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WATER CLUSTER MOTIFS IN STRUCTURALLY SIMILAR *N*-(2-AMINOETHYL)-
1-METHYLIMIDAZOLE-2-CARBOXAMIDE METAL COMPLEXES: SYNTHESIS,
CHARACTERIZATION, THERMAL AND ELECTRICAL PROPERTIES

By

Nina Saraei

B.S. Islamic Azad University 2008

M.S. University of Tabriz 2012

M.S. University of Louisville 2017

A Dissertation Submitted to the
Faculty of the College of Arts and Sciences
of the University of Louisville in Fulfillment
of the Requirements for the Degree of

Doctor of Philosophy in Chemistry

Department of Chemistry
University of Louisville
Louisville, KY

August 2020

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A Dissertation Approved on

August 5, 2020

By the following Dissertation Committee:

Advisor: Dr. Craig A. Grapperhaus

Dr. Robert M. Buchanan

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To my Dad, Mom and Brother

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ABSTRACT

WATER CLUSTER MOTIFS IN STRUCTURALLY SIMILAR *N*-(2-AMINOETHYL)-1-METHYLMIDAZOLE-2-CARBOXAMIDE METAL COMPLEXES: SYNTHESIS, CHARACTERIZATION, THERMAL AND ELECTRICAL PROPERTIES

Nina Saraei

August 5, 2020

Water is a remarkable molecule and in all of its forms exhibits an amazing collection of properties and functions. Besides its crucial role in life and many technological processes, water displays some unusual and anomalous properties at various interfaces and under different conditions. Although the role of hydrogen-bonding interactions and their fluctuations are well known to determine the properties of water, the main obstacle exists in the complexity of correctly describing the interactions between water molecules. The key to understanding the behavior of water is to collect precise structural data of various H-bonded water networks in diverse environments. In this dissertation, the formation of various water cluster motifs is investigated in a series of structurally similar complexes. Their thermal and electrical properties are studied using characterization techniques including, X-ray crystallography, UV-visible spectroscopy, IR, thermal analyses, electrochemical impedance spectroscopy (EIS) and two-probe resistance measurement studies. Chapter III focuses on a group of structurally related Ni(II) complexes containing N₃X (X = S or O) donors. The complexes crystallize with water of hydration forming extended H-bonding networks. The morphology of the network is dependent on small changes in the ligand framework leading to different orientations of the carboxamido oxygens, which influences the solid state packing, H-bonding patterns and accordingly thermal and electrical properties. Chapter IV builds on chapter III through

modification of the steric bulk around the carboxamido-O which result in isostructural complexes confining 1D coiled water wires in their crystal lattice and show quite similar packing pattern and thermal properties. Chapter V continues to study on electrical properties of one of synthesized complexes in Chapter IV. It explains the reversible surface conductivity changes upon variation of water vapor pressure for a single crystal.

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CHAPTER I

INTRODUCTION

1.1. Lay Summary

Water is the most crucial molecule in life and numerous technological processes. This molecule in all of its form displays a collection of amazing, unusual and anomalous properties based on the environmental conditions as well as characteristics of different involved media such as various surfaces or confined structures. Accordingly, one of the key factors to understand the behavior of water is to investigate structural features of this molecule and its interactions with other water molecules in different hydrogen-bonded (H-bonded) water networks. Therefore, X-ray crystallography is considered as a main tool to analyze H-bonding interactions between water molecules in expanded water networks confined within simple molecules or supramolecular assemblies. The obtained precise structural data reveals that the morphology of H-bonded water clusters can be engineered to favorite and predictable form through small changes in framework of host molecules. Different motifs of hydrogen bonding networks are associated with different solid state packing that influences directly on thermal and electrical properties of the compounds. In fact, design and modification of framework of host molecules results in formation of

materials with tunable properties, such as conductivity or thermal stability, as a requirement for designing devices such as moisture sensors/ switches.

1.2. Scope of Dissertation

This dissertation describes a series of studies on a group of Ni(II) compounds based on a *N*-(2-aminoethyl)-1-methylimidazole-2-carboxamide (HL¹) motif including Ni(L¹)₂, NiL², NiL³, NiL⁴, and NiL⁵ core as well NiL⁶ and its isostructural CuL⁶ complex. These studies include: 1) synthesis and structural characterizations; 2) thermal analyses 3) conductivity and electrical properties evaluation. A comprehensive list of the ligands and metals complexes synthesized and evaluated in this dissertation can be found in Figure 1.1.

Figure 1.1. Numbering scheme for all synthesized ligands and complexes.

The new ligands and metal complexes developed for the studies described in this dissertation were characterized by single crystal X-ray diffraction and infrared (IR), nuclear magnetic resonance (NMR) and ultraviolet-visible (UV-Vis) spectroscopies. Additionally, thermal analyses using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed. The conductivity of all complexes were evaluated using electrochemical impedance spectroscopy (EIS) in order to determine electrical properties of each complex. In some cases, changes in resistance at different environmental conditions were monitored using two-probe resistance measurement.

Chapter 1 provides an overview of the dissertation and introduces seven structurally similar complexes based on a *N*-(2-aminoethyl)-1-methylimidazole-2-carboxamide core that confine different motifs of water clusters in their crystal lattice. Chapter 2 specifies the experimental conditions, such as synthetic methodologies, yields, and characterization techniques for the complexes in this dissertation. This chapter also describes thermal analyses and conductivity measurement techniques used for these complexes. Chapter 3 describes the formation of various water clusters through different motifs of hydrogen bonding network. The X-ray crystallography proves that small changes in ligand framework can result in completely different packing styles and each one allows specific expansion pattern of hydrogen bonding. Accordingly, each H-bonding motif leads to formation of a specific water cluster in terms of dimensionality, continuity, and the strength of involved H-bonds. Crucially, thermal stability, dehydration temperature and conductivity measurement of each complex demonstrated the direct correlation with the characteristics of each hydrogen bonding pattern. Chapter 4 focuses on the syntheses of two isostructural complexes of Cu(II) and Ni(II) and comparison of their crystal structure,

packing style, water cluster motif, thermal stability and electrical properties. These studies revealed identical water cluster motifs for both complexes and accordingly quite similar thermal stability and dehydration temperature. Further, EIS studies on NiL^6 complex revealed that under dry conditions this complex behaves as ideal capacitor with no conductivity, while under wet conditions it acts as a capacitor with charge transfer along the surface. In Chapter 5, the resistance change in NiL^6 was monitored using two-probe resistance measurement set up and it revealed that upon surface adsorption/desorption of water the conductivity changes by three order of magnitude. It was observed that these significant changes in conductivity is reversible and the rate of the change is influenced by temperature and water vapor pressure. At higher temperatures the rate is slower and maximum conductivity requires longer time to achieve, while at higher vapor pressures the system reaches saturation (maximum conductivity) much faster. These results are consistent with EIS studies that show NiL^6 acts as an ideal capacitor under dry conditions, while in wet conditions two electrochemical processes are observed involving charge transfer along the surface of crystal through formation of a subsidiary water chain on the surface. Lastly, Chapter 6 contains concluding thoughts and future directions for the research in Chapters 3 – 5.

1.3. Significance of Water Structure

Water is a remarkable molecule with an amazing collection of properties and functions.¹ Besides its crucial role in biological and many technological processes,² water displays some unusual and anomalous properties at interfaces and under different conditions. Many chemists and biologists have been studied water in an attempt to achieve a comprehensive understanding of its properties in confined locations.^{3,4} For instance,

water can be found as thin films in contact with surfaces⁵ or embedded in confined environments, such as zeolites and minerals.⁶ Accordingly, proper understanding of the behavior of such interfacial and confined water molecules has scientific as well as technical importance. One specific example is effect on electrical conduction and the charge transfer mechanism with potential applications in electrochemistry, capillary microelectrodes and microfluidic devices.^{7,8}

H-bonding interactions and their fluctuations are well-known to effect the properties of water. A detailed introduction to H-bonding is provided in Section 3.1.2. However, the complexity of H-bonding presents a major obstacle to its thorough understanding and the role of interactions between water molecules.⁹⁻¹² In order to understand the behavior of water, precise structural data of various H-bonded water networks in diverse environments is needed.¹³⁻²³ Numerous studies that characterize discrete water clusters in various crystal hosts at room temperature have significantly advanced our understanding of these clusters and how they link together to form larger network of water molecules.¹³⁻²⁴ These results are also helpful in better understanding of the structure and behavior of water molecules in biological systems. In fact, organic compounds with functional moieties that are present in biological molecules can stabilize various water topologies in environments resembling those present in living systems.²⁵

1.4. Water Clusters

Water in confined geometries has obvious relevance in biology, geology, and other areas where the material properties are strongly dependent on the quantity and structure of confined water. Many biological processes are dependent on the properties of confined water. The size of confinement varies from 1 to 100 nm with a substantial fraction of these

water molecules located in the vicinity (within approximately 5 Å) of different kinds of biomolecules.²⁶ Since the presence of such water is necessary for life,²⁷ it is obvious that it is important to understand the structural and dynamical properties of water under these confined conditions.

The properties of confined water are also of central importance for many geological applications. Several studies used confined water to evaluate water properties at a temperature region of 150-230 K at ambient pressure^{28,29} to avoid immediate crystallization, either during cooling down from high temperatures or heating up from lower temperatures. It has been demonstrated that the confined water can avoid crystallization at any temperature if the geometrical restrictions are severe enough to prevent formation of a tetrahedral ice structure. For example through confining water in various porous materials, mixing water with a salt or hydrating surfaces or large biomolecules, the arrangement of water molecules in tetrahedral ice structure can be avoided. However, since many factors involve in this process such as the nature of interactions between water and surface, geometry of cavities confining water molecules or dispersion of water molecules in a solution, therefore determination of exact requirements to avoid formation of ice structure is difficult to provide.³⁰

Generally, in order to study the behavior of water at lower temperature, water molecules are confined within porous materials³¹⁻³⁴ that are classified based on their topology (in terms of order/ disorder), the pore diameter d (micro, $d < 20$ Å; meso, 20 Å $< d < 500$ Å; macro, $d > 500$ Å) as well as the degree of hydrophilicity or hydrophobicity. For example, there are numerous reports on confinement of water in disordered porous materials with hydroxyl groups on the surface (hydrophilic) such as molecular sieves,³⁵

mineral clays,³⁶ graphite oxide,³⁷ and cement-like materials^{38,39} in which due to the formation of water-surface interactions, filling of the pores are incomplete. However, in more ordered systems such as SBA-15⁴⁰ and MCM-41⁴¹⁻⁴⁴ there are less water-surface interactions and accordingly water dynamics seems to be more uniform.

Furthermore, X-ray crystallographic studies have demonstrated that supramolecular assemblies can be developed through networks of hydrogen-bonding interactions either between water molecules or between water molecules and organic structures.⁴⁵ In general, functional groups such as carboxylic acids, urea, amines and amides are the most common moieties that are involved in more complex H-bonding networks available in higher order assembled structures. In fact, investigation of numerous supramolecular assemblies has demonstrated that hydrogen bonds and other non-covalent interactions are the main driving forces in self-assembly process. In other words, hydrogen bonds due to their directionality and reversibility can be broadly engineered and result in formation of significantly diverse range of supramolecular assemblies such as hydrogen-bonded water clusters in the form of hexamers,^{46,47} octamers,^{17,48} decamers,^{18,49} and one-dimensional (1D) infinite water chains^{23-24,50-51} in diverse environments of various crystal hosts. Consequently, recently considerable number of studies have been devoted to study the topology of supramolecular structures in order to perform a reasonable design for functional materials. Accordingly an efficient design mainly relies on the concepts of coordination bond, hydrogen bonding, electrostatic and charge-transfer attractions and aromatic π stacking interactions.⁵²

One of the consequences in engineering supramolecular structures is the formation of various water clusters which leads to more comprehensive studies on the role and

behavior of water in confined environments. Although water seems to be a simple molecule, in fact this molecule has one of the most complex physical and chemical properties in liquid and solid phase and despite significant progress on understanding the complex behavior of water in different environments such as surface, confined media ,etc. yet some associated concepts such as mechanism of proton transfer are not completely clear.^{53,54} Investigation of water clusters of various sizes can lead to precise structural information on hydrogen-bonding motifs in diverse chemical environments. Furthermore, the combination of effective computational techniques with new laser spectroscopy experiments has generated substantial information regarding the intricate details of proton transfer mechanism in water clusters in terms of both structural and dynamic aspects.⁵⁵⁻⁵⁷ However, the dynamics resulting from the excess internal energy of the significantly expanded protonated water clusters $H(H_2O)^{n+}$ ($n > 20$) in the gas phase blurs the structural distinction and its spectroscopic manifestations.⁵⁸

Since the lattice of a crystal host could provide the environment to stabilize various topologies of neutral and ionic water clusters, recent studies have been focused on structural characterization and morphological characteristics of water clusters confined within various chemical entities.⁵⁹⁻⁶⁴ These topics continuously generate considerable interest on these topics from both theoretical and experimental point of views such as the crystallographic characterization of a neutral polyhedral $(H_2O)_{21}$ cluster has been recently reported by Ye et al.⁶⁵

1.5. 1D Water Clusters

At this juncture, 1D water chains are attracting a great deal of attention thanks to their vital role in the biological transport of water, protons, and ions.⁶⁶⁻⁶⁹ Earlier studies

show that transport of water or protons across the cell involves the assembly of highly mobile hydrogen-bonded water molecules into a single chain at the positively charged constricted pore of the membrane-channel protein, aquaporin-1.⁷⁰ Previous reports also indicate that water forms a 1D chain confined within a narrow hydrophobic carbon nanotube (CNT).⁷¹ The rate of proton transfer (PT) in these narrow structures is much higher than that of bulk water, often by more than 1 order of magnitude.⁷²⁻⁷³ The hydrophobic wall of a CNT provides an environment in which one-dimensional hydrogen bond (HB) networks replace the three-dimensional networks ordinarily present in bulk water. This difference in bonding may significantly affect excess proton hydration and transport. The rate of PT has been proved as a function of radius of the hydrophobic nanotubes. In fact, the rate of proton transport could be dramatically enhanced upon constricting a hydrophobic channel to dimensions where only a single-file water wire could be sterically accommodated.⁷² To understand the mechanism of PT, different theoretical methodologies through molecular dynamics simulation are performed to monitor the changes in electron density of water along the wire/chain. For instance, the rate of PT in bulk solution is influenced by the Grotthuss mechanism,⁷⁴ in which interconversion arises between Eigen and Zundel hydration structures⁷⁵⁻⁷⁷ while using multistate empirical valence bond (MS-EVB) methodology shows that within 1D water chains confined to a CNT, a proton is mainly hydrated in distorted Zundel (H_5O_2^+) form, unlike the distorted Eigen (H_9O_4^+) form seen in bulk water.^{75,78-79} Therefore, MS-EVB is one of the methodologies describing both hydration structures and the corresponding charge defect delocalization associated with the excess proton in the hydrogen-bond network.⁸⁰

CHAPTER II

EXPERIMENTAL DETAILS

2.1. Materials

All chemicals were purchased from commercial sources (Aldrich Chemical Company, VWR Scientific, TCI, Acros Organics and Alfa Aesar) and used as received unless otherwise noted. Isobutylene sulfide was prepared according to literature methods and stored under N₂ at -20 °C.^{81,82} Ethyl 1-methyl-1*H*-imidazole-2-carboxylate, H₂L², H₂L⁶ and NiL² were also prepared using the established literature procedures.⁸³⁻⁸⁵ Reagent grade solvents were purified with an MBraun solvent purification system or were dried using standard techniques and freshly distilled prior to use. In cases where anaerobic conditions were necessary, standard Schlenk line techniques along with the appropriate degassing of solvents by freeze-pump-thaw method and a N₂-filled glovebox were employed. A Pyrex chromatography column (1 inch i.d.) with a medium porosity frit was loaded with either aluminum oxide (activated, neutral Brockmann I standard grade, 150 mesh, 58Å) or silica gel (grade 62, 60-200 mesh, 150Å) for use in column chromatographic separations. Deuterated solvents were obtained from Cambridge Isotope Laboratories.

