, which gave an obvious color change of the reaction solution to deep reddish orange. From the reaction mixture, air-stable deep reddish orange crude product (1 from 4-formylimidazole or 2 from the 2-methyl derivative) was obtained by evaporation of the solvent in a relatively high yield (80% and 83% for compounds 1 and 2, respectively). The crude products are soluble in common polar organic solvents and recrystallized from acetonitrile by vapor diffusion of methanol to deposit block-shaped deep reddish orange crystals of 1-MeOH. For compound 2, platelet single crystals of 2·H₂O·Et₂O suitable for X-ray diffraction study were deposited by vapor diffusion of diethyl ether into a methanol solution. In the FT-IR measurement of both compounds, the crude and recrystallized products gave almost identical spectra, which showed v(C=N) stretching bands at 1619 and 1603 cm⁻¹ for 1 and 1625 and 1603 cm⁻¹ for 2 (Appendix 2). This suggests that like the abovementioned Fe^{II} complex ¹⁰, a certain Ni^{II} complex was selectively formed among several possible products. The elemental analyses of the vacuum-dried (partially efflorescent) samples suggested the empirical composition of [Ni(HL^H)₂](PF₆)₂·0.5MeOH and [Ni(HL^{Me})₂](PF₆)₂·MeCN·1.5MeOH for 1 and 2, respectively.

The χ_M T values of 1 and 2 at 300 K are 1.14 and 1.21 cm³ K mol⁻¹, respectively. These values are almost constant down to 20 K, then decrease sharply below 20 K due to their magnetic anisotropies (Appendix 3). No significant magnetic interactions between complex cations were observed. In addition, magnetizations at 1.9 K for both complexes (Appendix 3) did not reach the saturation values at 5 T, indicating the existence of magnetic anisotropies for both complexes. They are typical for magnetically isolated octahedral mononuclear nickel(II) complexes.

Absorption spectra of complexes 1 and 2 recorded in acetonitrile at room temperature are shown in Appendix 4. Both complexes displayed two absorption bands in the region of 200–550 nm. The absorption bands in the higher energy region around 200–330 nm can be assigned to ligand-centered (LC) π – π * and n– π * transitions, respectively. The lowest energy absorption band for the complexes around 450–550 nm is the metal-to-ligand charge transfer (MLCT) band.

2.4.2 Crystal Structures of the Nickel(II) Complexes

The molecular and crystal structures of 1·MeOH and 2·H₂O·Et₂O were confirmed by the single-crystal X-ray analysis at 188(2) K. Compound 1·MeOH crystallized in the orthorhombic system and a non-centrosymmetric space group $P_{21}_{21}_{21}$ with Z = 4 (Table 2.1), indicating conglomerate crystallization (spontaneous resolution of the enantiomers). The asymmetric unit consists of one [Ni(HL^H)₂]²⁺ cation, two PF₆⁻ anions, and a methanol molecule of crystallization. An ORTEP drawing of 1 is shown in Figure 2.1. The Ni^{II} center was coordinated by two HL^H ligands in a pseudo-octahedral coordination geometry. Each HL^H ligand has an E, Z configuration (mode (i) in Scheme 2) serving as tridentate coordination to a Ni^{II} center in a meridional fashion via pyridyl-N, imidazolyl-N, and one of the azine-N atoms close to the pyridyl substitution group. This coordination mode forms a five-membered chelate ring on the pyridine side and a six-membered one on the imidazole side. It is noted that the other azine-N atom remains uncoordinated, and the imidazole-NH group remains protonated.

Compound	1·MeOH	2·H ₂ O·Et ₂ O
Chemical formula	$C_{21}H_{22}F_{12}N_{10}NiOP_2$	$C_{26}H_{34}F_{12}N_{10}NiO_2P_2$
Formula weight	779.10	867.25
T/K	188(2)	188(2)
Crystal color and shape	orange, block	orange, platelet
Size of specimen/mm	$0.30 \times 0.26 \times 0.25$	$0.45 \times 0.30 \times 0.29$
Crystal system	Orthorhombic	Monoclinic
Space Group, Z	$P2_{1}2_{1}2_{1}, 4$	$P2_1/n, 4$
a/Å	8.6212(4)	12.5812(12)
b/Å	10.3267(6)	14.6221(12)
c/Å	33.20894(17)	19.9359(18)
<i>β</i> /°	90	98.664(3)
Ú/ų	2956.6(2)	3625.6(6)
$D_{ m calc}/ m g~cm^{-3}$	1.750	1.589
μ (Mo K α)/mm ⁻¹	0.8783	0.7270
$R_{ m int}$	0.0547	0.0628
No. reflns/params.	6767/426	8299/478
R1 [F^2 : $F_{o^2} > 2\sigma(F_{o^2})$]	0.0522	0.0903
$wR2$ (F^2 : all data)	0.1351	0.2966
GoF	0.872	1.084
Flack param.	0.022(7)	_

Table 2.1 Crystallographic Data of Compounds 1·MeOH and 2·H₂O·Et₂O.



Figure 2.1. An ORTEP drawing of $[Ni(HL^{H})_2](PF_6)_2$ ·MeOH (1·MeOH) with an atom-numbering scheme (ellipsoids are drawing at a 50% probability level).



Scheme 2.2. Possible configuration and their bridging or tridentate coordination modes for HL^{R} azines.

The coordination bond lengths and angles of **1** are summarized in Table 2.2, which indicates the nearly ideal octahedral coordination geometry around the Ni center, with minor deviations. The Ni–N bond lengths are in the range of 2.039(5)–2.095(5) Å,

which are typical for Ni^{II}–N(imine) coordination bonds.^{13,14} The five-membered chelate bite angles (N1–Ni1–N2 and N6–Ni1–N7) are smaller by ca. 10° than the six-membered chelate bite angles (N2–Ni1–N5, N7–Ni1–N10), as expected. The mutually *trans* bond angle of N2–Ni1–N7 for the azine-*N* donors (175.7(2)°) is close to the ideal value.

The packing structure of 1-MeOH is illustrated in Appendix 5. In the crystal structure, an explicit hydrogen bond was observed between one of the imidazole N-H group and the O atom of the methanol molecule of crystallization: N9(-H)...O1 2.710(8) A, but no other intermolecular interactions were found. In a previous study, of the Fe^{II} we reported the crystal structure analogous complex, [Fe(HL^{Me})2](PF₆)2·1.5H2O,¹⁰ in which a noble kryptoracemate resulted from a formation of a one-dimensional helical polymer by an intermolecular hydrogen-bonding interaction. In the present Ni^{II} complex 1·MeOH, although the compound was crystallized in a non-enantiogenic (Sohncke) space group, *P*2₁2₁2₁, the complex cation was crystallized in a discrete form (Appendix 5) and did not show the kryptoracemate phenomenon. Attempts were made to measure the solid-state CD spectra of a piece of a single crystal of 1 MeOH (in a KBr disk), but no CD signal was observed.

Compound	1·MeOH	2·H ₂ O·Et ₂ O
Ni1–N1, Ni–N6	2.094(4), 2.095(5)	2.110(4), 2.126(4)
Ni1–N2, Ni–N7	2.084(4), 2.082(4)	2.078(4), 2.093(4)
Ni1–N5, Ni–N10	2.047(5), 2.039(5)	2.068(4), 2.065(4)
N1–Ni1–N2, N6–Ni1–N7	79.22(19), 78.55(19)	78.80(16), 78.94(17)
N2–Ni1–N5, N7–Ni1–N10	87.99(18), 88.63(19)	88.95(16), 89.00(16)
N1–Ni1–N5, N6–Ni1–N10	167.20(18), 166.57(18)	166.81(16), 167.93(16)
N1–Ni1–N6, N5–Ni1–N10	88.85(18), 91.3(2)	91.91(18), 89.59(16)
N2–Ni1–N7	175.74(19)	165.77(16)
N1–Ni1–N7, N2–Ni1–N6	99.83(19), 97.26(17)	90.25(15), 92.25(16)
N1–Ni1–N10, N5–Ni1–N6	89.45(19), 93.27(19)	87.64(16), 93.46(16)
N2-Ni1-N10, N5-Ni1-N7	95.50(19), 92.97(19)	99.48(16), 102.60(16)

Table 2. 2. Selected bond lengths (l/Å) and angles (ϕ /°) around the Ni^{II} center in compounds 1·MeOH and 2·H₂O·Et₂O.

The compound, $2 \cdot H_2O \cdot Et_2O$, crystallized in the monoclinic system and centrosymmetric space group P_{21}/n with Z = 4 (Table 2.1). The molecular structure of the Ni^{II} complex cation in **2** (Figure 2.2) is very similar to that in **1**, except for the large deviation of the bond angles, e.g., N2–Ni1–N7 and N5–Ni1–N7 (Table 2.2), which resulted from steric congestion from the substituted methyl group at the imidazole ring.



Figure 2.2. An ORTEP drawing of the complex cation $[Ni(HL^{Me})_2]^{2+}$ in $2 \cdot H_2O \cdot Et_2O$ with an atomnumbering scheme (ellipsoids are drawing at a 30% probability level).