2.2 Physical Methods and Instrumentation

Elemental analyses for C, H, and N were performed by Midwest Microlab (Indianapolis, Indiana) on pre-dried samples. Electronic absorption spectra were recorded with an Agilent 8453 diode array spectrometer using 1 cm path length quartz cuvette. FT-IR spectra were recorded on a Thermo Nicolet Avatar 360 spectrometer with ATR attachment (4 cm^{-1} resolution). NMR spectra were obtained on a Varian Inova spectrometer (400-MHz) and referenced to the solvent peak. Matrix assisted laser desorption/ionization (MALDI) spectra were recorded using a Voyager Biospectrometry DE Workstation (Applied Biosystems, Foster City, CA, USA) and processed by Data Explorer SoftwareTM (Version 4.8) at University of Louisville. The matrix for MALDI experiment was prepared by dissolving 0.18 M *p*-nitroaniline (PNA) in 1:1 MeOH:CHCl₃ solution. The samples were dissolved in methanol and 0.75 ml aliquot of the solution was used for the dried-droplet method.⁸⁶

A Metrohm Autolab PGSTAT302N potentiostat/galvanostat, operating in potentiostat mode was used to collect the electrochemical impedance spectroscopy (EIS) measurements. A DC bias of -0.1 , 0 , or 0.1 V was applied throughout EIS measurements with an amplitude of $10\text{ mV}_{\text{RMS}}$ over the frequency range 100 kHz to 10 Hz . Two-probe resistance measurement studies were performed using In-House setup. TGA and DSC of the complexes were performed at Conn Center for Renewable Energy Research, using an SDT Q600 TA analyzer. A sample pan was loaded with $15\text{--}20\text{ mg}$ of metal complexes for each run. Data points were collected at a ramp rate of $2\text{ }^{\circ}\text{C min}^{-1}$ under a flowing (100 ml min^{-1}) N₂ stream.

X-ray crystal structures were determined by Dr. Mark Mashuta at the X-ray diffraction laboratory in the University of Louisville, Department of Chemistry. X-ray crystallographic data were obtained on either an Enraf-Nonius CAD4 diffractometer (equipped with a Mo tube and a scintillation detector) or on a Bruker SMART APEX CCD diffractometer. CCDC 1855263–66 and CCDC 1893397-98 contains the supplementary crystallographic data for this dissertation. Data can be obtained from The Cambridge Crystallographic Data Center at <https://www.ccdc.cam.ac.uk/structures> free of charge.

2.3. Chemical Syntheses

***N*-(2-Aminoethyl)-1-methyl-1*H*-imidazole-2-carboxamide (HL¹):**

Ethylenediamine (2.0 ml, 30. mmol) was added to a toluene solution of ethyl 1-methylimidazole-2-carboxylate (2.52 g, 16.4 mmol). The reaction mixture was refluxed with a Dean-Stark apparatus for 12 - 36 hours, whereupon ethanol was removed from the reaction mixture. Volatile components of the solution were removed on a rotary evaporator giving a yellow oil (2.33 g, 84.5% yield). Product formation was confirmed by NMR and infrared spectroscopy. ¹HNMR (DMSO): δ 2.05 (br, 2H), 2.63 (t, 2H), 3.28 (t, 2H), 3.98 (s, 3H), 6.82 (d, 1H), 6.88 (d, 1H), 8.14 (s, 1H). FT-IR (ATR), cm⁻¹: 1475 (m), 1505 (m), 1545 (s), 1663 (s).

***N'*-(Mercaptoethyl)-*N*-(2-aminoethyl)-1-methyl-1*H*-imidazole-2-carboxamide**

(H₂L³): This ligand was prepared in a manner analogous to that of H₂L². Ethylene sulfide (3.5 ml, 59 mmol) was added *via* syringe to a degassed benzene solution of HL¹ (1.0 g, 6.0 mmol). The reaction vessel was thoroughly purged with N₂ and then refluxed for 18 hours. Removal of the solvent and excess ethylene sulfide *in vacuo* gave a pale yellow residue

(1.16 g, 84.7% yield) of suitable purity. ^1H NMR (C_6D_6): δ 1.35 (br, 1H), 2.3–2.7 (m, 6H), 3.2–3.5 (m, 3H), 3.68 (s, 3H), 6.32 (d, 1H), 6.92 (d, 1H), 8.08 (s, 1H).

N-(2-((2-mercaptoethyl)amino)ethyl)-1-methyl-1*H*-imidazole-2-carboxamido

nickel(II) (NiL^3): A degassed green benzene solution (30 ml) of $\text{Ni}(\text{acac})_2$ (0.918 g, 3.57 mmol) was slowly added *via* cannula to a pale yellow solution of H_2L^3 (1.16 g, 5.08 mmol) of equal volume over a 1 – 2 hour period. During the course of addition, the color of the solution changed to a deep red, followed by precipitation of a red solid upon overnight stirring. The reaction mixture was filtered and the crude product was loaded onto an alumina column as an acetonitrile solution. The pure product was isolated as a red band after elution with 3:1 acetonitrile/methanol. X-ray quality single crystals (0.52 g, 52%) were grown upon evaporation of a methanol solution. Anal. calcd. for $\text{C}_9\text{H}_{14}\text{N}_4\text{OSNi}\cdot\text{H}_2\text{O}$: C, 35.67; H, 5.32; N, 18.49. Found: C, 35.74; H, 4.98; N, 18.45. +MALDI, m/z calcd for $\{[\text{NiL}^3]-\text{H}^+\}$ 285.023; found 285.188. ^1H NMR (CD_3OD): δ 1.18 (s, 1H), 2.16–3.45 (m, 8H), 3.78 (s, 3H), 6.29 (d, 1H), 6.92 (d, 1H). FT-IR (ATR), cm^{-1} : 1443 (m), 1636 (s). Electronic absorption (CH_3CN (22 °C)): λ_{max} (nm) (ϵ ($\text{cm}^{-1}\text{M}^{-1}$)) 368 (1075), 449 (135), 575 (45).

Bis-(N-(2-aminoethyl)-1-methyl-1*H*-imidazole-2-carboxamido) nickel(II) ($\text{Ni}(\text{L}^1)_2$): A

dry dry green toluene (20 ml) solution of $\text{Ni}(\text{acac})_2$ (0.85 g, 3.3 mmol) was added slowly *via* cannula to a toluene solution (18 ml) of HL^1 (0.65 g, 3.9 mmol). Upon complexation, a pale blue precipitate began to form, which appeared to become greener in color as more nickel was added. The light blue solid that precipitated upon overnight stirring was separated from the yellow supernatant by anaerobic filtration. Upon anaerobic washing with two 50 mL portions of dry toluene, the acetylacetone by-product was removed,

yielding the faint blue product. Upon drying under vacuum, the crude product was attained (0.70 g, 92% yield). Recrystallization from evaporation of an acetonitrile solution gave blue crystals. +MALDI, m/z calcd. for $\{[\text{Ni}(\text{L}^1)_2] - \text{H}^+\}$ 393.121; found 393.286. FT-IR (ATR), cm^{-1} : 1478 (m), 1597 (s), 3235–3275 (m). Electronic absorption (CH_2Cl_2 (22 ° C)): λ_{max} (nm) (ϵ ($\text{cm}^{-1} \text{ M}^{-1}$)) 319 (1110), 488 (75), 980 (85).

1-methyl-*N*-(2-((4-oxopent-2-ylidene)amino)ethyl)-1*H*-imidazole-2-carboxamido

nickel(II) (NiL^4): The ligand HL^4 was prepared via a metal-templated route. A 1:1 mixture of acetone/water (10 ml) was added to a crude $\text{Ni}(\text{L}^1)_2$ (0.15 g, 0.38 mmol). The reaction mixture was exposed to atmosphere for 24 hours, resulting in the formation of an orange solution. Evaporative crystallization of the acetone/water solution gave X-ray quality orange single crystals. Isolation of pure NiL^4 was achieved by washing the crystalline product with water and diethyl ether, respectively (0.053 g, 43% yield). Anal. calcd. for $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_2\text{Ni}$: C, 46.95; H, 5.25; N, 18.25. Found: C, 46.71; H, 5.17; N, 18.03. +MALDI, m/z calcd. for $\{[\text{NiL}^4] - \text{H}^+\}$ 307.062; found 307.253. ^1H NMR ($\text{C}_3\text{D}_6\text{O}$): δ 1.77 (s, 3H), 1.90 (s, 3H), 2.84 (t, 2H), 3.41 (t, 2H), 3.92 (s, 3H), 4.98 (s, 1H), 6.61 (d, 1H), 7.05 (d, 1H). FT-IR (ATR), cm^{-1} : 1500 (s), 1510 (s), 1590 (m), 1610 (s), 2850 (w), 2930 (w), 3120 (w). Electronic absorption (CH_3CN (22 °C)): λ_{max} (nm) (ϵ ($\text{cm}^{-1} \text{ M}^{-1}$)) 216 (754), 324 (580), 426 (168), 508 (108).

1-methyl-(methyl-(3-(2-ethylimino)butanoate)-1*H*-imidazole-2-carboxamido

nickel(II) (NiL^5): Complex $\text{Ni}(\text{L}^1)_2$ (0.40 g, 1.02 mmol) was dissolved in 25 mL of DI water and methyl acetoacetate (0.110 mL, 1.02 mmol) was then added. The solution was allowed to stir for 24 hours resulting in an orange solution. The solvent was removed *via* rotary evaporation yielding an orange solid (0.24 g, 73% yield). Orange plate crystals

suitable for X-ray analysis were obtained by slow evaporation of acetonitrile solution. Anal. calcd. for $C_{12}H_{16}N_4O_3Ni \cdot 3H_2O$: C, 38.23; H, 5.88; N, 14.86. Found: C, 38.49; H, 5.72; N, 15.34. +MALDI, m/z calcd. for $[NiL^5]^+$ 322.657; Found 322.978. 1H NMR ($CDCl_3$): δ 1.78 (s, 3H), 1.82 (s, 3H), 2.92 (t, 2H), 3.45 (t, 3H), 3.88 (s, 3H), 4.86 (s, 1H), 6.62 (d, 1H), 6.64 (d, 1H). FT-IR (ATR), cm^{-1} : 1050 (m), 1500 (s), 1585 (m), 1625 (s), 2835 (w), 2916 (w), 3085 (w). Electronic absorption (CH_3CN (22 °C)): λ_{max} (nm) (ϵ ($cm^{-1} M^{-1}$)) 209 (620), 250 (565), 305 (530), 380 (85), 475 (32).

N,N'-(ethane-1,2-diyl)bis(1-methyl-1H-imidazole-2-carboxamidato) nickel(II)

(NiL⁶): An aqueous solution (50 mL) of H_2L^6 (0.15 g, 0.543 mmol) was added dropwise to an aqueous solution (50 mL) of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ (0.135 g, 0.543 mmol) and sodium acetate (0.045 g, 0.543 mmol) while continuously stirring. The reaction was allowed to stir overnight and resulted in deep yellow solution. The solvent was removed on a rotary evaporator yielding an orange solid. The product was purified on an alumina column as an acetonitrile solution. The pure product was isolated as an orange band after elution with acetonitrile/methanol (3:1). X-ray quality single crystals were grown by vapor diffusion of acetonitrile solution into an aqueous solution of NiL^6 . Anal. Calcd. for $C_{12}H_{14}N_6O_2Ni \cdot 1.5H_2O$: C, 40.04; H, 4.76; N, 23.34. Found: C, 40.43; H, 4.74; N, 23.07. +MALDI, m/z calcd. for $\{[NiL^6]-H\}^+$ 333.06; Found 332.99. 1H NMR ($CDCl_3$): δ 3.35 (t, 4H), 4.00 (s, 6H), 6.60 (d, 2H), 6.80 (d, 2H). FT-IR (ATR), cm^{-1} : 1450 (s), 1600 (s), 3360 (s). Electronic absorption (CH_3CN (22 °C)): λ_{max} (nm) (ϵ ($cm^{-1} M^{-1}$)) 206 (2026), 256 (3227), 336 (2 3 3), 468 (12).

N,N'-(ethane-1,2-diyl)bis(1-methyl-1H-imidazole-2-carboxamidato) copper(II)

(CuL⁶): An aqueous solution (50 mL) of $Cu(C_2H_3O_2)_2 \cdot H_2O$ (0.35 g, 1.8 mmol) was added

dropwise to a stirring aqueous solution (50 mL) of H_2L^6 (0.49 g, 1.8 mmol) and sodium acetate (0.145 g, 1.77 mmol). The resulting purple solution was stirred overnight. The solvent was removed on a rotary evaporator yielding a red-purple solid which was purified on an alumina column. The pure product was eluted as a red band with acetonitrile/methanol (3:1). X-ray quality single crystals were grown by vapor diffusion of acetonitrile solution into an aqueous solution of CuL^6 . Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{N}_6\text{O}_2\text{Cu}$: C, 42.66; H, 4.18; N, 24.88. Found: C, 42.64; H, 4.23; N, 24.41. +MALDI, m/z calcd. for $\{[\text{CuL}^6]\text{-H}\}^+$ 338.05; Found 338.05. FT-IR (ATR), cm^{-1} : 1450 (s), 1604 (s), 3350 (s). Electronic absorption (CH_3CN (22 °C)): λ_{max} (nm) (ϵ ($\text{cm}^{-1} \text{M}^{-1}$)) 204 (2804), 258 (4728), 503 (33).