In the crystal structure, the intermolecular hydrogen-bonding interaction was observed between the imidazole N–H and azine-N groups: N9(–H9)…N8 2.714(6) Å, forming one-dimensional coordination polymers (Figure 2.3). In contrast to the corresponding Fe^{II} complex,¹⁰ this Ni^{II} complex **2**·H₂O·Et₂O crystallized in a centrosymmetric space group $P2_1/n$, indicating the crystal consists of the racemic mixture.



Figure 2.3. Intermolecular Hydrogen-Bonding Interaction Gives a one-Dimensional Polymer Chain in 2·H₂O·Et₂O. Color Code: Ni, Teal; P Orange; F, Yellow-Green; N, Blue; C, Gray; H, Silver.

2.5 CONCLUSIONS

In this study, we attempted to prepare transition-metal(II) complexes of an unsymmetrical azine-type ligand, HL^R, having 2-pyridyl and (2-methyl-)1*H*-imidazol-4-yl substituent groups. The desired azine could not be isolated in pure form from a simple stoichiometric reaction of hydrazine and respective aldehydes. However, in study using Fe^{II} salts, a highly our previous selective formation of [Fe(HLMe)2](PF6)2·1.5H2O was observed, and the complex was found to be a kryptoracemate as a result of a one-dimensional helical chain structure by hydrogenbonding interaction. At present, we have studied another two cases with nickel(II) salts: $[Ni(HL^{H})_2](PF_6)_2 \cdot MeOH (1 \cdot MeOH) and [Ni(HL^{Me})_2](PF_6)_2 \cdot H_2O \cdot Et_2O (2 \cdot H_2O \cdot Et_2O).$ In both cases, a highly selective formation of the unsymmetrical azine complex was observed among other possible symmetrical and unsymmetrical complexes.

In the crystal of 1·MeOH, the compound was crystallized in a non-enantiogenic (Sohncke) space group, $P2_12_12_1$. Still, the complex cation, $[Ni(HL^H)_2]^{2+}$, was only hydrogen-bonded to the solvated methanol molecule. In the crystal structure of **2**, ·H₂O·Et₂O there observed a one-dimensional hydrogen-bonded polymer chain made

from $[Ni(HL^{Me})_2]^{2+}$, but it was crystallized in a centrosymmetric space group, $P_{21/c}$. Thus, it can be concluded that the reason for the selective formation of an unsymmetric azine ligand in $[Fe(HL^{Me})_2](PF_6)_2 \cdot 1.5H_2O$ was not solely the formation of the characteristic hydrogen-bonded chain. The suitable tridentate chelate formation of *E*, *Z*-HL^R with mode (i) (in Scheme 2.2), which gives a five-membered chelate ring at the pyridyl coordination site and a six-membered chelate ring at the imidazolyl one, would probably be the most stable among the other coordination modes of symmetrical and unsymmetrical azine derivatives.

APPENDICES

Appendix 1: (a) ¹H NMR Spectrum of PAA.



Appendix 1: (b) ¹H NMR Spectrum of H₂ICA^H



Appendix 1: (c) ¹H NMR Spectrum of H₂ICA^{Me}



Appendix 1: (d) ¹H NMR Spectra of direct reaction products (partially separated by fractional crystallization) from pyridine-2-carboxaldehyde, imidazole-4-carboxaldehyde, and hydrazine monohydrate in methanol.



Appendix 1: (e) ¹H NMR Spectrum of direct reaction products from pyridine-2carboxaldehyde, 2-methylimidazole-4-carboxaldehyde, and hydrazine monohydrate in methanol.



Appendix 2. FT-IR spectra of (upper) [Ni(HL^H)₂](PF₆)₂ (1) and (lower) [Ni(HL^{Me})₂](PF₆)₂



Appendix 3: The X_M*T* vs *T* plots of **1** (red) and **2** (blue) (inset: Magnetizations of **1** (red) and **2** (red) at 1.9 K.



Appendix 4: Absorption spectra of 1 (black) and 2 (red) in acetonitrile at room temperature.



Appendix 5: Packing diagram of **1**·MeOH viewed along the crystallographic *a* axis. Color code: Ni, teal; P orange; F, yellow-green; O, red; N, blue; C, gray; H, silver.



Appendix 6: Packing diagrams of **2**·H₂O·Et₂O viewed along (upper) crystallographic *a* axis and (lower) crystallographic *b* axis. Color code: green, Ni; orange, P; yellow-green, F; red, O; blue, N; black, C; silver, H



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CHAPTER 3

Synthesis and Characterization of Iron(II) Complex with an Unsymmetrical Heterocyclic (2-Pyridyl)(4-imidazolyl)azine

ABSTRACT

A new iron(II) complex bearing unsymmetrical azine, [Fe(HL^H)₂](PF₆)₂·H₂O·MeCN (HL^H = 2-pyridylmethylidenehydrazono(4-imidazolyl)methane), was synthesized exclusively by a reaction of 2-pyridine carboxaldehyde, 4-formylimidazole, hydrazine monohydrate and FeCl₂·4H₂O (in a molar ratio of 2:2:2:1) in methanol, followed by the addition of an aqueous NH₄PF₆ solution. It was characterized using spectroscopic techniques, elemental analysis, magnetic measurement, and cyclic voltammetry. The molecular and crystal structure of the compound was revealed by X-ray analysis, where an iron(II) ion was surrounded by two HL^H azines with a planar E(py),Z(im)conformation, and tridentate $\kappa^3 N, N', N''$ coordination mode, forming a monomeric sixcoordinated and diamagnetic complex. The complex cations were linked by water molecules via intermolecular hydrogen-bonding interactions between the imidazole *N*–H and the neighboring uncoordinated azine-*N* atom, forming a 1D chain structure. The selective formation of this unsymmetrical azine (HL^H) from a stoichiometric mixture of the components would result from the steric preference of the five- and sixmembered chelate rings by the 2-pyridyl and 4-imidazolyl azine moieties, respectively, with the E(py),Z(im) conformation.

3.1 INTRODUCTION

N-heterocyclic-substituted azines ($R^1R^2C=N-N=CR^3R^4$: $R^1-R^4 = H$ or *N*-heterocyclic group) are characterized by their multiple nitrogen donor atoms and offer attractive prospects in coordination chemistry because of their ease of synthesis and accessibility ¹⁻⁴. They can be, most often, obtained by condensing suitable carbonyl compounds with hydrazine in excellent yields ⁵⁻⁸. Unsymmetrical azines are particularly interesting because of the ability of their functionality to link two dissimilar groups in useful ways ^{8,9}. One of the simplest examples with two different imine groups is having a pyridyl and an imidazolyl substituent on opposite sides (Figure 1: HL^R, R = H or 2-Me). These azines may allow fine-tuning of the coordination environment around the metal center ¹⁰⁻¹², opening doors to new and enhanced reactivity in catalytic processes ^{13,14}. They would also serve as building blocks for developing novel materials, including colorimetric chemo-sensors,¹⁵⁻¹⁷, luminescent compounds,^{18,19}, and organic electronics,²⁰⁻²², which hold significant promise for advanced technologies. With the above-enumerated prospects, the unsymmetrical azines are, however, arduous to prepare, because conventional synthetic methods, by reacting the corresponding two (e.g., pyridyl and imidazolyl) aldehydes with the stoichiometric amount of hydrazine suffer from drawbacks; the formation of product mixtures leads to low yields of the desired azines. We also attempted various synthetic methodologies, including mechanosynthesis and multiple synthetic approaches (Scheme 3.1), to selectively synthesize the unsymmetrical azines in high yields; however, these attempts were unsuccessful ^{3,6,23}.

In our previous studies, ²⁴, we reported the selective formation and structural characterization of an iron(II) complex bearing 2-pyridylmethylidenehydrazono(2-methyl-4-imidazolyl)methane (HL^{2-Me}) with the formula [Fe(HL^{2-Me})₂](PF₆)₂·1.5H₂O (**1Me**). This Fe^{II} compound crystallized out as a kryptoracemate, owing to the formation of a spiral 1D chain of the complex cations by hydrogen-bonding and π - π stacking interactions, and we suspected that such interactions would be the reason for



Figure 3.1. The azines and their abbreviations used in this study.

the exclusive crystallization of the unsymmetrical azine complex. Based on this assumption, we proceeded to investigate the synthesis and characterization of the analogous nickel(II) complexes containing HL^{2-Me} and its simpler imidazolyl derivative: $HL^{H} = 2$ -pyridylmethylidenehydrazono(4-imidazolyl)methane, which led to the desired complexes also in high yields ²⁵. Herein, to conclude our discussion on the selective formation of unsymmetric azine complexes, we will prepare and characterize the Fe^{II} complex containing HL^{4-Me} and compare the structure and properties with those of the corresponding HL^{2-Me} complex (**1Me**).



Scheme 3.1. Stepwise approach to synthesize unsymmetric azines.