2.4. Two-Probe Resistance Measurement

2.4.1 General Procedure

Surface resistance and surface resistivity are related, but distinct concepts, that are sometimes confused. Definitions of these terms can be found in the literature for two electrodes of specified configuration that are in contact with the same side of a material under the test, Figure 2.1.⁸⁷⁻⁹⁰ Surface resistance (R_s), equation 1, is the ratio of a DC voltage (V) to the current (I_s) flowing

$$R_s = V / I_s \quad (1)$$

Surface resistivity (ρ_s), equation 2, is determined by the ratio of DC voltage drop per unit length (V/L) to the surface current per unit width (I_s/D).

$$\rho_s = (V/L) / (I_s/D) \quad (2)$$

Figure 2.1. Basic setup for surface resistance and surface resistivity measurement.⁹¹

Surface resistivity is a property of the material. Theoretically, it should remain constant regardless of the method and configuration of the electrodes used for the surface resistivity measurement. In contrast, surface resistance depends on the material and the geometry of the electrodes used in the measurement. The physical unit of surface resistivity is ohm (Ω). While, the legitimate unit of the surface resistance is also the ohm, it is often expressed in ohm/square ($\Omega \text{ Sq}^{-1}$) to avoid confusion with surface resistivity.⁹¹

In this study, two-probe surface resistance measurements were performed on single crystals of NiL^6 in a glass reactor under hydrated (17 torr vapor pressure) and dehydrated conditions. An overview of the mounting procedure, experimental setup, and data collection method is provided in Figure 2.2 with a detailed written description of the process described below.

Figure 2.2. Experimental setup for two-probe resistance measurement and electrochemical impedance spectroscopy studies; (A) Single crystal of NiL⁶, (B) Crystal mounted on measurement chip (chip carrier), (C) Multimeter to verify connectivity, (D) Glass reactor enclosing sample, (E) Vacuum pump, (F) Water vessel, (G) Whole setup.

In a typical experiment, data were collected every six seconds with significant changes in resistance upon the process of adsorption/desorption of moisture. This process was repeated numerous times on different size crystals of NiL⁶ complex and the results are very reproducible. Similar experiments were also performed at different temperatures and various vapor pressures to investigate the adsorption/desorption process kinetically.

First, orange plate-shaped crystals of NiL^6 was grown by vapor diffusion of acetonitrile solution into an aqueous solution of the complex. A single crystal with dimensions of approximately 0.20 by 0.15 by 0.10 mm with no significant cracks was selected via visual inspection under an optical microscope, Figure 2.2 A. The selected crystal was mounted on a chip carrier. As shown in Figure 2.4 a chip carrier or a measuring chip consists of three integrated parts. The sample is placed at central part. At the peripheral parts, there are several spots where copper wires can be attached (labeled A, B, E and L). The left side has 4 spots where one end of copper wire is attached while the right side has only two spots with hanging copper wires. The crystal was mounted on the chip carrier using two-sided tape. One side of the tape was used attached to the base of the chip and the other side attached to the crystal to keep it in place while two copper leads (0.0003") were attached at opposite ends of the same crystal face using silver epoxy, Figure 2.2 B. After the leads were attached, the surface of the crystal was examined to ensure no significant cracks or breaks developed during the mounting process.

Next, the chip carrier with the crystal mounted on it was attached to a measurement probe containing the electrical leads and feedthroughs. In order to measure the current, a lock-in technique was employed in which a small AC voltage (0.01 V at 50 Hz frequency) was applied from the internal oscillator of a SR830 (Stanford Research) lock-in amplifier and the current was measured as schematically shown in Figure 2.3.

Figure 2.3. Lock-in amplifier and current measurement setup.

To verify that the contacts are viable a multimeter, Figure 2.2 C, was used to measure from the base of one of the contacts on the chip to correlated contact spot in an intermediate set up placed between probe and amplifier. For example if the contacts on the chip were to A and E, as shown in Figure 2.4, the multimeter would verify the viability of contacts by connecting the base of wire A on the chip to E contact spot in an intermediate set up. As long as the multimeter shows a resistance value it means the contacts are viable. After contact verification, the measurement probe was placed in a glass reactor equipped with provisions for evacuation, controlled gas/vapor exposure, and heating/cooling, Figure 2.2 D. This step was done caution to minimize mechanical disturbance to avoid breaking contacts between wires and the surface of NiL⁶ crystal.

The glass reactor was attached to a EDWARDS – E2M1.5 vacuum pump, Figure 2.2 E, equipped with a EDWARDS 1570 pressure gauge. With the valve to the reaction chamber containing the mounted crystal in the closed position, the vacuum pump was turned on and allowed to run for 15 minutes during which a stable vacuum of 8 torr was obtained. At this pressure, the current through the dehydrated crystal was measured and then the chamber connected to water vessel, Figure 2.2 F, opened to increase vapor pressure to 17 torr and record related current value. The vacuum valve was then opened again and

data were collected every six second for a defined period of time based on the type and target of experiment.

To rehydrate the crystal, the vacuum valve was closed. Then, the valve to the small vessel containing water was slowly opened while the pressure gauge was closely monitored. Once the desired vapor pressure was obtained, the valve to water vessel was closed. The vapor pressure was recorded (17 torr for maximum stable current) and current data collected for a defined period of time. Each experiment was repeated over multiple cycles to confirm reproducibility of the data.

Figure 2.4. Graphical view of the setup in Figure 2.2.

2.4.2. Evaluation of Pressure Effects

A series of experiments were conducted in order to monitor the changes in conductivity of NiL^6 single crystal at different vapor pressures. In the first experiment, a crystal was mounted and loaded into the glass reactor as described in section 2.4.1. The system was maintained at a pressure of 17 torr (maximum current) for 10 minutes and the current was recorded. The vacuum chamber was then carefully opened a small amount to decrease the vapor pressure to 16 torr. The valve was then closed and the system was kept at this pressure for 10 minutes and the current was measured. The process was repeated over several steps in which the pressure was lowered by 1 torr.

In the second experiment, a crystal was mounted and loaded into the glass reactor as described in section 2.4.1. The system was maintained at a pressure of 17 torr (maximum current) for 10 minutes and the current was recorded. Then, the valve to the water vessel was slightly opened until the pressure reached 18 torr. The valve was then closed and the system was kept at this pressure for 10 minutes and the current was measured. The process was repeated over several steps in which the pressure was increased by 1 torr.

2.4.3. Evaluation of Temperature Effects

A series of experiments were conducted in order to monitor the changes in conductivity of NiL^6 single crystal at different vapor pressures. For these experiments, a cylindrical furnace was used to enclose the glass reactor, Figure 2.2 D, in the apparatus of Figure 2.2 G. The first experiment was designed to compare maximum conductivity at a constant pressure (17 torr) and various temperatures greater than ambient conditions of 26 °C. A crystal was mounted and loaded into the glass reactor as described in section 2.4.1. The system was maintained at a pressure of 17 torr (maximum current) for 10 minutes and

the current was recorded. Then, the vacuum chamber was opened as described in section 2.4.1 to initiate desorption. The system was maintained under vacuum for 5 minutes and the current recorded. Then, the furnace was turned on and set to a temperature of 30 °C. The heating process took 20 minutes and 10 minutes was considered for getting the stable temperature. Then, the crystal was rehydrated by opening the valve to the water vessel until a vapor pressure of 17 torr was achieved. The pressure was maintained for 10 minutes to calculate average value of maximum current at this temperature. Then, the vacuum chamber was opened to initiate desorption. The system was held under vacuum for 5 minutes and the current recorded. This procedure repeated for 35 °C, 40 °C and 50 °C.

A similar set of experiments to evaluate temperature effects was conducted in which the data were initially collected at high temperature followed by a series of measurements at lower temperatures. A crystal was mounted and loaded into the glass reactor as described in section 2.4.1. Initially, the temperature was set to 50 °C. Then, a vacuum was applied for 5 minutes followed by exposure to 17 torr vapor pressure for 20 minutes. Once the system reached to its maximum conductivity over the define time frame, the same conditions ($P = 17$ torr, $T = 50$ °C) were maintained for another 10 minutes and the average value of maximum current was recorded. Afterwards, the temperature was lowered to 40 °C and system was kept under vacuum for 5 minutes followed by a 20 minute exposure to 17 torr vapor pressure. This procedure was repeated for each temperature and related maximum current was recorded.

2.4.4. Evaluation of Hydration Rates

To understand the correlation between temperature and the rate of hydration/moisture adsorption of NiL^6 , another variable temperature experiment was

designed. Using the methods described in section 2.4.3, the current was measured at a pressure of 17 torr and various temperatures. At each temperature, dehydrated crystal was exposed to a pressure of 17 torr and the current was recorded as a function of time until the maximum current was obtained.

2.5. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was performed using a Metrohm Autolab PGSTAT128N potentiostat/galvanostat operating in potentiostatic mode in collaboration with Alex Gupta and Professor Gautam Gupta. Data were collected on a single crystal of NiL^6 that was modified with two leads connected on the same crystal face as described in section 2.4.1. The leads were connected to the working/working sense and counter/reference electrode ports of the potentiostat. The crystal and contacts were enclosed in the glass reactor shown in Figure 2.4, and the vapor pressure was maintained at 17 torr (hydrated state) or 8 torr (dehydrated state) as noted in section 2.4.1. Impedance studies were conducted at ambient temperature ($\sim 26^\circ\text{C}$). A direct bias of 0 V was applied across NiL^6 with an alternating bias of ± 10 mV applied starting at a frequency of 100 kHz and ending at 0.1 Hz. Ten data points per decade of frequency were recorded. At each data point, real, imaginary, and combined impedances as well as the phase angle between applied voltage and current response were acquired. Raw impedance data were imported into Zview software where the data points were fitted to an equivalent circuit model using the method of least squares.⁹²

CHAPTER III

VARIOUS WATER CLUSTER MOTIFS IN A SERIES OF Ni(II) COMPLEXES BASED ON CHELATES CONTAINING *N*-(2-AMINOETHYL)-1- METHYLIMIDAZOLE-2-CARBOXAMIDE

3.1. Introduction

3.1.1. Significance

H-bonding interactions and their fluctuations are well known to determine the properties of water.⁹³⁻⁹⁶ The complexity of these interactions between water molecules can be used for many applications, but it is a major challenge to describe and understand these relationships.⁹⁷⁻¹⁰⁰ For example, metal organic frameworks (MOFs) have been used to absorb water for purification purposes.¹⁰¹ The structure and properties of water in confined environments such as MOFs continues to attract attention due its fundamental importance in our understanding of biological, chemical, and physical processes.¹⁰²⁻¹⁰³ For instance, the dielectric constant decreases dramatically when water is confined in small spaces.¹⁰⁴ The collection of precise structural data of various H-bonded water networks in diverse environments is of fundamental importance to understand the behavior of water in confined environments.¹⁰⁵⁻¹¹³ Numerous studies have led to characterization of several different discrete water clusters in various crystal hosts, significantly advancing our understanding

of how these clusters link together forming larger networks of water molecules.^{24,105-113} These results also help to better understand the structure and behavior of water molecules in biological systems. In fact, organic compounds with functional moieties that are present in biological molecules can stabilize various water topologies in environments resembling those present in living systems.¹¹⁴

Single crystal X-ray diffraction is an important tool to study cooperative H-bonding interactions between water molecules as well as between water molecules and organic molecules in the supramolecular assemblies.¹¹⁵ In general, functional groups such as carboxylic acids (RCOOH), urea ($(\text{R}_1\text{R}_2)\text{NCON}(\text{R}_3\text{R}_4)$), amines ($\text{R}_1\text{R}_2\text{R}_3\text{N}$), and amides ($\text{R}_1\text{CONR}_2\text{R}_3$) are commonly used to assemble higher order structures via H-bonding. H-bonding and other noncovalent interactions are driving forces behind the self-assembly process. The directionality, reversibility and strong bonding nature of the H-bonding have made it an attractive and useful approach to be investigated and engineered in supramolecular assembly. Accordingly, supramolecular chemistry is now in a phase of characterizing and understanding various H-bonded water clusters in the form of hexamers,¹¹⁶ octamers,¹¹³ decamers,¹¹⁷ and one-dimensional (1D) infinite water chains¹¹⁸⁻¹¹⁹ in diverse environments of various crystal hosts. In fact, the physical properties of water are influenced by the connectivity of H-bonding networks and dimensionality of void spaces within host environments associated with 1D,¹²⁰ 2D,¹²¹ and 3D¹²² supramolecular porous materials.

3.1.2. Hydrogen Bonding

The H-bond is a special type of dipole-dipole attraction between molecules, not a covalent bond to a hydrogen atom. It results from the attractive force between a hydrogen

atom covalently bound to a highly electronegative atom such as nitrogen, oxygen, or fluorine and a nearby highly electronegative atom. The polarity of the covalent bond between the H-bonding donor (D) and H results in a partial negative charge on D and a partial positive charge on H, Figure 3.1. The H-bonding is formed between partially positive H and the electronegative H-bonding acceptor (A).

Figure 3.1. H-bonding interactions between water molecules (left) and representation of H-bonding between the H-bond donor (D-H) and H-bond acceptor (A) showing partial charges and metric parameters (right).

The most important method for the identification of H-bonds even in complicated molecules is crystallography. Structural details, in particular distances between donor and acceptor which are smaller than the sum of the van der Waals radii can be taken as indication of the H-bonding strength. In fact, the strength of H-bonds are determined based on bond distances lengths (between donor and acceptor as well as between hydrogen and acceptor) and bond angle (angle between donor – hydrogen – acceptor), Table 3.1. In a given set of H-bonds, the strongest H-bonds are those closest to perfect geometry. It is customary to classify H-bondings as “weak”, “strong”, and “normal (medium)”. Strong H-bonds have bond angles close between 170 and 180 degrees. Weak H-bonds (make subsequent changes) have bond angles $< 120^\circ$ and $H\cdots A$ bond lengths $> 2.2 \text{ \AA}$. At these

distances, the van der Waals interaction may contribute as much as electrostatics to the total bond energy.

Table 3.1. Strength and characteristics of different types of H-bonds.

	Strong	Medium	Weak
Bond energy (kcal/mol)	14 - 40	4 - 14	0 - 4
Interaction type	mostly covalent	mostly electrostatic	electrostatic
Distances (Å)			
D --- A	2.2 – 2.5	2.5 – 3.2	3.2 – 4.0
H ··· A	1.2 – 1.5	1.5 – 2.2	2.2 – 3.2
D---H···A angle (°)	175 - 180	130 – 180	90 - 150

Of particular interest is the participation of water in H-bonding. Each water molecule can participate in up to four H-bonds; two as an H-bonding donor and two as an H-bonding acceptor. Because of this, water can participate in a variety of extended H-bonding network. For example, in the solid state (ice), intermolecular interactions lead to a highly ordered but loose structure in which each oxygen atom is surrounded by four hydrogen atoms; two of these hydrogen atoms are covalently bonded to the oxygen atom, and the two others (at longer distances) are H-bonded to the oxygen atom's unshared electron pairs. This open structure of ice causes its density to be less than that of the liquid state, in which the ordered structure is partially broken down and the water molecules are (on average) closer together. When water freezes, a variety of structures are possible depending on the conditions. Eighteen different forms of ice are known and can be interchanged by varying external pressure and temperature, and the most common forms are shown in Figure 3.2.

Figure 3.2. Common forms of snowflakes.¹²³

In fact, the ice crystals that make up snowflakes are symmetrical (or patterned) because they reflect the internal order of the crystal's water molecules as they arrange themselves in predetermined spaces (known as "crystallization") to form a six-sided snowflake. Ultimately, it is the temperature at which a crystal forms and to a lesser extent the humidity of the air that determines the basic shape of the ice crystal. Thus, we see long needle-like crystals at 23 °F and very flat plate-like crystals at 5 °F.

The intricate shape of a single arm of the snowflake is determined by the atmospheric conditions experienced by entire ice crystal as it falls. A crystal might begin to grow arms in one manner direction, and then minutes or even seconds later, slight changes in the surrounding temperature or humidity causes the crystal to grow in another way direction. Although the six-sided shape is always maintained, the ice crystal (and its six arms) may branch off in new directions. Because each arm experiences the same atmospheric conditions, the arms look identical.

3.1.3. Graph-Set Analysis

Graph-set analysis is a method to categorize H-bonding patterns topologically and disentangle related motifs systematically and consistently.¹²⁴ Graph sets are descriptions, like an empirical formula or a space group, that provide the simplest representation of a more complex feature. They represent the type of H-bonding pattern including the number of donors and acceptors and the type of network.

A graph set is defined by a pattern designator (G), the degree of H-bonding (r), and the number of donors (d) and acceptors (a); $G^a_d(r)$.¹²⁴ The G term has values of S , C , R or D depending on the H-bonding pattern. A designation of S (self) denotes an intramolecular H-bonding between a single donor and a single acceptor with no extended network. The term C (chain) is used to for infinite H-bonding chains that repeat through the crystal lattice. An R (ring) term is used for H-bonding arranged in finite structures, while D (dimers) is used for noncyclic dimers and other finite H-bonded networks. The parameter r refers to the degree of the H-bonding motif and is equal to the number of atoms in the smallest repeating unit of the set. The parameters d and a refer to the number of different kinds of donors and acceptors. If d and a are not specified a value of one is assumed.

Examples of graph sets are provided in Figure 3.3. Panel A shows a D pattern for a single H-bond and since $r = 2$, $a = 1$, and $d = 1$, these two are not explicitly written. Panel B shows a C pattern and $r = 7$ is the number of covalent/H-bonds from H of one H-bonding to A or the next DH. Since $a = 1$ and $d = 1$, they are not explicitly written. Panel C shows both C and R patterns and $a = 2$, $d = 1$ for the chain containing 8 bonds. Since the chain contains a ring, the ring is noted in brackets after the chain. The ring contains 4 atoms comprised of 2 acceptors and 1 donor. Panel D shows two identical rings (R pattern).

Figure 3.3. Examples of graph sets. A) D pattern ($r = 2$, $a = 1$, and $d = 1$); B) C pattern ($r = 7$, $a = 1$, and $d = 1$); C) C pattern ($r = 8$, $a = 2$, and $d = 1$) enclosing R pattern ($r = 4$, $a = 2$, and $d = 1$); D) two identical R patterns ($r = 4$, $a = 2$, and $d = 1$).

Graph sets can be assigned by manual inspection of the crystal data. Alternately, programs such as Mercury¹²⁵ have automated features to calculate graph sets from a provided data set. To manually assign the graph sets in a crystal, all of the different types of H-bonds are first identified. Second, H-bonding types are ranked by chemical priority using an adaptation of the Cahn-Ingold-Prelog rules (IUPAC, 1970) as following; i) First, examine at the atoms directly attached to the stereocenter of the compound. A substituent with a higher atomic number takes precedence over a substituent with a lower atomic number. Hydrogen is the lowest possible priority substituent, because it has the lowest atomic number. ii) Second, if there are two substituents with equal rank, proceed along the two substituent chains until there is a point of difference. First, determine which of the chains has the first connection to an atom with the highest priority (the highest atomic number). That chain has the higher priority and second, if the chains are similar, proceed down the chain, until a point of difference. iii) If a chain is connected to the same atom

twice or three times, check to see if the atom it is connected to, has a greater atomic number than any of the atoms that the competing chain is connected to. If none of the atoms connected to the competing chain(s) at the same point has a greater atomic number, then the chain bonded to the same atom multiple times has the greater priority. If however, one of the atoms connected to the competing chain has a higher atomic number, then that chain has the higher priority.¹²⁶

The third step after applying the Cahn-Ingold-Prelog rules is to generate a motif, selecting the highest priority H-bonding, H(1), and finding all occurrences of this bond in the array. To identify a motif, choose one molecule as the starting point and identify all molecules that are attached to it by H(1). Then proceed from each of these molecules to all others bonded to them by H(1), etc. until a molecule is encountered which has no additional attached molecules, or until it is obvious that the set is infinite. Fourth, assign a graph set to the motif. Fifth, repeat steps three and four until graph sets have been assigned to all H-bonding types.

3.1.4. Focus of Chapter III

This chapter focuses on a group of structurally related Ni(II) complexes containing N_3X ($X = S$ or O) donors. The complexes crystallize with water of hydration forming extended H-bonding networks. The morphology of the network is dependent on small changes in the ligand framework leading to different orientations of the carboxamido oxygens, which influences the solid state packing and H-bonding patterns. Three different network structures are observed including 1D water chains (streams), 2D tapes of infused rings (cascades), and isolated water dimers (pools).¹²⁷ The results presented in this chapter have previously been published.¹²⁷

3.2. Results and Discussion

3.2.1. Synthesis and Characterization

A series of Ni(II) compounds, NiL^2 , NiL^3 , $\text{Ni}(\text{L}^1)_2$, NiL^4 , and NiL^5 , based on a *N*-(2-aminoethyl)-1-methylimidazole-2-carboxamide (HL^1) core were synthesized as shown in Scheme 3.1. The N_3S chelate H_2L^2 and its nickel complex, NiL^2 , were prepared as previously reported.¹²⁸ Similar methods were employed to yield the new chelate H_2L^3 and NiL^3 . Complex $\text{Ni}(\text{L}^1)_2$ was isolated from a mixture of compounds formed upon addition of HL^1 to $\text{Ni}(\text{acac})_2$ in dry toluene. Addition of acetone/water or methyl acetylacetonate/water to the mixture containing $\text{Ni}(\text{L}^1)_2$ yields complexes NiL^4 or NiL^5 , respectively.

Scheme 3.1. Synthetic pathways for Ni(II) complexes containing N_3X (X = S/O) donors.

The UV-visible spectra of NiL^3 , $\text{Ni(L}^1\text{)}_2$, NiL^4 , and NiL^5 were recorded in acetonitrile or dichloromethane, Figures 3.4 - 3.7. The spectrum of NiL^3 is similar to that previously reported for the square planar complex, NiL^2 , with charge transfer bands at 368, 449, and 575 nm.¹²⁸ In contrast, the electronic spectrum of $\text{Ni(L}^1\text{)}_2$ shows low intensity d–d transitions at 488 and 980 nm consistent with an octahedral environment. The spectrum of NiL^4 displays absorbances at 216, 324, 426, and 508 nm assigned to charge transfer bands. Similarly, NiL^5 has bands as at 209, 250, 305, 380, and 475 nm.

Figure 3.4. UV-visible spectrum of NiL^3 in CH_3CN .

Figure 3.5. UV-Vis spectrum of $\text{Ni}(\text{L}^1)_2$ in CH_2Cl_2 .

Figure 3.6. UV-Vis spectrum of NiL^4 in CH_3CN .

Figure 3.7. UV-Vis spectrum of NiL^5 in CH_3CN .

The FT-IR spectra of NiL^2 , NiL^3 , $\text{Ni}(\text{L}^1)_2$, NiL^4 , and NiL^5 were collected on solid samples by attenuated total reflectance (ATR correction), Figures 3.8 - 3.13. The spectra of these complexes show distinct C–N and C=O stretches associated with the carboxamide moiety that are shifted relative to HL^1 due to deprotonation, Table 3.2. The $\nu_{\text{C=O}}$ stretches in NiL^2 and NiL^3 are identical, 1660 cm^{-1} . There is a slight shift to 1610 and 1590 cm^{-1} in NiL^4 and NiL^5 , respectively. For complexes NiL^2 , NiL^3 , and $\text{Ni}(\text{L}^1)_2$, the amine N–H stretching frequencies are observed in the range of $3200\text{--}3300\text{ cm}^{-1}$. The absence of spectral features between $2400\text{--}2600\text{ cm}^{-1}$ indicates the thiol group has been deprotonated upon Ni(II) coordination in complexes NiL^2 and NiL^3 . A $\nu_{\text{C=N}}$ stretch is clearly visible at 1590 cm^{-1} and 1585 cm^{-1} in complexes NiL^4 and NiL^5 , respectively. In NiL^5 , a medium-strength peak at 1050 cm^{-1} is consistent with the presence of a C–O–CH₃ bond in the structure.

Figure 3.8. FT-IR spectrum of HL¹.

Figure 3.9. FT-IR spectrum of NiL².

Figure 3.10. FT-IR spectrum of NiL³.

Figure 3.11. FT-IR spectrum of $\text{Ni}(\text{L}^1)_2$.

Figure 3.12. FT-IR spectrum of NiL^4 .

Figure 3.13. FT-IR spectrum of NiL^5 .

Table 3.2. Selected stretches (cm^{-1}) in FT-IR spectra of HL^1 and five Ni(II) complexes.

Moiety	HL^1	NiL^2	NiL^3	$\text{Ni(L}^1)_2$	NiL^4	NiL^5
C = O	1670	1660	1660	1590	1610	1590
C – N	1544	1540	1540	1510	1510	1510

3.2.2. X-ray Crystallography

The structure of NiL^2 has previously been reported.¹²⁸ Crystals of NiL^2 , NiL^3 , $\text{Ni(L}^1)_2$, NiL^4 , and NiL^5 include water of hydration through H-bonding interactions with the metal–ligand complex. Details of the crystallization process for each complex are provided in Chapter 2. Crystal data and structure refinement details for NiL^3 , $\text{Ni(L}^1)_2$, NiL^4 , and NiL^5 are listed in Table 3.3. A summary of bond distances and angles for all five Ni(II) complexes are listed in Table 3.4 with a summary of H-bonding metric parameters provided in Table 3.5.

Table 3.3. Crystal data and structure refinement of NiL³, Ni(L¹)₂, NiL⁴, and NiL⁵.

Identification code	NiL ³	Ni(L ¹) ₂	NiL ⁴	NiL ⁵
Empirical formula	C ₉ H ₁₄ N ₄ NiO ₁ S·H ₂ O	C ₁₄ H ₂₂ N ₈ NiO ₂ ·H ₂ O	C ₁₂ H ₁₆ N ₄ NiO ₂ ·3H ₂ O	C ₁₂ H ₁₆ N ₄ NiO ₃ ·H ₂ O
Formula weight	303.03	411.12	361.05	341.01
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2/ <i>n</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions				
<i>a</i> (Å)	11.9515(15)	9.1756(19)	6.8975(18)	9.2792(6)
<i>b</i> (Å)	4.8375(6)	10.590(2)	9.130(2)	13.6005(8)
<i>c</i> (Å)	22.198(3)	9.4434(19)	12.645(3)	21.7240(13)
<i>α</i> (deg)	90.00	90.00	92.821(4)	90.00
<i>β</i> (deg)	103.424(2)	98.876(3)	92.276(4)	95.3700(10)
<i>γ</i> (deg)	90.00	90.00	104.339(4)	90.00
<i>V</i> (Å ³)	1248.3(3)	906.7(3)	769.4(3)	2729.6(3)
<i>Z</i>	4	2	2	8
<i>d</i> _{calcd} (Mg m ⁻³)	1.612	1.506	1.558	1.660
Abs coeff (mm ⁻¹)	1.717	1.103	1.290	1.444
<i>F</i> (000)	632	432	380	1424
Cryst size (mm ³)	0.25 × 0.25 × 0.25	0.35 × 0.33 × 0.30	0.50 × 0.03 × 0.01	0.24 × 0.14 × 0.03
<i>θ</i> range for data coll. (°)	1.75 to 25.12	2.91 to 25.08	2.90 to 25.11	1.77 to 25.12
Index ranges	-14 ≤ <i>h</i> ≤ 14 -5 ≤ <i>k</i> ≤ 5 -26 ≤ <i>l</i> ≤ 26	-10 ≤ <i>h</i> ≤ 10 -12 ≤ <i>k</i> ≤ 12 -11 ≤ <i>l</i> ≤ 11	-8 ≤ <i>h</i> ≤ 8 -10 ≤ <i>k</i> ≤ 10 -15 ≤ <i>l</i> ≤ 15	-10 ≤ <i>h</i> ≤ 11 -16 ≤ <i>k</i> ≤ 16 -25 ≤ <i>l</i> ≤ 25
Reflns collected	8216	6422	5732	19 823
Independent reflections	2227 [<i>R</i> (int) = 0.0359]	1621 [<i>R</i> (int) = 0.0141]	2709 [<i>R</i> (int) = 0.0231]	4861 [<i>R</i> (int) = 0.0435]
Completeness to theta max	99.4%	99.9%	99.1%	99.8%
Absorption correction	SADABS	SADABS	SADABS	SADABS
Max., min transmission	1.000 and 0.636	0.710 and 0.571	0.871 and 0.613	1.000 and 0.754
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/params	2227/5/210	1621/0/155	2709/28/257	4861/0/452
Goodness of fit on <i>F</i> ²	1.083	1.008	1.052	1.057
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^{a,b}	<i>R</i> ₁ = 0.0449 <i>wR</i> ₂ = 0.1148	<i>R</i> ₁ = 0.0219 <i>wR</i> ₂ = 0.0567	<i>R</i> ₁ = 0.0280 <i>wR</i> ₂ = 0.0579	<i>R</i> ₁ = 0.0364 <i>wR</i> ₂ = 0.0593
<i>R</i> indices (all data) ^{a,b}	<i>R</i> ₁ = 0.0472 <i>wR</i> ₂ = 0.1164	<i>R</i> ₁ = 0.0222 <i>wR</i> ₂ = 0.0569	<i>R</i> ₁ = 0.0356 <i>wR</i> ₂ = 0.0588	<i>R</i> ₁ = 0.0561 <i>wR</i> ₂ = 0.0628
Largest diff. peak and hole (e·Å ⁻³)	0.900 and -0.458	0.308 and -0.280	0.394 and -0.331	0.601 and -0.302

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$, where $w = q/\sigma^2(F_o^2) + (qp)^2 + bp$. GOF = $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

Table 3.4. Selected bond distances (Å) and bond angles (°) for the five Ni(II) complexes.

Bonds	NiL²	NiL³	Ni(L¹)₂	NiL⁴	NiL⁵
Ni1–N1	1.893(3)	1.885(3)	2.1348(13)	1.9013(19)	1.889(2)
Ni1–N3	1.869(3)	1.863(3)	2.0133(13)	1.8517(18)	1.842(2)
Ni1–N4	1.904(3)	1.892(3)	2.1494(13)	1.8444(19)	1.843(2)
Ni1–S1	2.1810(11)	2.1668(11)			
Ni1–O2				1.8350(15)	1.8578(18)
Ni2–O5					1.8521(18)
Ni2–N5					1.898(2)
Ni2–N7					1.840(2)
Ni2–N8					1.847(2)
N1–Ni1–N3	83.77(12)	83.55(13)	78.50(5)	83.55(8)	83.74(10)
N3–Ni1–N4	85.32(12)	85.30(14)	80.27(5)	86.22(8)	86.21(10)
N1–Ni1–N4	168.94(12)	168.59(15)	158.53(5)	169.67(8)	169.88(10)
N4–Ni1–S1	90.57(9)	90.66(11)			
S1–Ni1–N1	100.47(9)	100.55(10)			
N4–Ni1–O2				97.97(8)	97.53(9)
O2–Ni1–N1				92.25(8)	92.50(9)
N5–Ni2–N7					83.81(10)
N7–Ni2–N8					85.91(10)
N5–Ni2–N8					169.14(10)
N8–Ni2–O5					97.30(9)
O5–Ni2–N5					92.90(9)

Table 3.5. Selected H-bonding metrics for the five Ni(II) complexes.