3.2 EXPERIMENTAL SECTION

3.2.1 Materials and Methods

All chemicals and solvents used for synthesizing the Fe complex were of reagent grade and were used without further purification. The chemicals, 2-pyridine carboxaldehyde, 1H-imidazole-4-carboxaldehyde, iron(II) chloride tetrahydrate, and ammonium hexafluorophosphate were purchased from FUJIFILM Wako Co. Ltd. All reactions were performed under aerobic conditions. Infrared spectra (KBr pellets; 4000–400 cm⁻¹) were recorded using a JASCO FT-001 Fourier transform infrared spectrometer. Absorption spectra were recorded using a Shimadzu UV/Vis-1650 spectrophotometer in the 200-800 nm range at room temperature in acetonitrile. Proton (¹H) NMR spectra were recorded on a Varian NMR system PS600 spectrometer. The chemical shifts, δ , are given in parts per million relatives to TMS ($\delta = 0$) and refer internally to the residual proton chemical shift in the deuterated solvent. Elemental analyses were conducted at the Advanced Science Research Center of Okayama University. Magnetic susceptibilities were measured using a Quantum Design MPMS XL5 SQUID magnetometer in a 1.9–300 K temperature range under an applied magnetic field of 0.1 T at the Okayama University of Science. Diamagnetism corrections were applied using Pascal's constants. The cyclic voltammetry measurements were carried out in a standard one-compartment cell under a dinitrogen atmosphere at 25 °C equipped with a platinum wire counter electrode, an Ag/Ag⁺ (Ag/0.01 M AgNO₃) reference electrode, and a glassy carbon working electrode using an ALS Model 612E electrochemical analyzer. The measurements were performed in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) as the supporting electrolyte. The concentration of the compound was 1.0 mM. The scan rate was 100 mV s⁻¹.

3.2.2 Synthesis of the iron(II) complex (1H).

A solution of FeCl₂·4H₂O (0.477 g, 2.00 mmol) in 30 mL of methanol, a methanol solution (60 mL) containing 2-pyridine carboxaldehyde (0.432 g, 4.00 mmol) and 1*H*-

imidazole-4-carboxaldehyde (0.387 g, 4.00 mmol), and a methanol solution (30 mL) of hydrazine monohydrate (0.207 g, 4.00 mmol) were mixed in this order, followed by the addition of aqueous solution (20 mL) of NH₄PF₆ (0.652 g, 4.00 mmol). The resulting mixture was stirred at 60 °C for 3 h. After the concentration of the solution under reduced pressure, the resulting dark blue precipitate was collected by filtration. The crude product was dissolved in acetonitrile and the resulting solution underwent filtration. The filtrate was subsequently concentrated using a rotary evaporator, resulting in the formation of a dark precipitate. This precipitate was subjected to recrystallization in methanol, and once again, the resulting solution was concentrated to yield an amorphous dark blue solid crystal. Crystals suitable for single-crystal Xray diffraction (SC-XRD) analysis were obtained using a vapor diffusion technique from a mixture of acetonitrile and chloroform. Yield: 1.70 g (91%). Anal. Found: C, 32.17; H, 3.07; N, 18.76%. Calcd for C22H25F12FeN11O2P2 (1H·2H2O·MeCN): C, 32.03; H, 2.94; N, 18.64%. ¹H-NMR (DMSO-*d*₆), 1H: δ: 13.50 (s, 2H), 10.09 (s, im–CH=N, 2H), 8.63 (s, py–CH=N, 2H), 8.30 (d, J = 7.7 Hz), 8.00 (dd, J = 20.9 and 3.4 Hz, 2H), 7.91 (td, J = 7.7 and 1.4 Hz, 2H), 7.67 (s, 2H), 7.37 (ddd, J = 7.2, 5.6 and 1.3 Hz, 2H) 7.00–7.17 (m, 2H), 1Me: δ: 13.30 (s, 2H), 10.10 (s, im–CH=N, 2H), 8.68 (s, py–CH=N, 2H), 8.42 (d, J = 6.7 Hz, 2H), 8.23 (d, J = 7.3 Hz, 2H), 8.10 – 7.79 (m, 2H), 7.67 (s, 2H), 7.57 - 7.30 (m, 2H) 2.12 (s, 6H). IR (KBr pellet): VN-H 3160, VC=N (imine) 1623, 1602; VP-F (PF6⁻) 837, VFe-N 559 cm⁻¹.

3.2.3 Crystallography.

The SC-XRD data for **1H**·H₂O·MeCN were collected at 210(2) K using a Rigaku RAXIS RAPID II imaging plate area detector employing graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The structure was solved by the direct method, utilizing the SIR2014 software package ²⁶, and refined on *F*² by full-matrix least-squares techniques using the SHELXL2014 program package ²⁷. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the calculations with

riding models. All analyses were performed using the Crystal Structure software package ²⁸.

3.3 RESULTS AND DISCUSSION

3.3.1 Selective formation of the unsymmetric ligand complex.

A possible and the most straightforward method for preparing [Fe(HL^H)₂](PF₆)₂ (**1H**) involves a reaction between stoichiometric amounts of the unsymmetrical (2-pyridyl)(4-imidazolyl)azine (HL^H) and a suitable iron(II) salt, followed by the addition of hexafluorophosphate salts (Scheme 1; upper). However, a direct approach of reacting 2-pyridine carboxaldehyde, 1*H*-imidazole-4-carboxaldehyde, and hydrazine in equimolar amounts to obtain the desired unsymmetrical azine, HL^H, has proven to be notoriously difficult ²⁵. To overcome this limitation, we employed a modified



Scheme 3.2. Preparation of the iron complex: [Fe(HL^H)₂](PF₆)₂

approach, in which the ligand components (the two aldehydes and hydrazine) and an appropriate metal salt were combined in stoichiometric amounts in a concerted reaction, as previously reported ^{24,25}. Specifically, 2-pyridine carboxaldehyde, 4-formylimidazole, and FeCl₂·4H₂O were reacted in a molar ratio of 2:2:1 in methanol, followed by the addition of a stoichiometric amount of hydrazine monohydrate. This resulted in a distinct color change of the reaction solution to deep blue. An aqueous solution of NH₄PF₆ was added to the reaction mixture, affording an air-stable deep blue crude product of the complex PF₆ salts (Scheme 1; lower) by evaporation of the

solvent in an excellent yield (91%). The product was soluble in acetonitrile and sparingly soluble in methanol at room temperature, and the purity was confirmed by elemental analyses, IR, and ¹H NMR spectroscopy. The IR spectrum of the product displayed a prominent band at 3160 cm⁻¹, indicating N–H stretching, and the C=N stretching bands were observed at 1623 and 1602 cm⁻¹, while the presence of the counter ion (PF₆-) was confirmed by a strong band at 837 cm⁻¹ (Figure S1). Elemental analysis suggested an empirical composition of [Fe(HL^H)₂](PF₆)₂·2H₂O·MeCN.

Magnetic susceptibility measurement of complex **1H** showed diamagnetic behavior in the temperature range of 5–300 K in the solid state (Appendix 5). The negligible $\chi_M T$ value for the complex is attributed to temperature-independent paramagnetism. This result is consistent with the ¹H NMR spectrum (Figure 3.3 and Appendix 3) and the Fe–N bond lengths in Table 3.3.

The ¹H NMR spectra of complexes 1H and 1Me are depicted in Figure 3.2 and Appendix 4 respectively. These spectra showed three characteristic signals in the low-field region, corresponding to the imidazole N–H (a broad signal around δ 13.7), the imino proton located next to the imidazolyl group (C=N-N=CH-im; δ 10.09) and the imino proton next to the pyridyl group (py-CH=N-N=C; δ 8.63). There were no additional peaks that might suggest the presence of a mixture of symmetrical and



Figure 3.2. ¹H NMR Spectrum of 1H in DMSO- d_6 at 22°C.

unsymmetrical azines. Thus, this spectrum indicated the selective formation of a single azine and its iron(II) complex.

Electronic spectra of the complexes, **1H** and **1Me**²⁴ recorded in acetonitrile at room temperature are shown in Figure 3.2 and the data are summarized in Table 3.1. The absorption bands in the higher energy region around 240–360 nm for both complexes can be assigned to ligand-centered (LC) π – π * and n– π * transitions. The lowest energy absorption band for the complexes around 450–800 nm can be ascribed as the metal-to-ligand charge transfer (MLCT) band ^{29,30}. Complexes **1H** and **1Me** exhibited nearly identical MLCT transition energy bands, implying the identical coordination environment around the Fe^{II} center in both complexes.

Compound	$\lambda_{max}/nm (\epsilon/M^{-1}cm^{-1})$
1H	261 (sh, 5623)
	295 (sh, 3947)
	342 (7078)
	663 (725)
1Me	274 (10102)
	359 (4763)
	679 (558)

Table 3.1. UV-Vis spectral data of 1H, and 1Me in methanol at room temperature.



Figure **3**.3. UV-VIS absorption spectra of acetonitrile solutions of 1H and 1Me, measured at room temperature.