D–H...A	H...A (Å)	D...A (Å)	D–H...A (°)
NiL²			
O2–H2oa...O1	1.90(5)	2.756(4)	163(5)
O2–H2ob...O2 ⁱ	1.96(5)	2.892(5)	168(5)
O2–H2oc...O2 ⁱⁱ	2.01(5)	2.892(5)	174(5)
N4–H4...S1 ⁱⁱⁱ	2.57(4)	3.409(3)	163(4)
Symmetry codes: i = (–x, 2 – y, 1 – z); ii = (–x, 1 – y, 1 – z); iii = (x, 1 + y, z).			
NiL³			
O2–H2oa...O1	1.93(3)	2.818(4)	175(6)
O2–H2ob...O2 ⁱ	1.92(10)	2.788(5)	169(16)
O2–H2oc...O2 ⁱⁱ	1.96(9)	2.794(5)	157(12)
N4–H4...S1 ⁱⁱⁱ	2.50(6)	3.417(4)	173(4)
Symmetry codes: i = (–x, –y, –z); ii = (–x, 1 – y, –z); iii = (x, –1 + y, z).			
Ni(L¹)₂			
O2–H2o ⁱⁱ ...O1	2.010(18)	2.7979(13)	162.8(19)
N4–H4na...O1 ⁱⁱⁱ	2.072(19)	2.9431(17)	173.1(16)
Symmetry codes: ii = (0.5 – x, y, 1.5 – z); iii = (–0.5 + x, 1 – y, –0.5 + z).			
NiL⁴			
O3–H3oa...O1	1.938(18)	2.720(2)	175(2)
O3–H3ob...O5 ⁱ	2.09(2)	2.873(3)	178(2)
O4–H4oa...O1	2.01(2)	2.803(3)	173(3)
O4–H4ob...O4 ⁱⁱⁱ	1.98(5)	2.765(3)	172(7)
O4–H4oc...O5 ^{iv}	2.04(3)	2.800(3)	166(6)
O5–H5oa...O3 ⁱⁱ	2.04(3)	2.786(3)	160(3)
O5–H5ob...O5 ^v	2.06(6)	2.827(3)	169(7)
O5–H5oc...O4 ^{vi}	2.08(3)	2.800(3)	154(7)
Symmetry codes: i = (x, y, –1 + z); ii = (1 – x, –y, 1 – z); iii = (2 – x, 1 – y, –z); iv = (x, y, 1 + z); v = (2 – x, –y, 2 – z); vi = (x, y, 1 + z).			
NiL⁵			
O7–H7oa...O1	2.01(3)	2.775(3)	174(3)
O7–H7ob...O4 ⁱ	2.18(4)	2.942(3)	169(4)
O8–H8oa...O7	2.06(3)	2.871(4)	173(3)
O8–H8ob...O4 ⁱⁱ	2.11(4)	2.879(3)	167(3)
Symmetry codes: i = (1 – x, –0.5 + y, 0.5 – z); ii = (1 + x, 1.5 – y, 0.5 + z).			

Complex NiL³ crystallizes as an orange cube that is structurally similar to NiL². Both complexes are in the monoclinic space group *P*2₁/*c*. The asymmetric unit of NiL³ contains one equivalent of NiL³ and a disordered water of hydration, Figure 3.14. The Ni is coordinated in a pseudo-square planar environment defined by the N₃S chelate with metric parameters similar to NiL². The water of hydration is modeled with a full occupancy

oxygen, O2, and one full occupancy hydrogen, H2oa. The remaining hydrogen atom is positionally disordered with 50% occupancy each for H2ob and H2oc.

Figure 3.14. ORTEP¹²⁹ representation of the asymmetric unit of NiL^3 with thermal ellipsoids shown at the 50% probability level.

The water of hydration in NiL^3 participates in three H-bonding interactions. The first is with the carboxamide oxygen O1 of the metal complex in the asymmetric unit. The H-bonding is nearly linear with an $\text{O2-H2oa}\cdots\text{O1}$ angle of $175(6)^\circ$. The donor-acceptor ($\text{D}\cdots\text{A}$) and hydrogen-acceptor ($\text{H}\cdots\text{A}$) distances of $2.818(4)$ and $1.93(3)$ Å, respectively, are consistent with a strong interaction. The two additional H-bonding interactions are symmetry generated water molecules; $\text{O2-H2ob}\cdots\text{O2}^{\text{i}}$ ($-x, -y, -z$) and $\text{O2-H2oc}\cdots\text{O2}^{\text{ii}}$ ($-x, 1-y, -z$).

Figure 3.15. 1D H-bonding "stream" of water in complex NiL^3 . Each O2 atom is bonded to one full occupancy H atom and two partial, 50% occupancy H atoms (see text). H-bonding interactions are denoted by black dashed lines. Graph sets are displayed by dotted colored lines as follows: $\text{C}^2_2(4)$ (blue); $\text{D}^3_3(7)$ (red); $\text{C}^1_1(4)$ (green). Atoms generated by symmetry as marked as follows: i = $(-x, -y, -z)$, ii = $(-x, 1 - y, -z)$, iii = $(x, -1 + y, z)$.

The extended H-bonding network in NiL^3 can be described as a 1D zig-zag chain of water along the b direction that is anchored to stacked metal complexes, Fig. 3.15. Using the graph set notation¹²⁴, the 1D water molecule chain is described as $\text{C}^2_2(4)$ (blue dotted line). The $\text{C}^2_2(4)$ chains are held between carboxamide oxygens (O1 and O1ⁱⁱ) by a $\text{D}^3_3(7)$ motif (red dotted line). Further, the Ni complexes stack through a $\text{C}^1_1(4)$ chain involving $\text{S1}^{\text{iii}} \cdots \text{H4} - \text{N4} - \text{Ni}$ (green dotted line). A similar network is observed in NiL^2 . The $\text{N} - \text{H} \cdots \text{S}$ H-bonding in NiL^2 and NiL^3 orient the complexes into an AAAA stacking arrangement. Each carbonyl O of the host interacts with a single water molecule, which is confined in 1D channels.

Complex $\text{Ni}(\text{L}^1)_2$ crystallizes from acetonitrile as blue plates in the monoclinic space group $P2_1/n$. The asymmetric unit contains one equivalent of $[\text{L}^1]^-$, one Ni atom that sits on the special position $(0.75, y, 0.75)$, and one water of hydration. The Ni is coordinated by two equivalents of $[\text{L}^1]^-$ in a pseudo-octahedral N_6 environment, Figure 3.16. The $[\text{L}^1]^-$ ligand serves as a meridional chelate with imidazole (N1), amido (N3), and amino (N4) donors.

Figure 3.16. ORTEP representation of $\text{Ni}(\text{L}^1)_2$ with thermal ellipsoids shown at the 50% probability level. Atoms generated by symmetry as marked as follows: i = $(1.5 - x, y, 1.5 - z)$, ii = $(0.5 - x, y, 1.5 - z)$.

The asymmetric unit of $\text{Ni}(\text{L}^1)_2$ also contains an O atom, O2, on a special position $(0.25, y, 0.75)$ associated with the water molecule. The symmetry generated hydrogen atom H2o^{ii} $(0.5 - x, y, 1.5 - z)$ on O2 serves as an H-bonding donor to the carboxamido O1 of the metal complex with an $\text{O2-H2o}^{\text{ii}}\cdots\text{O1}$ angle of $162.8(19)^\circ$. The $\text{D}\cdots\text{A}$ and $\text{H}\cdots\text{A}$ distances are $2.7979(13)$ and $2.010(18)$ Å, respectively. There is a symmetrically

equivalent H-bonding interaction between O2–H2o and O1ⁱⁱ that completes a water bridge between neighboring metal complexes defined as a C²₂(10) H-bonding motif (green dotted line), Figure 3.17. The carboxamide also serves as an H-bonding acceptor with N4–H4NA to form a C²₂(12) pattern, Figure 3.18. There are no water–water interactions in the extended network.

Figure 3.17. Bridging H-bonding interactions in complex Ni(L¹)₂. H-bonding interactions are denoted by black dashed lines. The graph set C²₂(10) is noted by the dotted green line. Atoms marked with ii are symmetry generated (0.5 – x, y, 1.5 – z).

Figure 3.18. C²₂(12) H-bonding motif in Ni(L¹)₂.

Single crystals of NiL^4 were collected from an acetone/water mixture as orange needles in the triclinic space group $P\bar{1}$. Orange plate crystals of NiL^5 in the monoclinic space group $P2_1/c$ were obtained from acetonitrile solution by slow evaporation. The asymmetric unit of NiL^4 contains one equivalent of NiL^4 and three waters of hydration, Figure 3.19. The asymmetric unit of NiL^5 consists of two, crystallographically distinct equivalents of NiL^5 and a total of two waters of hydration, Figure 3.20. The Ni centers of NiL^4 and NiL^5 sit in similar N_3O donor environments arranged in pseudo-square planes. The only difference in the donor ligands is the substitution of the methyl group (C12) in NiL^4 with a methoxy group (O3–C12) in NiL^5 .

Figure 3.19. ORTEP representation of the asymmetric unit of NiL^4 with thermal ellipsoids shown at the 50% probability level.

Figure 3.20. ORTEP representation of the asymmetric unit of NiL^5 with thermal ellipsoids shown at the 50% probability level.

The three waters of hydration in NiL^4 are involved in extensive H-bonding interactions, Figure 3.21. The absence of H-bonding between the host layers of NiL^4 allows an ABAB stacking arrangement. This generates void spaces between alternating layers allowing the host carbonyl O to interact with two water molecules. This allows for multi-dimensional H-bonding motifs. The carboxamido oxygen O1 of the metal complex interacts with the O3 and O4 containing water molecules. The O3–H3oa $\cdots$ O1 angle is $175(2)^\circ$ with a D $\cdots$ A distance of $2.720(2)$ Å and an H $\cdots$ A distance of $1.938(18)$ Å. The O4–H4oa $\cdots$ O1 interaction is similar with an angle of $173(3)^\circ$, a D $\cdots$ A distance of $2.803(3)$ Å, and an H $\cdots$ A distance of $2.01(2)$ Å. Additionally, the O3 containing water molecule acts as an H-bonding donor to O5ⁱ ($x, y, -1 + z$) and an H-bonding acceptor to O5ⁱⁱ ($1 - x, -y, 1 - z$). The O4 containing water molecule has a disordered H-atom, modeled as H4ob and

H4oc that participates in H-bonding interactions with O5ⁱ and O4ⁱⁱⁱ ($2 - x, 1 - y, -z$), respectively.

The extended H-bonding in NiL⁴ creates a cascade water network. The water molecules are arranged in three R²₄(8) rings (dotted blue lines) fused together in a stair-step fashion generating a larger R⁸₈(16) pattern, Figure 3.21. Each R⁸₈(16) ring is a part of a pair of infinite chains best described as a C³₃(6) (dotted red line) in the *a*-direction and a C⁵₅(10) (dotted green line) along the *b*-direction, Figure 3.22.

Figure 3.21. Infused H-bonding rings in complex NiL⁴. Each O4 and O5 atom is bonded to one full occupancy H atom and two partial, 50% occupancy H atoms. H-bonding interactions are denoted by black dashed lines. The three R²₄(8) graph sets are noted by the dotted blue lines. Atoms generated by symmetry as marked as follows: i = (*x*, *y*, $-1 + z$), ii = ($1 - x$, $-y$, $1 - z$), vii = ($1 - x$, $-y$, $-z$).

Figure 3.22. 2D H-bonding water “cascade” in complex NiL^4 . H-bonding interactions are denoted by black dashed lines. Graph sets are noted by dotted colored lines as follows: $\text{C}^3_3(6)$ (red) and $\text{C}^5_5(10)$ (green). Atoms marked with viii are symmetry generated ($4 - x$, $1 - y$, $-z$).

The substitution of the methyl substituent in NiL^4 with a methoxy group in NiL^5 results in significant changes in the H-bonding network. In NiL^5 , there are two metal complexes and two waters of hydration in the asymmetric unit. The carboxamido oxygen O1 associated with Ni1 accepts an H-bonding from O7. The $\text{O7-H7oa}\cdots\text{O1}$ angle is $174(3)^\circ$ with a $\text{D}\cdots\text{A}$ distance of $2.775(3) \text{ \AA}$ and an $\text{H}\cdots\text{A}$ distance of $2.01(3) \text{ \AA}$. The carboxamido oxygen O4 associated with Ni2 is an H-bonding acceptor from both O7 and O8 containing water molecules. The $\text{O7-H7ob}\cdots\text{O4i}$ ($1 - x$, $-0.5 + y$, $0.5 - z$) angle is $169(4)^\circ$ with a $\text{D}\cdots\text{A}$ distance of $2.942(3) \text{ \AA}$ and an $\text{H}\cdots\text{A}$ distance of $2.18(4) \text{ \AA}$. The $\text{O8-H8ob}\cdots\text{O4ii}$ ($1 + x$, $1.5 - y$, $0.5 + z$) interaction is similar with an angle of $167(3)^\circ$, a $\text{D}\cdots\text{A}$ distance of $2.879(3) \text{ \AA}$, and an $\text{H}\cdots\text{A}$ distance of $2.11(4) \text{ \AA}$. Additionally, the O8 containing water molecule acts as an H-bonding donor to O7.

The extended H-bonding in NiL^5 forms isolated pools of water, Figure 3.23., as a result of the substitution of $-\text{CH}_3$ in NiL^4 with $-\text{OCH}_3$ in NiL^5 results. The methoxy groups serve as a gate to generate isolated void spaces within an ABBA stacking arrangement. The water molecules are arranged in $\text{R}^4_6(12)$ rings (dotted blue line) comprised of carboxamido atoms O4 and O4^{iii} ($2 - x, 1 - y, 1 - z$) and four water molecules. The rings are anchored between stacks of metal complexes via direct H-bonding interactions between O7 and O1. Notably, the methoxy substituents ($\text{O3}-\text{C12}$) of neighboring stacks are in close contact creating a barrier between adjacent rings of water.

Figure 3.23. Isolated H-bonding “pool” of water in complex NiL^5 . H-bonding interactions are denoted by black dashed lines. The $\text{R}^4_6(12)$ graph set is noted by the dotted blue line. Atoms generated by symmetry as marked as follows: i = $(1 - x, -0.5 + y, 0.5 - z)$, ii = $(1 + x, 1.5 - y, 0.5 + z)$, iii = $(2 - x, 1 - y, 1 - z)$.

3.2.3. Conductivity Studies

The electrical impedance of crystals of NiL^2 , NiL^4 , and NiL^5 were evaluated by electrochemical impedance spectroscopy (EIS). No peak (time constant) is observed in the plot of phase angle vs. frequency indicating no faradaic electrochemical processes occur within crystals at the biases applied (Figure 3.24).¹³⁰ The total impedance, Z , is a combination of real (Z') and imaginary (Z'') contributions.¹³¹ Data for NiL^2 , NiL^4 , and NiL^5 are summarized in Table 3.6. At high frequency (~ 100 kHz), the real component represents the system resistance. Under these conditions, Z' values with no applied bias are 730, 650, and 580 Ω for NiL^2 , NiL^4 , and NiL^5 , respectively. The imaginary component involves inductive and capacitive contributions to impedance. The capacitance was determined by fitting measured impedance data to an electrical circuit model using the method of least squares.⁹² Several models were evaluated and convergence was only achieved for a capacitor circuit. The capacitance for all three complexes ranges from $1.12 \times 10^{-10} - 1.27 \times 10^{-10}$ F.

Analysis of the Nyquist representation (Z' and $-Z''$) for the complexes shows that Z'' changes with frequency, in the high frequency domain, while Z' remains relatively constant (Figure 3.25). This indicates that the vast majority of the system impedance is caused by capacitive elements, rather than resistive elements.¹³² The impedance of an ideal capacitor is inversely proportional to frequency.¹³¹ This trend is observed for the control capacitor (0.22 μF , Sangamo USA), 1, 4, and 5 (Figure 3.25).

Figure 3.24. Bode representations of EIS data for 22 μF capacitor control (A), NiL^2 (B), NiL^4 (C) and NiL^5 (D) show the phase angle and impedance behavior as a function of frequency. The inverse relation between Z and frequency and constant $\sim 90^\circ$ phase angles in all four plots are characteristics of capacitors.

Table 3.6. Capacitance (with associated chi-squared values) and Z' at 100 kHz (indicative of equivalent series resistance) for the capacitor control and complexes NiL^2 , NiL^4 , and NiL^5 at various applied DC biases. Also depicted is the equivalent circuit model used to fit EIS data and determine capacitance.

Sample	DC Bias (V)	Circuit	Chi-squared	Capacitance (F)	Z' @ 100 (Ω)
Capacitor	-0.1		1E-20	2.08E-07	3.84
	0		1E-20	2.08E-07	3.82
	0.1		1E-20	2.07E-07	6.63
NiL^2	-0.1		1E-20	1.31E-10	1346.88
	0		1E-20	1.25E-10	729.26
	0.1		1E-20	1.30E-10	984.91
NiL^4	-0.1		1E-20	1.07E-10	659.57
	0		1E-20	1.12E-10	650.04
	0.1		1E-20	1.07E-10	637.31
NiL^5	-0.1		1E-20	1.23E-10	512.69
	0		1E-20	1.27E-10	577.06
	0.1		1E-20	1.33E-10	529.32

The similarities in measured capacitances and system resistances for NiL^2 , NiL^4 , and NiL^5 are attributed to the nearly identical π -stacking distances of the metal complexes of ~ 3.4 Å. Charge transfer appears to propagate through the metal complex stacks with the water of hydration serving a structural role. It is envisioned that the water structure could serve as a conduit for proton conduction, which is a focus of continued efforts.

Figure 3.25. Nyquist representations of EIS data for 22 μF capacitor control (A), NiL^2 (B), NiL^4 (C) and NiL^5 (D). Data in B, C, and D were truncated at $-Z'' = 80,000 \text{ } \Omega$ to illustrate similarities with (A) and omit the diffusion-related noise observed at low frequencies.

3.2.4. Thermal Analyses

TGA and DSC traces of complexes NiL^2 , NiL^3 , NiL^4 , and NiL^5 are shown in Figures 3.26. – 3.33. In complexes NiL^2 and NiL^3 , there is a clear dehydration step beginning near 50 °C with a mass loss of 6.09 and 6.12%, respectively, upon reaching 150 °C. The mass change is consistent with the loss of one water molecule per complex from the lattice. Decomposition of the ligand framework of NiL^2 and NiL^3 occurs above 200 °C and 250 °C, respectively. Degradation is accompanied by a phase transition as indicated by the endothermic process observed by DSC.^{133,134} In NiL^4 and NiL^5 dehydration begins at, or below, room temperature and is complete by 70 °C with a mass loss of 14.89% (three water molecules) and 9.698% (two water molecules), respectively. Both NiL^4 and NiL^5 display complete mass loss by 320 °C attributed to sublimation of the complexes, which was confirmed experimentally. A phase transition, as observed by DSC, occurs prior to sublimation.

Figure 3.26. TGA of NiL^2 .

Figure 3.27. DSC of NiL^2 .

Figure 3.28. TGA of NiL^3 .

Figure 3.29. DSC of NiL^3 .

Figure 3.30. TGA of NiL^4 .

Figure 3.31. DSC of NiL^4 .

Figure 3.32. TGA of NiL^5 .

Figure 3.33. DSC of NiL^5 .

The H-bonding motif in the hydrated crystals correlates with the temperature range of the dehydration process. For NiL² and NiL³, the 1D chain requires a higher temperature to break the relatively strong H-bonding interactions within the channel and between the water and structural O atoms. For NiL⁴ and NiL⁵, the water motif is more open with a greater variability in the types and strengths of H-bonding interactions. The relatively low temperature required to initiate dehydration suggests that cleavage of the weakest interactions initiates complete dehydration through a breakdown of the H-bonding network. A detailed analysis based on H-bonding distances and angles is not possible due to relatively small changes in H-bonding parameters with respect to their standard deviations, Table 3.5.

3.3. Conclusion

The H-bonding motifs in the related planar Ni(II) complexes NiL², NiL³, NiL⁴, and NiL⁵ vary as a function of the crystal packing of the host molecules, Scheme 3.2. The interlayer H-bonding interactions in NiL² and NiL³ results in an AAAA stacking arrangement, which positions the carbonyl O atoms to interact water molecules confined in 1D channels. The absence of H-bonding stacking interactions between the layers of NiL⁴ result in an ABAB stacking arrangement with large void spaces between alternating layers. The –OCH₃ group in NiL⁵ act as a gate to generate isolated void spaces resulting in pools of water as a result of the ABBA stacking arrangement. The mass quantity of water stored per volume of crystal is dependent on the packing arrangement. The pools of NiL⁵ contain the least amount of water at 10.96 mg cm⁻³. The streams of NiL² and NiL³ hold approximately twice as much water as NiL⁵ with values of 20.72 and 23.97 mg cm⁻³, respectively. The cascades of NiL⁴ retain 116.7 mg cm⁻³, which is 10 times the water of

NiL⁵. The capacitances and system resistances are relatively constant for NiL², NiL⁴, and NiL⁵ and can be attributed to the nearly identical π -stacking distances of the metal complexes. The H-bonding motifs facilitate orientation of the metal stacks to support propagation of the charge carriers, but do not appear to be directly involved in charge propagation. The thermal properties of the hydrated structures correlate with the differences in the H-bonding motifs. These results offer promise for the rational design of H-bonding motifs based on small changes in the host framework with predictable physical properties.

Scheme 3.2. Stacking arrangements of complexes NiL^2 , NiL^3 , NiL^4 and NiL^5 .

From a design standpoint the *N*-(2-aminoethyl)-1-methylimidazole-2-carboxamide building block (and related motifs) can be assembled as solids with tunable conductivity. This could be accomplished by varying the ligand backbone or other substituents to modulate the spacing between complexes in the stack. Further, modification of the steric bulk around the carboxamido-O can be used to control the H-bonding motif and dehydration temperatures. The combination of these two effects can be employed to design materials that undergo structural changes upon dehydration with quantifiable effects on the charge transfer properties of the materials. Studies of this type are presented in chapter V.

CHAPTER IV

1D WATER WIRES IN ISOSTRUCTURAL Cu(II) & Ni(II) COMPLEXES: SYNTHESIS, CHARACTERIZATION, AND THERMAL ANALYSES

4.1. Introduction

In Chapter III a series of structurally related hydrated (N₃X)Ni(II) complexes, where X = S or O, was synthesized and characterized. The complexes contained a common *N*-(2-aminoethyl)-1-methylimidazole-2-carboxamide motif on one-half of the chelate ligand and variable NX motifs on the other half. Changes in the NX motif resulted in variation of the H-bonding network allowing the isolation and characterization of H-bonding streams, pools, and cascades. In the current chapter, the synthesis and characterization of the related symmetric ligand *N,N'*-(ethane-1,2-diyl)bis(1-methyl-1*H*-imidazole-2-carboxamide) (H₂L⁶) and its Cu(II) and Ni(II) complexes are described. The crystal structures with this new ligand reveal one-dimensional water wires.

Structural engineering of supramolecular motifs, such as metal-organic frameworks (MOFs), with desired topologies and properties including catalytic activity, electrical conductivity, magnetic properties, and pharmacological activity^{135- 136} constitute a major area of supramolecular chemistry. The self-assembly of supramolecular structures depends on a variety of factors. These include interactions between the metal and the ligands,

solvent, and solution conditions such as pH. Organic ligands that are capable of intermolecular interactions such as π - π stacking¹³⁷ and H-bonding in addition to van der Waals forces assist in building the network.¹³⁸⁻¹³⁹ The choice of the organic ligand depends on steric and electronic factors, the flexibility and length of the ligands, and the relative position of the functional groups.¹⁴⁰ MOFs are attractive materials for preparing proton conductors due to their highly designable structure and diverse topological architecture.¹⁴¹⁻¹⁴³ Smaller and more easily accessible metal complexes that possess supramolecular properties such as extended π - π stacking, extensive H-bonding and porous networks are also viable candidates to generate solid state materials for proton conduction.¹³⁷

The design and engineering of host environments for stabilizing various discrete water clusters are well documented.¹⁴⁴⁻¹⁴⁵ Water clusters in confined environments, such as 1D coiled waters, display enhanced proton conductivity in response to electrochemical potential gradients.¹⁴⁶⁻¹⁴⁸ Furthermore, 1D water chains play a vital role in the biological transport of water, protons, and ions.¹⁴⁹⁻¹⁵² The transport of water or protons across the cell membrane involves the assembly of highly mobile water molecules H-bonded into a single chain at the positively charged constricted pore of the membrane-channel protein, aquaporin-1.¹⁵³

This chapter focuses on the synthesis and characterization of isostructural Cu(II) and Ni(II) complexes of the N₄ chelate ligand H₂L⁶. The X-ray characterization of these complexes shows that these structures are hydrated forming 1D coiled water chains through H-bonding networks within crystal lattices that are described in detail and related to the thermal stability of the complexes. The results presented in this chapter have previously been published¹⁵⁴

4.2. Results and Discussion

4.2.1. Synthesis and Characterization

The ligand H_2L^6 was prepared through a single step via the condensation of one equivalent of ethylenediamine with two equivalents of ethyl 1-methylimidazole-2-carboxylate.¹⁵⁵ The isostructural complexes CuL^6 and NiL^6 were synthesized through the reaction between N',N' -(ethane-1,2-diyl)bis(1-methyl-1*H*-imidazole-2-carboxamide) (H_2L^6) and acetate salts of Cu(II) and Ni(II), respectively, Scheme 4.1. The CuL^6 complex was isolated as dark red powder, while the NiL^6 complex yielded an orange powder. The UV–visible spectra of CuL^6 and NiL^6 were recorded in acetonitrile, Figures 4.1 and 4.2. The electronic spectrum of the square planar CuL^6 complex displays charge transfer bands at 204 and 258 nm and a d-d transition at 503 nm. Similarly, complex NiL^6 shows absorbances at 206, 256 and 336 nm associated with charge transfer bands and a d-d transition at 468 nm.

Scheme 4.1. Synthetic pathway for complexes CuL^6 and NiL^6 .

Figure 4.1. UV-visible spectrum of CuL^6 in CH_3CN .

Figure 4.2. UV-visible spectrum of NiL^6 in CH_3CN .

The FT-IR spectra of CuL^6 and NiL^6 were collected on crystalline samples by attenuated total reflectance (ATR correction), Figures 4.3 – 4.5. The spectra of CuL^6 and NiL^6 show distinct C-N and C=O stretches associated with the carboxamide moiety that are shifted relative to H_2L^6 due to deprotonation. The $\nu_{\text{C=O}}$ stretches in CuL^6 and NiL^6 are 1604 and 1600 cm^{-1} , respectively and are shifted from 1635 cm^{-1} in H_2L^6 . Additionally, the $\nu_{\text{C-N}}$ stretches in CuL^6 and NiL^6 are identical with a value of 1450 cm^{-1} that is shifted from 1527 cm^{-1} in H_2L^6 , Table 4.1.

Table 4.1. Selected stretches (cm^{-1}) in FT-IR spectra of H_2L^6 , CuL^6 , and NiL^6 .

Moiety	H_2L^6	CuL^6	NiL^6
C = O	1635	1604	1600
C – N	1527	1450	1450

Figure 4.3. FT-IR spectrum of H_2L^6 .

Figure 4.4. FT-IR spectrum of CuL⁶.

Figure 4.5. FT-IR spectrum of NiL⁶.

4.2.2. X-ray Crystallography

Single crystals of CuL^6 and NiL^6 were analyzed by single crystal X-ray diffraction in collaboration with Dr. Mark Mashuta. Data has been deposited in the Cambridge Crystallographic Data Center as CCDC-1893397 and CCDC-1893398. Crystal data and structure refinement details are listed in Table 4.2.

Complex CuL^6 crystallizes as red cubes that isostructural with the orange cube crystals of NiL^6 . Both complexes are in the monoclinic space group $P2_1/c$. The complexes contain water of hydration through H-bonding interactions with the metal-ligand complex. A summary of bond distances and angles for CuL^6 and NiL^6 is listed in Table 4.3 with a summary of H-bonding metric parameters presented in Table 4.4.

The asymmetric unit of CuL^6 contains two equivalents of CuL^6 and four molecules of water of hydration, Figure 4.6. Three waters of hydration are modeled with full occupancy oxygen (O5, O6, and O7) and hydrogen atoms. Additionally, the fourth water molecule is modeled with half occupancy oxygen (O8) and hydrogen atoms. The Cu(II) centers (Cu1 and Cu2) are coordinated in a pseudo-square planar environment and bond distances between Cu(II) centers and each of donors (N1, N3, N4, N5, N7, N9, N10 and N11) are at the range of 1.913(2) – 1.984(2) Å, which are nearly longer than reported values for the counterpart bonds in NiL^6 , Table. 4.3.

Table 4.2. Crystal data and structure refinement for CuL⁶ and NiL⁶.