The electrochemical behaviors of complexes **1H** and **1Me** were compared, and the cyclic voltammograms (CVs) of both complexes are given in Appendix 3. Complexes **1H** and **1Me** showed one reversible oxidation wave at +0.66 and +0.71 V (vs. Fc⁺/Fc), respectively, corresponding to the Fe^{III/II} redox couple. Both complexes also showed one reversible reduction around -1.2 V (vs. Fc⁺/Fc), which is tentatively assigned to the reduction of the coordinated ligands ^{31,32}. The two complexes are redox active from the voltammograms, and there seemed to be no subtle difference. The presence of a methyl substituent, as an electron-donating group, contributes to little variations in oxidation and reduction potentials.

3.3.2 Crystal structure.

The crystal structure of **1H**·H₂O·MeCN was determined at 210(2) K. The crystallographic data are provided in Table 3.2, and the selected bond lengths and angles are listed in Table 3.3. Within the orthorhombic space group of *Pbca*, the asymmetric unit of compound **1H**·H₂O·MeCN consisted of one [Fe(HL^H)₂]²⁺ cation,



Figure **3.4**. An ORTEP drawing of $[Fe(HL^H)_2](PF_6)_2 \cdot H_2O \cdot MECN (1H \cdot H_2O \cdot MECN)$ with an atomnumbering scheme (ellipsoids are drawn at a 30% probability level).

two PF₆⁻ anions, one water molecule, and one molecule of acetonitrile (Figure 3.4) with Z = 8. The Fe^{II} center is coordinated by two HL^H azines, adopting a pseudo-octahedral coordination geometry. Each azine, configured in the E(py),Z(im) arrangement (Figure 3.5), acts as a planar tridentate ligand, forming a five-membered chelate ring with pyridyl-*N* atom and a six-membered chelate ring with an imidazolyl-*N* atom as well as one of the azine-*N* atoms. Notably, the other azine nitrogen atom remains uncoordinated, consistent with prior reports ^{24,25}.



Scheme 3.3. Possible configurations for HL^H

The Fe–N bond lengths of **1H** range from 1.940(2) to 1.972(2) Å are characteristic of low-spin Fe^{II} species, like those in **1Me**. The five-membered N–Fe–N chelate bites angles are 81.61(17) and 81.79(8)°, and the six-membered ones are 91.53(7) and 91.35(8)°. Compared these coordination bond lengths and angles to those of the corresponding HL^{2-Me} complex of **1Me**, there were no significant differences. This contrasts with the case between the analogous bis(4- imidazolyl)azine (H₂ICA^H) and (H₂ICA^{2-Me}) bis(2-methyl-4-imidazolyl)azine complexes. Complex [Fe(H₂ICA^H)₂](ClO₄)₂ was diamagnetic (low-spin state) at room temperature, while [Fe(H₂ICA^{2-Me})₂](ClO₄)₂ was paramagnetic (high-spin state), owing to the intramolecular steric repulsion from the substituted methyl group. However, in the case of unsymmetric HL^H and HL^{2-Me} azine complexes, **1H** and **1Me** display very similar absorption spectra and magnetic properties, irrespective of the presence of the methyl group in **1Me**. In addition, for the symmetrical PAA, H₂ICA^H, and H₂ICA^{2-Me} azines, the formation of the iron(II) dinuclear complexes bridged by the azines was observed, but in the case of the unsymmetrical HL^H and HL^{2-Me} azines isolation of the corresponding dinuclear complexes failed in the previous and present studies.

Compound	1H·H ₂ O·MeCN
Chemical formula	C22H23F12FeN11OP2
Formula weight	803.27
T/K	210(2)
Crystal color and shape	Dark-blue, block
Crystal system	Orthorhombic
Space group, Z	Pbca, 8
a/Å	8.9070(5)
b/Å	18.0884(9)
c/Å	37.232(2)
U/ų	5998.6(6)
$D_{\text{calc}}/\text{g cm}^{-3}$	1.779
μ (Mo K $lpha$)/mm ⁻¹	0.7254
Rint	0.0408
No. reflns/params.	6869/443
$R_1 [F^2: F_0^2 > 2\sigma(F_0^2)]$	0.0497
wR_2 (F^2 : all data)	0.1179
GoF	1.038

Table 3.2. Crystallographic data of compound 1H·H₂O·MeCN.

Table 3.3. Selected bond lengths (l/Å) and angles ($\phi/^{\circ}$) in compound 1H·H₂O·MeCN.

Fe1–N1	1.9675(17)	Fe1–N6	1.972(2)
Fe1–N2	1.9404(17)	Fe1–N7	1.9440(17)
Fe1–N5	1.9592(17)	Fe1-N10	1.954(2)
N1–Fe1–N2	81.61(17)	N6-Fe1-N7	81.79(8)
N2–Fe1–N5	91.53(7)	N7-Fe1-N10	91.35(8)
N1–Fe1–N5	172.97(7)	N6-Fe1-N10	173.09(7)
N1–Fe1–N6	91.70(8)	N5-Fe1-N10	89.17(8)
N2–Fe1–N7	174.15(8)		
N1–Fe1–N7	94.37(7)	N2-Fe1-N6	94.03(8)
N1-Fe1-N10	89.63(8)	N5-Fe1-N6	90.31(8)
N2-Fe1-N10	92.87(8)	N5-Fe1-N7	92.58(7)

In the crystal structure of **1H**, water molecules connect the $[Fe(HL^{H})_{2}]^{2+}$ cations via hydrogen bonds. Intermolecular hydrogen bonding interactions were observed between the imidazole N–H and the oxygen of the water molecule: $[N4-H4\cdots O1 = 2.741(2) \text{ Å}]$, and between the hydrogen of the water molecule and azine-N atom $[N3\cdots H-O1 = 2.923 (3) \text{ Å}]$. This arrangement leads to a zigzag arrangement of the molecules in the crystal packing (Figure 6). In addition, the imidazole hydrogen atom, N9–H9, is also involved in a hydrogen bond with the acetonitrile N11 atom $[N4-H4\cdots N11 = 2.894(3) \text{ Å}]$. However, in our previous study on **1Me**, a 1D helical chain structure was observed, resulting from several interactions, such as hydrogen bonds, CH– π interactions, and π – π stacking interactions between the pseudo-enantiomers.



Figure 3.5. 1D chain arrangement in $1H \cdot H_2O \cdot MeCN$ built by hydrogen bonds between $[Fe(HL^H)_2]^{2+}$ monomeric units and water molecules.

Azines	Complexes	The bite angle of a five-membered chelate	The bite angle of a six-membered chelate	Transoid angle of tridentate azine	Ref.
PAA	[Fe(PAA) ₂]X ₂	82.11(11), 83.20(10)	90.4(10), 91.53(11)	171.56(11), 173.12(10)	35,38
	[Ni(PAA) ₂]X ₂	78.86(17), 78.92(17)	87.95(17), 88.15(18)	167.09(10), 168.78(9)	11,39
H ₂ ICA ^H	[Fe(H ₂ ICA ^H) ₂](ClO ₄) ₂	78.13(17), 77.0(2) 79.65(11), 73.8(3)	95.9(2), 94.31(19) 98.9(3), 92.96(11)	172.73(9), 171.96(8)	33,37
H ₂ ICA ^{2-Me}	$[Fe(H_2ICA^{2-Me})_2](ClO_4)_2$	77.04(11), 73.9(2)	84.36(12), 87.4(2)	161.29(11), 160.94(12)	33,37
HL ^H	[Fe(HL ^H) ₂](PF ₆) ₂	81.61(17), 81.79(8)	91.53(7), 91.35(8)	172.97(7), 173.09(7)	This work
	$[Ni(HL^H)_2](PF_6)_2$	79.22(19), 78.55(19)	87.99(18), 88.63(19)	167.20(18), 166.57(18)	25
HL ^{2-Me}	[Fe(HL ^{2-Me}) ₂](PF ₆) ₂	81.17(11), 80.69(11), 81.77(10), 81.17(11)	91.73(11), 91.45(11) 91.18(10), 91.93(11)	172.77(10), 171.91(11), 172.47(10), 172.67(10)	24
	[Ni(HL ^{2-Me}) ₂](PF ₆) ₂	78.80(16), 78.94(17)	88.95(16), 89.00(16)	166.81(16), 167.93(16)	25

Table **3**. 4. Five- and six-membered chelate bite angles and transoid angles ($f/^{\circ}$) formed by symmetrical and unsymmetrical azines in the Fe^{II} and Ni^{II} complexes.

3.3.3 Selective formation of unsymmetric azine complexes.

The theoretically expected yield for the unsymmetric azine by a stoichiometric mixture of two kinds of aldehydes and hydrazine is 50%, and that for the Fe^{II} complex with two azine molecules is only 25% ²⁴. However, the previous reports on this type of unsymmetrical azine complexes had excellent yields of more than 80%. We explained that the formation of the unsymmetrical azine in **1Me** might have been related to the formation of the helical hydrogen-bonding chain, which would lower the solubility of the compound ^{24,34}. In contrast, our earlier studies on nickel(II) complexes bearing the same azines (HL^H and HL^{2-Me}) resulted in the selective formation of similar complexes in excellent yields. We explained this tremendous outcome by emphasizing the hydrogen bonding expressed by the complexes in their solid states, similar to those mentioned above in helical 1D chain ²⁷.