Identification code	CuL ⁶	NiL ⁶
Empirical formula	C ₄₈ H ₅₆ Cu ₄ N ₂₄ O ₈ ·7H ₂ O	C ₄₈ H ₅₆ Ni ₄ N ₂₄ O ₈ ·6.4H ₂ O
Formula weight	1477.44	1447.31
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	24.117(5)	23.767(2)
<i>b</i> (Å)	7.0125(15)	7.0356(6)
<i>c</i> (Å)	18.203(4)	18.0114(15)
α (deg)	90.00	90.00
β (deg)	105.597(3)	105.4480(10)
γ (deg)	90.00	90.00
<i>V</i> (Å ³)	2965.1(11)	2902.93
<i>Z</i>	2	2
<i>d</i> _{calcd} (Mg m ⁻³)	1.657	1.656
Abs coeff (mm ⁻¹)	1.502	1.365
<i>F</i> (000)	1524	1504
Cryst. Color and habit	Red block	Orange block
Cryst size (mm ³)	0.21 × 0.17 × 0.12	0.24 × 0.17 × 0.10
θ range for data coll. (°)	3.03 to 26.75	3.12 to 27.25
Index ranges	-30 ≤ <i>h</i> ≤ 30 -8 ≤ <i>k</i> ≤ 8 -23 ≤ <i>l</i> ≤ 23	-30 ≤ <i>h</i> ≤ 29 -8 ≤ <i>k</i> ≤ 9 -23 ≤ <i>l</i> ≤ 22
Reflns collected	24001	23403
Independent reflections	6272 [<i>R</i> (int) = 0.0295]	6449 [<i>R</i> (int) = 0.0211]
Completeness to theta max	99.6%	99.7%
Absorption correction	multi-scan	multi-scan
Max., min transmission	0.975 and 0.815	0.978 and 0.855
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/params	6272/8/451	6449/3/432
Goodness of fit on <i>F</i> ²	1.087	1.031
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^{a,b}	<i>R</i> ₁ = 0.0405	<i>R</i> ₁ = 0.0282
<i>R</i> indices (all data) ^{a,b}	w <i>R</i> ₂ = 0.1031 <i>R</i> ₁ = 0.0433 w <i>R</i> ₂ = 0.1048	w <i>R</i> ₂ = 0.0683 <i>R</i> ₁ = 0.0337 w <i>R</i> ₂ = 0.0709
Largest diff. peak and hole (e·Å ⁻³)	0.625 and -0.357	0.450 and -0.252

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$, where $w = q / \sigma^2(F_o^2) + (qp)^2$ + bp. GOF = $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined.

Table 4.3. Selected bond distances (Å) and bond angles (°) in CuL⁶ and NiL⁶ complexes.

Bonds	CuL ⁶	NiL ⁶
M1-N3	1.913(2)	1.8305(14)
M1-N4	1.934(2)	1.8469(14)
M1-N1	1.957(2)	1.8838(14)
M1-N5	1.970(2)	1.8971(14)
M2-N10	1.919(2)	1.8381(15)
M2-N9	1.922(2)	1.8404(15)
M2-N7	1.974(2)	1.9001(14)
M2-N11	1.984(2)	1.9013(15)
Angles		
N3-M1-N4	82.90(10)	84.75(6)
N3-M1-N1	84.08(10)	85.13(6)
N4-M1-N1	166.97(9)	169.81(6)
N3-M1-N5	166.44(10)	169.81(6)
N4-M1-N5	83.63(9)	85.06(6)
N1-M1-N5	109.39(9)	105.06(6)
N10-M2-N9	82.87(10)	84.44(6)
N10-M2-N7	166.47(10)	169.41(7)
N9-M2-N7	83.85(10)	84.97(6)
N10-M2-N11	83.22(10)	84.77(7)
N9-M2-N11	166.08(10)	169.18(6)
N7-M2-N11	110.02(10)	105.81(6)

Table 4.4. Selected H-bond metrics for CuL⁶ and NiL⁶ complexes.

D-H...A	H...A (Å)	D...A (Å)	D-H...A (°)
CuL⁶			
O5-H5ob...O(3) ⁱ	1.94(2)	2.777(3)	169(4)
O5-H5oa...O(6)	1.843(19)	2.698(3)	178(4)
O6-H6ob...O(5) ⁱ	1.914(19)	2.769(3)	177(4)
O6-H6oa...O(1)	1.89(2)	2.742(3)	170(4)
O7-H7ob...O(2)	1.99(2)	2.814(3)	164(5)
O7-H7oa...O(2) ⁱⁱ	1.91(2)	2.738(3)	167(4)
O8-H8oa...O(4)	1.98(3)	2.837(6)	168(9)
Symmetry codes: i = (-x, y + 1/2, -z + 1/2); ii = (-x + 1, -y + 1, -z + 1).			
NiL⁶			
O5-H5oa...O(6)	1.88(3)	2.691(2)	175(3)
O5-H5ob...O(3) ⁱ	2.00(3)	2.7718(19)	172(2)
O6-H6ob...O(1) ⁱⁱ	1.93(3)	2.7256(19)	174(3)
O6-H6oa...O(5) ⁱⁱⁱ	1.937(17)	2.766(2)	174(2)
O7-H7oa...O(2) ^{iv}	1.94	2.7538(18)	169.0
O7-H7ob...O(2) ^v	2.04	2.8454(19)	173.0
Symmetry codes: i = (-x, -y + 1, -z + 1); ii = (x, y, z + 1); iii = (-x, y + 1/2, -z + 3/2); iv = (x, -y + 3/2, z + 1/2); v = (-x + 1, y + 1/2, -z + 1/2).

Figure 4.6. ORTEP representation of the asymmetric unit of CuL^6 with thermal ellipsoids shown at the 50% probability level.

The molecules of water of hydration in CuL^6 participates in multiple H-bonding interactions. The O7 water molecule bridges two symmetrically equivalent metal complexes through H-bonding interactions of H7oa and H7ob with the carboxamide oxygen atoms O2^{ii} ($-x+1, -y+1, -z+1$) and O2 (x, y, z), respectively. These two H-bonds are slightly bent with an $\text{O7-H7oa}\cdots\text{O2}^{\text{ii}}$ ($-x+1, -y+1, -z+1$) angle of $167(4)^\circ$ and $\text{O7-H7ob}\cdots\text{O2}$ angle of $164(5)^\circ$. The donor-acceptor ($\text{D}\cdots\text{A}$) and hydrogen acceptor ($\text{H}\cdots\text{A}$) distances of $\text{O7-H7oa}\cdots\text{O2}$ are $2.738(3)$ Å and $1.91(2)$ Å, respectively and are consistent with a strong interaction. Similarly, ($\text{D}\cdots\text{A}$) and ($\text{H}\cdots\text{A}$) distances of $\text{O7-H7ob}\cdots\text{O2}$ are

2.814(3) Å and 1.99(2) Å, respectively and indicate characteristics of a strong interaction. Both O5 and O6 are involved in 3 H-bonding interactions each and contribute both as H-bond donors and acceptors. Each serves as a H-bond donor to a carboxamido O of the ligand backbone. O5 exists in a nearly linear H-bonds with O3ⁱ ($-x, y+1/2, -z+1/2$) with a O5-H5ob...O3ⁱ angles of 169(4)° and (D...A) and (H...A) distances of 2.777(3) Å and 1.94(2) Å, respectively.

A similar H-bonding interaction is observed between O6 and O1 with a O6-H6oa...O1 angle of 170(4)° and (D...A) and (H...A) distances of 2.742(3) Å and 1.89(2) Å. In addition, O5 and O6 water molecules are linked through a pair of strong H-bonding interactions in which each serves as a donor and acceptor. As a donor, O5 exists in nearly linear H-bonds with O6 with a O5-H5oa...O6 angle 178(4)° and (D...A) and (H...A) distances of 2.698(3) Å and 1.843(19) Å, respectively. The O6 water molecule serves as an donor with a nearly linear H-bond to O5ⁱ ($-x, y+1/2, -z+1/2$) with a O6-H6ob...O5ⁱ angle of 177(4)° and related (D...A) and (H...A) distances of 2.769(3) Å and 1.914(19) Å. The water molecule O8 participates in only one H-bond, with the caboxamido oxygen O4. The absence of an extended H-bonding network for O8 is consistent with its lower occupancy (50%) in the crystal lattice. The O8-H8oa...O4 angle is slightly bent, 168(9)°. The (D...A) and (H...A) distances of 2.837(6) Å and 1.98(3) Å, respectively, are associated with a strong H-bonding interaction. The extended H-bonding networks in CuL⁶ can be described as 1D coiled zigzag chains of water along the *b* direction that are anchored to stacked metal complexes, Figures 4.7 and 4.8. Using the graph set notation,¹²⁴ the 1D water coiled chain is described as C²₂(4) (blue dotted line). The C²₂(4) chains are held between carboxamide oxygens (O1 and O3) by two D²₂(5) motifs (red dotted line). Further,

carboxamide oxygens O2 also participate in $R^2_4(8)$ motif (green dotted line) which result in formation of isolated water pools. These pools are orienting the complexes into a twisted AAAA stacking arrangement.

The asymmetric unit of NiL^6 contains two equivalents of NiL^6 and four waters of hydration, Figure 4.9. Each Ni center is coordinated to four donors (four N atoms of the ligand) in a pseudo square planar geometry with bond distances in the range of 1.830 – 1.901 Å which are shorter than the reported counterpart values in CuL^6 , Table 4.3. Three waters of hydration are modeled with full occupancy oxygen atoms, O5, O6, and O7. The fourth water molecule, O8, is modeled with 20% occupancy. The Ni center of NiL^6 similar to CuL^6 sits in the same N_4 donor environment arranged in pseudo square planes. The four water molecules of hydration in NiL^6 are involved in H-bonding interactions similar to CuL^6 (Figure 4.10, Table 4.4).

Figure 4.7. The 1D H-bonding wire of water in complex CuL^6 . H-bonding interactions are denoted by black dashed lines. The graph sets are noted by dotted colored lines as follows: $C^2_2(4)$ (blue); $D^2_2(5)$ (red); $R^2_4(8)$ (green). Atoms generated by symmetry are marked as follows: $\text{iii} = (-x, \frac{1}{2}+y, \frac{1}{2}-z)$, $\text{iv} = (x, 1+y, z)$, $\text{v} = (1-x, 2-y, 1-z)$.

Figure 4.8. An extended view of the water wire in CuL^6 . Hydrogen atoms of the ligands are omitted for clarity.

Figure 4.9. ORTEP representation of the asymmetric unit of NiL^6 with thermal ellipsoids shown at the 50% probability level.

Figure 4.10. The 1D H-bonding wire of water in complex NiL^6 . H-bonding interactions are denoted by black dashed lines. The graph sets are noted by dotted colored lines as follows: $C^2_2(4)$ (blue); $D^2_2(5)$ (red); $R^4_4(8)$ (green). Atoms generated by symmetry are marked as follows: $\text{vi} = (-x, \frac{1}{2}+y, \frac{1}{2}-z)$, $\text{vii} = (-x, 1-y, -z)$, $\text{viii} = (x, y, -1+z)$, $\text{ix} = (-x, -\frac{1}{2}+y, -\frac{1}{2}-z)$, $\text{x} = (-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, $\text{xi} = (-x, \frac{1}{2}+y, -\frac{1}{2}-z)$, $\text{xii} = (-x, 2-y, -z)$, $\text{xiii} = (-1+x, 1.5-y, -\frac{1}{2}+z)$, $\text{xiv} = (-1+x, y, -1+z)$.

4.2.3. Thermal Analyses

TGA and DSC traces of complexes CuL^6 and NiL^6 are shown in Figures 4.11 – 4.14. In complexes CuL^6 and NiL^6 , there is a clear dehydration step beginning near 40 °C with a mass loss of 10.13 and 7.96%, respectively, upon reaching 120 °C. The mass change is consistent with loss of four water molecules per complex CuL^6 and 3.2 water molecules per complex NiL^6 from the lattice. Decomposition of the ligand frame work of CuL^6 and NiL^6 occurs above 280 °C and 300 °C, respectively. Degradation is accompanied by a phase transition as indicated by the endothermic process observed by DSC.^{133,134} The mass of the residue is consistent with the formation of the metal oxide. In comparison to previously reported compounds confining 1D water chains¹²⁷, complex CuL^6 and NiL^6 also show the same correlation between H-bonding motif of the hydrated crystals and temperature range of the dehydration process. Similarly, the 1D coiled chains require a higher temperature to break the strong H-bonding interactions within the channel and between the water and structural O atoms.

Figure 4.11. TGA of CuL⁶.

Figure 4.12. DSC of CuL⁶.

Figure 4.13. TGA of NiL^6 .

Figure 4.14. DSC of NiL^6 .

4.2.4. Electrochemical Impedance Spectroscopy (EIS)

The impedance of crystal NiL^6 was evaluated using electrochemical impedance spectroscopy (EIS). Two peaks (time constants) were observed in the Bode representation of phase angle vs. frequency, Figure 4.15 (red trace) indicating the presence of two interfacial electrochemical processes in NiL^6 under the experimental conditions explained in Chapter 2 (2.5). The presence of two time constants is also confirmed by the Nyquist representation, Figure 4.15, which shows two semicircles. A single time constant is typically modeled with a single RC element (resistor and constant phase element in parallel).¹³⁰ Therefore, in this case, we modeled the system¹⁵⁶ with two RC elements to account for each time constant and an additional resistive element, R1, which accounts for the equivalent series resistance of the system, including wires and contacts (R-(CPE1//R2)-(CPE-2//R3)), Figure 4.16. The phase peak at high frequency in Figure 4.15 A, the left-hand semicircle in Figure 4.15 B, and the R2//CPE1 element in Figure 4.16 correspond to time constant 1. Conversely, the phase peak at lower frequency in Figure 4.15 A, the right-hand in complete semicircle in Figure 4.15 B, and the R3//CPE2 element in Figure 4.16 correspond to time constant 2. Parameters obtained by fitting the impedance data to the equivalent circuit model are presented in Table 4.5.

The total impedance, Z, is a combination of real (Z') and imaginary (Z'') contributions to impedance.¹⁵⁷ At high frequency (~100kHz), the real (resistive) component of impedance represents the approximate system resistance. For NiL^6 , the system resistance (RES, Table 4.5) is approximately 360 Ω . The imaginary component, Z'', constitutes both capacitive and inductive contributions to the overall impedance. In this case, both resistive and capacitive elements contribute to the system impedance. The

capacitances for time constants 1 and 2 were determined to be approximately 0.1 nF and 1 μ F, respectively. The presence of two time constants in NiL⁶ suggests the presence of two different types of domains within the structure of the material. Introducing additional water as a dielectric into a capacitive system decreases the electric field strength, which decreases the voltage and in turn increases the capacitance. Because the capacitance of time constant 2 is several orders of magnitude higher than that of time constant 1, we postulate that the domain corresponding to time constant 2 is significantly more water-permeable and amenable to charge conduction. This wet domain (time constant 2) could be associated with water wire clusters within 2, while the dry domain corresponds to time constant 1 which was preliminarily associated with charge transfer through desiccated regions of 2 which are water-deficient.¹⁵⁴ Further studies of this type are discussed in Chapter 5 including an alternate circuit model for the data.

Figure 4.15. Bode (A) and Nyquist (B) representations of impedance data for NiL⁶. Dots represent individual data points, while lines represent the equivalent circuit fit.