Table 3 provides a summary of chelate bite angles and the transoid angle of the related azines in their Fe^{II} and Ni^{II} complexes. For PAA complexes the six-membered chelate angles (89.9(10)–91.53(11)°) are approximately right angles, and the transoid angles (168.8(9)–173.12(10)°) are approaching linearity ^{15,38–40}. However, the lone pair

electrons of the pyridyl-N atom in the six-membered ring were not efficiently matched to the accepting metal(II) d-orbital. Instead, the overlap between the pyridyl-*N* donor orbital and metal(II) d-orbital is sterically preferable for the five-membered chelate, though the bite angles of the chelate were $80.11(11)-83.20(10)^\circ$. In the case of Fe^{II} symmetrical imidazole-type azine complexes, the H2ICA2-Me complex exhibited comparatively smaller six-membered chelate and transoid angles than those of the corresponding H₂ICA^H complex, owing to the steric interaction from the substituted methyl group at 2-position of imidazole ring to the other azine ligand plane⁴¹. For the five-membered chelate bite angles of the H₂ICA^{2-Me} and H₂ICA^H complexes, there is no remarkable difference between them. Still, they were significantly smaller than those of the PAA complexes and the lone pair electrons of the imidazolyl-N atom were not so matched to the accepting metal(II) d-orbital. Complexes formed with unsymmetrical HL^H and HL^{2-Me} ligands exhibited similar chelate bite angles for both five- and six-membered structures, irrespective of the metal ions (Fe^{II} and Ni^{II}). These facts indicate that the steric repulsion from the substituted methyl group on the imidazolyl ring had no effects on these complexes. The five- and six-membered chelate rings formed by the pyridyl and imidazolyl groups, respectively, as the terminal azine substituents with the E(py),Z(im) conformation could be more preferable than the other *Z*(py),*E*(im) conformation which would give a six-membered chelate ring for the pyridyl and a five-membered one for the imidazolyl moieties. We conclude that the steric predominance of the successive five- and six-membered chelate rings with the *E*(py),*Z*(im) conformation is crucial for selective formation of the unsymmetrical azine complexes. We should, however, note that the predominance is largely dependent on the metal-ligator coordination bonds, so other transition metal ions, such as Mn^{II}, Cu^{II}, and Cr^{III} may give a different result of selectivity.
3.4 CONCLUSION

Despite our previous achievements in synthesizing and characterizing unsymmetrical azines (HL^H and HL^{2-Me}) complexes of Fe^{II} and Ni^{II} in excellent yields, the underlying reasons behind the selective formation of these unsymmetrical azines remained elusive. While we have posited reasons such as the labile nature of the C=N bonds in the azines, solubility of the resulting complex salts, and diverse interactions exhibited by the complex ions as major contributing factors to this selectivity, we were convinced that there is a more profound understanding yet to be uncovered. We revisited the possibility of steric factors resulting from the chelate bite angles of the symmetrical and unsymmetrical azines in the complexes. The five-membered chelate ring formed by the (2-pyridyl)azine part of $HL^{\mathbb{R}}$ with E(py),Z(im) conformation was sterically preferable to the possible six-membered chelate ring formed with the Z(py), E(im) conformed HL^R, as similar to the discussion in the PAA complexes. In contrast, for the (4-imidazolyl)azine part the formation of a six-membered chelate ring with E(py), Z(im) conformation was predominant over the five-membered chelate ring formed by the *Z*(py),*E*(im) azine. The existence of methyl group at the 2-position of the imidazole ring did not give any intramolecular steric hindrance to the other azine ligand, which was observed in the related H₂ICA^{2-Me} complex. Thus, we conclude that a combination of the sterically favorable five- and six-membered chelate rings for the 2-pyridyl and 4-imidazolyl azine parts, respectively, is the main reason for the selective formation of unsymmetrical azines with the E(py), Z(im) conformation.

APPENDICES

Appendix 1: Plausible structures





Appendix 2: FT-IR spectra of [Fe(HL^H)₂](PF₆)₂ (1H)



Appendix 3: Cyclic voltammograms of **1H** and **1Me** (scan rate 100 mVs⁻¹).

Appendix 4: 1H NMR Spectrum of 1Me



Appendix 5: The $\chi_M T$ vs *T* plots of the complex 1H



Appendix 6: Packing diagram of 1·2H₂O·MeCN viewed along the crystallographic *a* axis. Color code: Fe, violet; P orange; F, yellow-green; O, red; N, blue; C, gray; H, silver.



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CHAPTER 4

Exclusivity and Selectivity in the Formation of Iron(II) and Nickel(II) Complexes with Unsymmetrical Heterocyclic Multidentate Azine Ligands: (2-Pyridyl)(4-(2-Methyloxazolyl))azine.

ABSTRACT

High-yield synthesis of new selectively formed six-coordinated Fe^{II} and Ni^{II} complexes, $[Ni(L)_2](PF_6)_2$ (1), and $[Fe(L)_2](PF_6)_2 \cdot MeOH$ (2)was achieved, where L denotes 2-methyl-4-(((-pyridin-2-ylmethylene)hydrazineylidene)methyl)oxazole. The compounds were synthesized by reacting a mixture of 2-pyridine carboxaldehyde, 2-methyloxazole-4-carbaldehyde, and FeCl2·4H2O or NiCl2·6H2O in a molar ratio of 2:2:1 with two equivalents of hydrazine monohydrate in methanol, followed by the addition of an aqueous NH₄PF₆ solution. The physical characterization of the coordination complexes was conducted using various spectroscopic techniques (FT-IR, ¹H-NMR, and UV-vis), along with X-ray diffraction. The molecular and crystal structures of the compounds were elucidated, revealing that each metal ion (Ni^{II} and Fe^{II}) in 1 and 2, was coordinated by two unsymmetrical L azines in a planar tridentate $\kappa^{3}N$, N', N'' mode. Both complexes 1 and 2 crystallized in the orthorhombic space group Pca21. Notably, none of these complexes exhibited interactions via intermolecular hydrogen bonding, unlike observations in our previous reports. Also, the selective formation of this unsymmetrical azine (L^{Me}) from the stoichiometric mixture of the components perhaps spawns from the steric preference of the five- and six-membered chelate rings by the 2-pyridyl and 4-(2-methylimidazolyl) azine moieties, respectively, with the E(py),Z(ox) conformation.

4.1 INTRODUCTION

The discovery of pyridine aldazine (PAA), specifically 1,2-bis(pyridine-2ylmethylene) hydrazine, marked a significant turning point in diimine (C=N-N=C) chemistry. In this compound, two pyridine-2-ylmethanimine binding units are directly linked by imine nitrogen atoms, as illustrated in Figure 1a. The presence of a flexible N-N bond in the central part of the ligand allows for unhindered rotation. Between 1958 and 1960, Stratton and Busch conducted pioneering research into the coordination behaviors of PAA, unmatched at the time.^{1,2} They uncovered a fascinating realm of Metallo-supramolecular chemistry associated with PAA. Notably, PAA has the remarkable ability to form metal helicates. Stratton and Busch proposed that when PAA interacts with transition metal ions, it can yield octahedral complexes represented by the formula $[M_2(PAA)_3]^{4+}$ (M = Co²⁺, Fe²⁺, etc.). These complexes consist of three strands enfolded around two metals in a spiral fashion, representing the first recognized examples of triple helicates in the field of chemistry.^{3,4}

Furthermore, their investigations documented that when these helical complexes are subjected to exchange reactions through heating or standing, they transform to their respective mononuclear complexes denoted as [M(PAA)₂]²⁺. The ligand adopts a tridentate coordination mode in these complexes, with one imine residue remaining uncoordinated. This restructuring process is a remarkable phenomenon in coordination chemistry.^{1,2}

Sheldrick et al. drew inspiration from Stratton and Busch's studies. They reported the X-ray crystal structure of a dinuclear triple-helical cobalt (II) complex formed using the pyridylmethyl ketazine ligand.⁵ Hanon et al. made groundbreaking contributions by structurally characterizing the PAA's dimeric Ag(I) triple helicate.⁶ They suggested that the obtained structures might be influenced by the relative positions of the N atoms on the terminal pyridine ring and in the central part of the ligand (PAA). Additionally, PAA exhibits a strong chelating ability with metal ions due to the

proximity of the pyridine ring N atom and the imine N atom within the ligand's body.⁷⁻⁹

Sunatsuki et al. for the first time also structurally characterized the dimeric Fe(II) triple helicate of the ligand, IAA (Figure 4.1b), and its methyl- and ethyl-derivatives which showed remarkable magnetic and electrochemical properties.⁷

Motivated by the intriguing behaviors displayed by complexes involving the symmetrical azine ligands, namely PAA and IAA (shown in Figure 4.1), we embarked on an exploration of unsymmetrical azine ligands that feature both pyridyl- and imidazolyl- substituents. In a groundbreaking endeavor, we conducted a concerted reaction, resulting in the synthesis and characterization of the chiral structure of a Kryptoracemate Fe(II) complex featuring the (pyridyl)(2-methylimidazolyl)aldazine ligand (Figure 4.1c). This achievement marked the first instance of such a structure being characterized.⁸

With a growing interest in unsymmetrical ligands, we expanded our investigations to assess their bonding capabilities when interacting with Ni(II) ions. Our reports uncovered intriguing bonding patterns that led to the formation of metallo-supramolecules. However, it's noteworthy that none of these interactions resulted in the formation of helical structures or Kryptoracemate structures. Our research, therefore, contributes to understanding the diverse bonding behaviors exhibited by these unique ligands.⁸⁻¹⁰

Fueled by the findings and as part of our ongoing research efforts in the quest for metal complexes featuring unsymmetrical azine ligands with potential significance, we aim to investigate the influence of other heteroatoms, such as oxygen (O), sulfur (S), and others, as electron pair donors for coordination. And to establish their preferred modes when these groups of ligands coordinate with metal ions. This chapter, presents the synthesis, crystal structure, and a comprehensive spectroscopic analysis of nickel(II) and iron(II) complexes that incorporate the (pyridyl)(2-methyl oxazolyl) aldazine ligand.

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Figure 4.1. Symmetrical (a, and b) and unsymmetrical (c) azine ligands

MATERIALS AND METHODS

4.2.1 Chemicals and Physical Methods

All chemicals and solvents used for synthesizing the Fe and Ni complexes were of reagent grade and were used without further purification. First, 2-pyridine carboxaldehyde, 2-methyl-1,3-oxazole-4-carboxaldehyde, iron(II) chloride tetrahydrate, nickel(II) chloride hexahydrate, and ammonium hexafluorophosphate were purchased from FUJIFILM (Tokyo, Japan). All reactions were performed under aerobic conditions. Infrared spectra (KBr pellets; 4000–400 cm⁻¹) were recorded using a JASCO FT-001 Fourier transform infrared spectrometer (JASCO, Tokyo, Japan). Absorption spectra were recorded using a Shimadzu UV/Vis-1650 spectrophotometer (Kyoto, Japan) in the 200–900 nm range at room temperature in acetonitrile. ¹H NMR spectra were recorded on a Varian MNR system PS600 spectrometer (Los Angeles, CA, USA). The chemical shifts, δ , are given in parts per million relatives to TMS ($\delta = 0$) and refer internally to the residual proton chemical shift in the deuterated solvent. Elemental analyses were conducted at the Advanced Science Research Center of Okayama University.

4.2.2 Preparation of Metal Complexes 4.2.2.1 Synthesis of [Ni(L)₂]₂(PF₆)₂ (1)

A mixture of 2-pyridine carboxaldehyde (0.1947g, 1.8mmol) and 2-methyl-1,3oxazole-4midazole-4-carboxaldehyde (0.2004g, 1.8mmol) was dissolved in 20mL of methanol. To this solution, 0.0940g NiCl₂·6H₂O (0.90 mmol) in 10 mL of methanol, followed by the addition of 0.0992g hydrazine monohydrate (1.8 mmol) in 10 mL of methanol, and 0.2935g NH₄PF₆ (1.8mmol) in 20 mL of water. The resulting mixture was stirred at 60 °C for 3 h. Subsequently, the solution was concentrated using a rotary vacuum evaporator, forming a deep orange precipitate. The crude product was then dissolved and sequentially washed in methanol, and acetonitrile, and finally recrystallized by slow evaporation to deposit deep orange microcrystals. Crystals suitable for SC-XRD were obtained from a mixture of acetonitrile and methanol. Yield: 0.67g (95%). Anal. Found: C, 35.71; H, 3.00; N, 16.18%. Calcd for C₂₅H_{24.5}F₁₂NiN_{9.5}O₂P₂ (for [NiL₂](PF₆)₂·1.5MeCN (1·1.5CH₃CN)): C, 35.80; H, 2.94; N, 15.87%. IR (KBr pellet): vc=N (imine) 1641.6 and 1605.9 cm⁻¹ (fs) vP-F (PF₆⁻) 851.4(s).

4.2.2.2 Synthesis of [Fe(L)₂]₂(PF₆)₂ (2)

Complex **2** was synthesized following the same procedure as in complex 1, except using iron(II) chloride tetrahydrate instead of nickel(II) chloride hexahydrate. A dark blue precipitate was obtained. Yield: 0.67g (96%). Anal. Found: C, 33.45; H, 3.20; N, 15.04%. Calcd for C₂₄H₂₇F₁₂ FeN₉O₄P₂ (for 2·2H₂O·CH₃CN): C, 35.44; H, 3.62; N, 17.83. IR (KBr pellet cm⁻¹): vc=N (imine) 1641.6 and 1605.9 cm⁻¹ (fs) vP-F (PF₆⁻) 851.4 cm⁻¹ (vs).

¹H NMR (600MHz CH₃CN-*d*₃), δ, **2**: 10.06 (d, J= 17.6Hz, 2H), 8.79 - 8.63 (m, 2H), 8.42 (d, J = 17.1Hz, 2H), 8.17 (d, J= 25.5Hz, 2H), 8.04 - 7.76 (m, 2H), 7.37 (s, 2H), 6.14 - 5.81 (m, 2H) 2.33 (s, 6H).

4.2.3 Single crystal X-ray diffraction (SC-XRD) analysis.

The crystallographic data of **1** and **2** were collected on the Rigaku RAXIS RAPID II imaging plate area detector using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 190(2) K. The structures were solved by the direct method, utilizing the SIR2014 software package,¹¹, and refined on F² by full-matrix least-squares techniques using the SHELXL2014 program package.¹² All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the calculations with riding models. All analyses were performed using the Crystal Structure software package.¹³

Details of the crystal structures, data collection, and refinement are summarized in Table 4.1.

4.3 RESULTS AND DISCUSSION

In our previous research, we focused on the formation of the HL^R ligands in the presence of metal ions such as Fe(II) and Ni(II), favoring octahedral coordination. Our investigations revealed that these ligands consistently acted as tridentate ligands in all complex formations. Additionally, when adopting the tridentate coordination mode, they exhibited two possible coordination modes when coordinated meridionally with a metal ion, as illustrated in Figure 4.2. Coordination mode (i) involved the imidazole moiety in a six-membered chelate ring, while the pyridine moiety formed a five-membered ring. Conversely, mode (ii) showed the reverse arrangement. It's noteworthy that all our complexes consistently exhibited coordination mode (i) with the ligands. This intriguing coordination behavior, coupled with other considerations such as confirming the certainty of complexes formed and ensuring that hydrogen bonds did not influence the complexes with the desired unsymmetrical ligands, drove our motivation for this current study to explore these behaviors in more depth.

Initial efforts to exclusively synthesize these ligands as standalone entities proved to be quite challenging, resulting in complex mixtures that posed significant separation difficulties.⁹ Moreover, based on existing literature and theoretical predictions, our previous complexes were not expected to exceed a 25% yield due to the inherent propensity for mixtures to form in concerted reaction systems. Nonetheless, we achieved these complexes with an exceptional yield.^{8,9}

As a continuation of our work on unsymmetrical azine with heteroaromatic substituents, herein we report the synthesis and characterization of Fe(II) and Ni(II) complexes bearing the unsymmetric azine ligand: 2-methyl-4-pyridine-2-ylmethylene)hydrazineylidene)methyl)oxazole L, obtained in one-pot reaction systems. We observed the formation of new octahedral coordination complexes:

[FeL₂]²⁺ and [NiL₂]²⁺. The new compounds have been characterized based on spectroscopic data in both solid and liquid states via IR, UV, ¹H-NMR, SC-XRD, and CV measurements.



Figure 4.2. Two possible coordination modes, i and ii, by tridentate coordination of the HLR ligand family to a metal ion.

4.3.1 Synthesis and characterization of the of Fe(II) and Ni(II) complexes bearing Unsymmetric (2-Pyridyl)(4-(2-methyloxazolyl))azine

Complexes 1 and 2, were prepared following published procedures, or modifications of published procedures.^{8,9} The crude products were soluble in common polar organic solvents and recrystallized from a solution of acetonitrile and methanol. The purity of complex **1** was initially monitored by FT-IR measurements and confirmed later by elemental analysis. In the case of complex 2, its purity was initially monitored by both FT-IR and ¹H-NMR measurement which was later agreed on by elemental analysis. FT-IR spectra showed for both complexes a strong and medium peak at 1641.6 and 1605.9 cm⁻¹ respectively for C=N stretching, and a firm peak at 851.4 cm⁻¹ assignable to the counter anion, PF₆⁻.

The ¹H NMR spectrum of complex 2, reveals no impurities (Appendix 2). The spectrum is obvious, indicating the presence of only one molecule. In the spectrum, we observed eight distinct signals for the complex. The chemical shift at 10.06 ppm corresponds to the imino proton (-CH=N-N=C) closest to the oxazolyl group. Additionally, the signal at 8.71 ppm corresponds to the imino proton (-CH=N-N=C) near the pyridyl group.

Electronic spectra of complexes, **1** and **2** recorded in methanol at room temperature are shown in Appendix 1. The two complexes displayed two absorption bands in the region of 200–800 nm. Both complexes displayed an intense absorption band with λ_{max} (molar absorptivity, ε) at 326 nm (46370 for **1** and 36020 for **2**) assignable to ligand-centered (LC) π – π * and n– π * transitions. Complex 1 showed a shoulder peak with λ_{max} (molar absorptivity, ε) at 420 nm (5090). However, complex 2 showed a broad and intense absorption band in the visible region with λ_{max} (molar absorptivity, ε) at 629 nm (3060) which can be ascribed as the metal-to-ligand charge transfer (MLCT) band.^{14,15}

4.3.2 Crystal Data for Complexes

Crystals of the nickel complex, **1** suitable for SC-XRD were obtained by diffusion of methanol into a solution of the complex in acetonitrile. In contrast, those of iron complex, **2** were obtained by diffusion of diethyl ether into a solution of the complex in acetonitrile, and their structures were determined by X-ray crystallography. Both Compounds, **1**, and **2**·MeOH crystallized in the orthorhombic system, space group *P*ca2₁ with their respective Z values of 8 and 4 (Table 4.1). The molecular structure of compound **1** revealed two independent structures that are not linked up by any interaction as observed in our previous work^{8,9} in its ORTEP drawing as shown in Figure 4.3. The asymmetric unit consists of two [Ni(L)₂]²⁺ cations and four PF₆⁻anions. Selected bond lengths and angles for the molecules are listed in Table 4.2. Each Ni^{II} ion binds two L ligands and has a pseudo-octahedral coordination geometry. Each ligand in the *E*–*Z* configuration serves as a tridentate ligand and coordinates meridionally to the metal ion with the oxazole nitrogen, one pyridine, and one azine nitrogen atom, and the other azine nitrogen atom and the O atom of the oxazole ring remaining uncoordinated.

Compound	1	2
Formula	$\mathrm{C}_{22}\mathrm{H}_{20}\mathrm{F}_{12}\mathrm{N}_8\mathrm{NiO}_2\mathrm{P}_2$	C ₂₃ H ₂₄ F ₁₂ FeN ₈ O ₃ P ₂
Formula Weight	777.08	806.27
Crystal System	Orthorhombic	Orthorhombic
T/K	190(2)	190(2)
a/Å	18.3567(10)	37.690(4)
b/Å	9.2382(5)	9.1542(9)
c/Å	33.6008(14)	9.0645(9)
$V/Å^3$	5698.1(5)	3127.4(6)
Space Group	<i>P</i> ca2 ₁ (#29)	<i>P</i> ca2 ₁ (#29)
Ζ	8	4
D_c/gcm^{-3}	1.812	1.712
F000	3120.00	1624.00
µ/cm ⁻¹	9.119	6.980
Rint	0.0576	0.2123
<i>R</i> ₁ (I>2σ)	0.0456	0.0839
R (All reflns)	0.0639	0.1882
wR_2 (All reflns)	0.1205	0.2089
GOF	1.089	0.962
Flack parameter	0.449(5)	0.27(2)

Table 4.1. Crystallographic data and structure refinement for compounds 1 and 2.



Figure 4.3. An ORTEP drawing of the complex cation $[NiL_2](PF_6)_2$ in 1 with an atom numbering scheme (ellipsoids are drawn at a 25% probability level).

Table 4.2 summarizes the coordination bond lengths and angles of **1**, revealing a nearly ideal octahedral coordination geometry around the Ni center, with only minor

deviations. The Ni–N bond lengths are in the range of 2.074(5)–2.134(5) Å, which are typical for Ni^{II}–N(imine) coordination bonds.^{16,17} The N–Ni–N angles for the sixmembered chelate rings (87.9(2)–88.75(19)°) are approximately right angles and are significantly larger than those for the five-membered chelate rings (78.40(18)–79.5(2)°). As anticipated, the bite angles in the five-membered chelate rings are approximately 9° smaller than those in the six-membered chelate rings. However, the mutual trans bond angles of N2-Ni1-N6 and N10-Ni2-N14 for the azine-N donors measure 165.6(2) and 168.5(2), respectively, which deviate significantly from the ideal values. This substantial deviation from the ideal angles could potentially be attributed to steric hindrance, possibly induced by the methyl substituent on the oxazole ring.

	Bond Distances/ Å		
Ni1 – N1	2.082(5)	Ni1 - N2	2.096(5)
Ni1 – N4	2.090(4)	Ni1 - N5	2.134(5)
Ni1 – N6	2.091(5)	Ni1 - N8	2.084(5)
Ni2 – N9	2.085(5)	Ni2-N10	2.074(5)
Ni2-N12	2.088(5)	Ni2 – N13	2.115(5)
Ni2-N14	2.078(5)	Ni2-N16	2.080(5)
	Bond Angles/deg		
N1 - Ni1 - N2	78.7(2)	N1 - Ni1 - N4	166.6(2)
N1 - Ni1 - N5	91.29(19)	N1 - Ni1 - N6	93.10(18)
N1 - Ni1 - N8	89.3(2)	N2 - Ni1 - N4	87.9(2)
N2 - Ni1 - N5	89.87(19)	N4 - Ni1 - N5	88.60(19)
N2 - Ni1 - N8	103.8(2)	N4 - Ni1 - N8	94.0(2)
N4 - Ni1 - N6	100.04(18)	N5 - Ni1 - N8	166.18(19)
N5 - Ni1 - N6	78.40(18)	N2 - Ni1 - N6	165.6(2)
N6 - Ni1 - N8	87.79(19)		
N9-Ni2-N14	93.63(19)	N9 - Ni2 - N12	167.64(19)
N10 - Ni2 - N12	88.2(2)	N13 - Ni2 - N14	78.80(18)
N12 - Ni2 - N13	90.11(18)	N9 - Ni2 - N13	89.22(18)
N12-Ni2-N16	92.45(19)	N10 - Ni2 - N14	168.5(2)
N9-Ni2-N10	79.5(2)	N14 - Ni2 - N16	88.75(19)
N9-Ni2-N16	90.86(19)	N13 - Ni2 - N16	167.53(18)
N10-Ni2-N13	91.82(19)	N12 - Ni2 - N14	98.35(18)
N10-Ni2-N16	100.45(19)		

Table 4.2. Selected bond lengths (l/Å) and angles ($\phi/^\circ$) around the Ni^{II} center in compound 1

The packing structure of **1** is illustrated in Appendix 3. In the crystal structure, neither intra- nor intermolecular interactions were observed. The compound showed no bonding, as each molecule is independent of the other in their lattice.

The molecular structure of the Fe(II) complex in **2**, as depicted in Figure 4.4, closely resembles that of **1**. However, it's important to note that in **1**, there are two molecules present in its ORTEP drawing. Also, bond angles in **1** exhibit larger deviations than those observed in **2**. Additionally, in **2·MeOH** the asymmetric unit comprises a $[Fe(L)_2]^{2+}$ cation, two PF₆-anions, and a molecule of methanol. Selected bond lengths and angles for complex **2**, are detailed in Table 4.3. The Fe^{II} ion binds two L ligands, adopting a pseudo-octahedral coordination geometry. Each ligand, configured in the *E-Z* isomerism, acts as a tridentate ligand, coordinating meridionally to the metal ion through the oxazole nitrogen, one pyridine, and one azine nitrogen atom. The other azine nitrogen atom and the O atom of the oxazole ring remain uncoordinated. The Fe-N coordinate bond distances range from 1.923(12) Å to 2.015(9) Å (Table 3). Notably, the N-Fe-N angles for the six-membered chelate rings fall within the range of 91.7(4)° to 92.3(5)°, closely approximating right angles, and are significantly larger than those in the five-membered chelate rings, which range from 79.8(5)° to 80.3(4)°.



Figure 4.4. An ORTEP drawing of the complex cation $[FeL_2](PF_6)_2$ in 2^{MeOH} with an atom numbering scheme (ellipsoids are drawn at a 25% probability level).

The packing structure of 2·MeOH is illustrated in Appendix 4. Within the packing arrangement of this compound, no hydrogen bonds were observed. It's worth noting that the individual compounds do not interact within the molecules themselves or between neighboring methanol molecules.

	Bond Distances/ Å		
Fe1 – N1	1.962(10)	Fe1 - N2	1.983(11)
Fe1 - N4	2.015(9)	Fe1 - N5	1.981(9)
Fe1 - N6	1.923(12)	Fe1 - N8	1.956(10)
	Bond Angles/deg		
N1 - Fe1 - N2	80.3(4)	N1 - Fe1 - N4	172.0(4)
N1 - Fe1 - N5	90.8(4)	N1 - Fe1 - N6	90.3(5)
N1 - Fe1 - N8	89.7(4)	N2 - Fe1 - N4	91.7(4)
N2 - Fe1 - N5	91.3(5)	N4 - Fe1 - N5	90.0(4)
N2 - Fe1 - N8	96.6(4)	N4 - Fe1 - N8	90.7(4)
N4 - Fe1 - N6	97.7(5)	N5 - Fe1 - N8	172.1(5)
N5 - Fe1 - N6	79.8(5)	N2 - Fe1 - N6	167.0(5)
N6 - Fe1 - N8	92.3(5)		

Table 4.3. Selected bond lengths (l/Å) and angles ($\phi/^{\circ}$) around the Fe^{II} center in compound 2

Where the formation was attributed to the presence of hydrogen bonding interactions found or exhibited by the complexes in Chapter 2 and Chapter 3, our current compounds, 1 and 2·MeOH exhibit a distinct absence of hydrogen bonding interactions. Nonetheless, it's noteworthy that these compounds exclusively form complexes with the desired ligands. Through our findings, we have gained insights that suggest that the formation of the unsymmetrical azine-based ligands, was due to the steric preference and dominance of the successive five- and six-membered chelate rings of the E(py),Z(ox) conformations. As well as being the most thermodynamically stable option among various possibilities in the presence of metal ions. Based on the results derived from complexes 1 and 2, it is indeed commendable to affirm that these unsymmetrical azine-based ligands demonstrate remarkable thermodynamic stability in the presence of metal salts.

4.4 CONCLUSION

This chapter presents the successful synthesis of new Fe(II) and Ni(II) complexes with the unsymmetrical ligand, (2-Pyridyl)(4-oxazolyl) azine, achieving an exceptional yield. These complexes consist of two tridentate N, N', and N'' binding subunits, and the Fe(II) and Ni(II) ions exhibit a pseudo-octahedral geometry.

In our previous reports on analogous Fe(II) and Ni(II) complexes with (2-Pyridyl)(4imidazolyl) azines, the exclusive and selective formations of these complexes were attributed to the presence of hydrogen bonds within the complexes. Our current findings, along with those presented in Chapter 3, suggest that the selective formation of unsymmetrical azine ligands in both previous and current complexes cannot be solely attributed to characteristic hydrogen bonds. Rather, it appears to be influenced significantly by the steric preferences of the chelate five- and six-membered rings. The primary factor contributing to the selective formation of sterically preferred fivemembered chelate rings for the 2-pyridyl moiety and six-membered chelate rings for the 4-(2-methyloxazoyl) azine. While no specific thermodynamic experiments assessing stability were conducted, it is plausible that thermodynamic stability played a role in favoring the formation of unsymmetrical azine ligands among the various possible molecules in the presence of Fe(II) and Ni(II) metal ions.

Furthermore, our observations support the conclusion that these unsymmetrical azine groups of ligands effectively serve as tridentate chelate molecules, adopting an E, Z-configuration with mode (i) (as shown in Figure 4.2).

APPENDICES

Appendix 1: A UV-Vis electronic absorption spectrum of an acetonitrile solution of 1, and 2 measured at room temperature.



Appendix 2: ¹H NMR Spectrum of 2



Appendix 3: Packing diagram of 1 viewed along the crystallographic a-axis. Color code: Ni, violet; P, black; F, green; O, red; N, blue; C, gray.



Appendix 4. Packing diagram of 2·MeOH viewed along the crystallographic *b-axis*. Color code: Fe, yellow; P black; F, green; O, red; N, blue; C, gray.



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CHAPTER 5

5.1 SUMMARY, AND CONCLUSION,

This thesis is dedicated to the synthesis and structural characterization of iron(II) and nickel(II) complexes featuring unsymmetrical azine-based ligands, specifically, (pyridyl)(imidazolyl)azine and (pyridyl)(oxazolyl)azine. These compounds were exclusively obtained in high yields.

In Chapter One, we conducted a comprehensive review of the chemistry of diimine functionality (azine). The emphasis was placed on various synthetic methodologies, encompassing traditional techniques, modified approaches, and advanced methods for obtaining Schiff-based molecules, namely azines. These molecules exhibit three distinct configurations as free ligands: EE, EZ, and ZZ. Among these, the EE configuration is the most stable; however, when they coordinate with most metals, they assume the EZ configuration. Additionally, we delved into some applications and discussed the fascinating nature of these complexes.

Chapter Two outlines the synthesis of nickel(II) complexes of 2-((((1H-imidazol-4-yl)methylene)hydrazineylidene)methyl)pyridine, [Ni(HL^H)₂](PF₆)₂ and 2-((((2-methyl-1H-imidazol-4-yl)methylene)hydrazineylidene)methyl)pyridine, [Ni(HL^Me)₂](PF₆)₂. This chapter also provides insights into their respective molecular structures.

The metal complexes were prepared using a one-pot reaction, which deviates from the conventional approach, and resulted in exclusively high yields for all the compounds with the desired unsymmetrical ligands, HL^{H} and HL^{Me} , among other possibilities. [Ni(HL^H)₂](PF₆)₂ crystallized in orthorhombic noncentrosymmetric space group *P*2₁2₁2₁, while [Ni(HL^{Me})₂](PF₆)₂ crystallized in the monoclinic and centrosymmetric space group *P*2₁/n.

In conclusion, the findings presented in Chapter Two mirror the serendipitous synthesis observed in our well-known selective formation of the Kryptoracemate Iron(II) Complex with an Unsymmetric Azine Ligand in a concerted reaction, where the complex with the desired unsymmetric azine ligated the Ni(II) metal ions. The molecular structure of 2-((((1H-imidazol-4-yl)methylene)hydrazineylidene)methyl)pyridine of Fe(II) complex introduced in Chapter Three, as $[Fe(HL^{H})_{2}](PF_{6})_{2}$ revealed that $[Fe(HL^{H})_{2}](PF_{6})_{2}$ H₂O crystallized in orthorhombic space group *Pca*2₁ with *Z* = 4.

Chapter Three delves into the characterization of the pseudo-octahedral Fe(II) complex involving the tridentate ligand 2-((((1H-imidazol-4yl)methylene)hydrazinylidene)methyl)pyridine, referred to as HL^H. The complex's structure was elucidated through elemental analysis, FT-IR measurements, UV-Vis spectroscopy, and single-crystal X-ray diffraction (SC-XRD). It was further confirmed by ¹H-NMR analysis. The properties of our elucidated complex, [Fe(HL^H)₂](PF₆)₂H₂O (1H) were compared and contrasted with those of our previously characterized kryptoracemate complex, [Fe(HL^{Me})₂](PF₆)₂ **1.5**H₂O (**1Me**). In the case **1H**, molecules were linked by water molecules via hydrogen bonds, resulting in a zigzag 1D arrangement. Additionally, both complexes, 1H and 1Me, exhibited favorable properties, electrochemical as demonstrated through cyclic voltammetry measurements.

In conclusion, the results presented in this chapter offer much-needed clarity and definitively address the uncertainty surrounding whether the complexes synthesized and described in Chapter Two are indeed the exclusive complexes bearing the desired unsymmetrical azine-based ligands, HL^R. This clarification holds particular significance, especially in light of the challenges posed by the paramagnetic nature of the Ni(II) complexes in Chapter Two, which hindered further characterization via ¹H-NMR.

Chapter Four provides an in-depth exploration of the coordination mode of a novel unsymmetrical azine-based ligand, viz 2-methyl-4-(((-pyridin-2-ylmethylene)hydrazinylidene)methyl)oxazole (L), of Ni(II) and Fe(II) complexes. The synthesis of these complexes, [Ni(L)₂](PF₆)₂ and [Fe(L)₂](PF₆)₂ is detailed. The molecular structures of both complexes unveil the tridentate nature of the ligand (L),

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as it coordinates the various metal ions in mode (i), as illustrated in scheme 2 of Chapter Two and Figure 2 of Chapter Four. These complexes crystallized within an orthorhombic system with the space group *P*ca21. In the ORTEP structure of the Ni(II) complex, two molecules were observed, while the Fe(II) complex displayed only one. Importantly, neither of these complexes exhibited inter- or intramolecular bonding in their packing structures. This observation significantly reinforces our assertion that the unsymmetrical azine ligands, HL^R and L, are indeed the most thermodynamically stable ligands among the various possibilities.

5.2 RECOMMENDATIONS

A synthetic methodology needs to be developed for the successful preparation and characterization of unsymmetrical azine molecules containing both heterocyclic and heteroaromatic moieties.

Complexes of the ligands with metals such as Co, Mn, and Cu, should be prepared and characterized.

A comprehensive investigation into the electrochemical properties of both the ligands and their corresponding complexes is essential. This analysis should focus on their unique two-electron redox tunability, a characteristic that is uncommon in most firstrow transition metal complexes.

The chemistry of azine molecules, particularly those with heteronuclear moieties, holds significant potential as a source for future supra-molecules, metallo-enzyme chemistry, material science, drug prototypes, and more. Research efforts to explore their biodiversity potential should be continued.