Figure 4.16. Equivalent circuit used to fit impedance data for NiL⁶.

Table 4.5. Parameters calculated from fitting impedance data for NiL⁶ complex to the equivalent circuit.

R_{ES} (Ω)	Time Constant	R_{CT} (Ω)	n	Q (F sⁿ⁻¹)	C (F) = R^{(1-n)/n} Q^{1/n}
363.3	1	197000	0.998	9.46E-11	9.25578E-11
	2	1125000	0.634	9.70E-7	1.02015E-06
χ²		0.0056			

4.3. Conclusion

The H-bonding motifs in isostructural planar CuL⁶ and NiL⁶ complexes are identical due to similar crystal packing of the host molecules, Figures 4.7 and 4.10. The interlayer H-bonding interactions in CuL⁶ and NiL⁶ result in a twisted AAAA stacking arrangement, which positions the carbonyl O atoms to be in interaction with water molecules confined in coiled 1D chains. The thermal properties of the hydrated structures correlate with the identical H-bonding motifs. The H-bonding motifs facilitate orientation of the metal stacks to support propagation of the charge carriers. Based on EIS there are two types of domains present in the structure which correlate with two distinct charge transfer pathways. The effects of H-bonding interactions and the adsorption/desorption of moisture on the conductivity of NiL⁶ is examined in Chapter 5.

CHAPTER V

REVERSIBLE CONDUCTIVITY CHANGES UPON ADSORPTION/DESORPTION
OF MOISTURE IN SINGLE CRYSTALS CONTAINING 1D COILED ZIG-ZAG
CHAINS OF WATER

5.1. Introduction

Water is a remarkable molecule and its complex molecular behavior continues to generate intense scientific interest.^{158,159} It plays a crucial role in biochemical processes¹⁶⁰⁻¹⁶² and the development of biomimetic artificial water channels have led to a greater understanding of the hydrodynamics of water in confined environments.¹⁶³⁻¹⁶⁶ There are also numerous examples of water clusters of various shapes and sizes in different host matrix environments.¹⁶⁷⁻¹⁷² The pores and channels generally are lined with organic moieties containing carbonyl, amine, or hydroxyl groups that facilitate hydrogen bonding. Within these channels, water serves as a conduit for proton mobility along water wires according to the Grotthuss¹⁷³⁻¹⁷⁵ and vehicle mechanisms.¹⁷⁶ Dehydration of the channel may be irreversible due to collapse of the structure or reversible via single crystal to single crystal structural transformations with considerable changes in the material properties between the hydrated and dehydrated states.^{177,178} Recently, materials that undergo reversible structural transformation upon hydration have been employed to study proton

propagation relevant to proton-exchange membranes or humidity sensors. Several metal-organic framework (MOF) materials demonstrate high proton conductivity under humid (94 – 98%) conditions attributed to an extended hydrogen-bonding network within the material upon hydration.¹⁷⁹⁻¹⁸⁴ One of the MOFs demonstrated potential applicability as a humidity sensor with a five orders of magnitude enhancement in conductivity when the relative humidity was increased from 40% to 95%.¹⁸⁵ Similarly, an iron based perovskite $\text{BaFeO}_{2.5-x}(\text{OH})_{2x}$,¹⁸⁶ an open-framework chalcogenide,¹⁸⁷ and a porous organic molecular material¹⁸⁸ demonstrated reversible increases in conductivity upon adsorption of water into the lattice. Proton conductivity has also been observed in coordination polymers through extended water networks between 2D layers¹⁸⁹ and in single crystals of coordination polymers.¹⁹⁰ Further evaluation identified two mechanisms for the enhanced conductivity at higher humidity of the single crystal with a lower barrier route attributed to a proton hopping mechanism through the interior of the crystal and a higher barrier route associated with mass transport on the crystal surface.¹⁹⁰

Water also displays unique properties when confined to a 2D surface. For instance, the structure and dynamics of water at mineral surfaces varies significantly from bulk water due to surface-specific hydrogen bonding, orientation, and ordering that is dependent on the hydrophilicity/hydrophobicity of the mineral surface.¹⁹¹ Relative to bulk water, water confined into 2D layers participate in fewer hydrogen bonds per molecule with decreased H-bond life times and increased lateral diffusion.¹⁹² Charge propagation through water on surfaces has largely been attributed to the presence of Zundel¹⁹³ and Eigen¹⁹⁴ ions or small water clusters¹⁹⁵ that influence surface electrical and ionic conduction via an electrochemically mediated charge transfer process. The pH of the ambient environment

dictates the direction to or from the host matrix of the charge transfer. The organization of water on surfaces has also been exploited to enhance proton conductivity. Unlike the materials that undergo structural changes upon adsorption of water into the lattice, the surface adsorption of water relies on interactions with surface features to organize water networks. For example, oxygen deficiencies in a 2D $\text{Ti}_3\text{C}_2/\text{TiO}_2$ composite provides a surface capable of detecting water over a wide relative humidity range (9 – 97%) through changes in conductivity. Ultrafast humidity detection was obtained using 2D graphene oxides that used changes in impedance to detect changes in humidity near the sensor associated with activities such as speaking, breathing, or whistling.¹⁹⁶

In Chapter 4, the HB motifs in the isostructural complexes CuL^6 and NiL^6 were described as 1D water wire aligned along the crystallographic *b*-axis. The EIS of these complexes reveals the presence of two of domains in the structure, which correlate with two distinct charge transfer pathways. The current chapter focuses on the changes in conductivity of NiL^6 crystals upon adsorption/desorption of moisture. The obtained results demonstrate significant and reversible change in conductivity associated with surface bound water molecules on the 010 crystal face. The results presented in this chapter will be included in a manuscript in preparation for submission.¹⁹⁷

5.2. Results and Discussion

5.2.1. Crystal Structure of Water Wire

As described in Chapter 4 section 4.2.2, the crystal structure of NiL^6 contains water molecules that H-bond with carboxamide oxygens that act as anchor spots to orient water into single file water wires in the lattice, Figure 5.1.A. In fact, crystals of NiL^6 contain two

crystallographically distinct NiL^6 equivalents and four unique water sites; three of which are full occupancy and one with partial occupancy. Individual water wires composed of O5 and O6 water molecules are arranged as $C^2_2(4)$ coiled chains. The 1-D wires are anchored by carboxamide oxygens (O1 and O3) through additional H-bonds. Between the 1-D water wires are two additional water molecules. The structural water molecule is H-bonded in a $R^2_4(8)$ ring motif with O2 carboxamide oxygens. The volatile O8 water molecule (not shown) sits nearest the 1-D water chain 7.68 and 7.65 Å from O5 and O6, respectively, and is in close contact with O7, 4.02 Å. Notably, O8 only participates in one H-bond consistent with its lower occupancy (20%) in the crystal lattice, Figure 5.1.A. In fact, the 1D water wires propagate along the b-axis to form parallel channels along the 010 face of the crystal. To index the crystal faces, the short edge of an orange, plate shaped single crystal of NiL^6 was mounted on a glass fiber, Figure 5.1.B. The goniometer was then rotated to collect data along the 010 face. The data clearly identifies the broad, flat face of the NiL^6 crystals as the 010 plane.

Figure. 5.1. A) Illustration of the extended hydrogen bonding network in NiL^6 highlighting the positions of the water wire (O5 and O6), structural water (O7), and volatile water (O8) relative to the nickel complex. B) Single crystal of NiL^6 .

5.2.2. Reversible Conductivity

A single plate-shaped crystal of $\text{NiL} \cdot \text{H}_2\text{O}$ was mounted on a measurement chip that was loaded into a two-probe resistance measurement system that allowed for precise control of the water vapor pressure, Figure. 5.2 and 5.3. A potential of 0.01 V was applied to determine the current of the intact crystal under initial, atmospheric conditions of $T = 26^\circ\text{C}$ and $P_{\text{H}_2\text{O}} = 25.2$ torr. As shown in Figure 5.4, a constant current of 52 ± 3 nA was maintained for 7 - 8 minutes. Upon applying vacuum to reduce $P_{\text{H}_2\text{O}}$ to 8 torr, the current rapidly dropped to a steady value of 8 ± 3 pA (*dry conditions*). Then, water vapor was introduced to the system until the $P_{\text{H}_2\text{O}}$ reached 17 torr. Within several minutes a constant current of 52 ± 3 nA was re-established (*wet condition*). Multiple cycles of desorption and adsorption were performed with reproducible results. The behavior is consistent with modulation of surface conductivity through the formation and disruption of organized water motifs demonstrated by the initial EIS studies section 4.2.4 of the prior chapter. The phenomenon is reproducible using different crystals of NiL^6 , although the value of current under wet conditions is dependent on the crystal size and electrode placement.

Figure 5.2. Schematic of the two probe AC resistance measurement using a lock-in technique.

Figure 5.3. Glass apparatus for *in-situ* electrical resistance measurements and electrochemical impedance spectroscopy studies.

Figure 5.4. Reversible conductivity measured on a single crystal of NiL^6 upon desorption/adsorption of moisture. The maximum conductivity was reached at 17 torr of water vapor pressure (the lowest current value is in the range of 10 pA and not zero).

From the structural point of view, x-ray data verifies that the presence of π - π stacking between adjacent imidazole rings along the *b*-axis provides a robust framework for making hydrogen bonds with, Figure 5.5. This robust framework does not collapse under vacuum and remains intact even after numerous cycles of desorption/adsorption, therefore prevents disintegration of water chains during desorption stage of the experiment. However, fine powder of NiL⁶ obtained from grinding the single crystals loses its crystallinity completely within two days and therefore cannot maintain the robust framework and accordingly water wires.

Figure 5.5. Viewing along *b*-direction shows π - π stacking distances of adjacent imidazole rings.

5.2.3. Electrochemical Impedance Spectroscopy (EIS)

As noted in Chapter 4 section 4.2.4, preliminary EIS studies on NiL⁶ showed two time constants in both Bode and Nyquist representations demonstrating the presence of two charge transfer pathways. In this chapter, these studies are done under dehydrated and hydrated conditions and results are discussed in details. In fact, in order to study the charge transfer mechanism in NiL⁶ in greater detail and refine the capacitor or resistor characteristics upon adsorption (*wet*) and desorption (*dry*) conditions, additional EIS experiments were performed. Specifically, EIS was performed under vacuum (8 torr), *dry condition*, as well as at $P_{\text{H}_2\text{O}} = 17$ torr, *wet condition*, and parameters such as capacitance (C), constant phase (n) and (Q) factor were calculated based on the fitted circuit models that explain the differences in charge transfer under hydrated and dehydrated conditions.

A single crystal of NiL⁶ mounted on the chip carrier was enclosed in the system used to measure two probe resistance. A vacuum of 8 torr was applied for 5 minutes after which the resistance was measured to confirm the dehydrated state, ($i = 5\text{-}10$ pA). While maintaining the system under vacuum in two-probe resistance measurement setup, EIS data was collected in collaboration with the working/working sense and counter/reference electrode ports of a Metrohm Autolab PGSTAT128N potentiostat/galvanostat, who fit the data in an electrical circuit model using the method of least squares. In this model, the data was fit using single Constant Phase Element (CPE), Figures 5.6. Selected parameters including capacitance and capacitor ideality are tabulated in Table 5.1.

As shown in Figures 5.7, there is no peak (time constant) in the plot of phase angle vs. frequency indicating no Faradic electrochemical processes occur within the dehydrated NiL⁶ single crystal at the applied biases. The total impedance, Z, is a combination of real

(Z') and imaginary (Z'') contributions. At high frequency (~ 100 kHz), the real component represents the system resistance and the imaginary component involves inductive and capacitive contributions to impedance. Also, analysis of the Nyquist representation (Z' and $-Z''$) for NiL^6 shows that Z'' changes with frequency, in the high frequency domain, while Z' remains relatively constant, Figures 5.8. This indicates the majority of the system impedance is caused by capacitive elements, rather than resistive elements. The impedance of an ideal capacitor is inversely proportional to frequency and this trend is observed for dehydrated NiL^6 which demonstrates that it behaves as a capacitor with a small degree of non-ideality (n , a measure of capacitor ideality, is approximately 0.960 - 0.962 for the dehydrated NiL^6 ; $n = 1$ for an ideal capacitor). The measured capacitance of dehydrated NiL^6 is approximately 0.148 – 0.150 nF, which indicates a rather poor ability to store a charge across the double layer (through water chain). This is due to the low density of dielectric (adsorbed water) under dehydrating conditions (vacuum / 8 torr). In fact, this result is intuitive since dehydrated NiL^6 crystal cannot serve as a medium for charge transfer, hence the lack of resistive elements in the circuit model, despite the presence of structural water wires within the material cannot facilitate internal charge transfer. Instead, in this state, charge is built between the electrodes, across the crystalline material which acts as a dielectric.

Figure 5.6. Equivalent circuit used to fit impedance data of dehydrated single crystal of NiL^6 .

Figure 5.7. Bode (A) and Nyquist (B) representations of impedance data for the dehydrated single crystal of NiL^6 . Dots represent individual data points, while lines represent the equivalent circuit fit. The data truncated with CPE Fit.

Table 5.1. Parameters calculated from fitting impedance data for dehydrated single crystal of NiL^6 to the equivalent circuits.

Equivalent circuit	n	C (F)
CPE	0.962 ± 0.001	$1.48\text{E-}10 \pm 2.26\text{E-}12$

The crystal of NiL^6 was then exposed to 17 torr water vapor pressure for 10 minutes to rehydrate the structure. This was confirmed with a two-probe resistance measurement, which showed a maximum current of ~ 56 nA, and While maintaining the system exposed to 17 torr $P_{\text{H}_2\text{O}}$ in two-probe resistance measurement setup, EIS data was collected in collaboration with the working/working sense and counter/reference electrode ports of a Metrohm Autolab PGSTAT128N potentiostat/galvanostat. The Bode representation, Figure 5.9 part A, shows at least two visually apparent peaks corresponding to two time constants, signifying the presence of at least two interfacial electrochemical processes (two

modes of interfacial charge transfer). The presence of two time constants is confirmed by the Nyquist representation, Figure 5.9 part B, which shows two semicircles.

A single time constant is typically modeled with a single R//C element (resistor and constant phase element in parallel). Therefore, as shown in Figure 5.8, the high-frequency time constant encompasses the constant phase element for the bulk material, as observed in the case of the dehydrated material (note that the values of C_{material} are on the same order of magnitude in both the hydrated and dehydrated states), and a resistor which contains the probe contact resistance and circuit equivalent series resistance ($R_{\text{ES+contact}}$). The low-frequency time constant encompasses a R//C element which arises due to bridging the electrical contacts with water which serves as a conductive dielectric, Figure 5.10. In fact, the capacitance measured for the second time constant, is three orders of magnitude greater than that of the first time constant. This is attributed to adsorption of water molecules on the surface that introduce a dielectric into a capacitive system which decreases the electric field, the voltage (electric potential energy), and in turn increases the capacitance. Clearly, the capacitance is significantly higher for the second time constant in the hydrated NiL^6 compared to the dehydrated state. Selected parameters including capacitance, resistance and capacitor ideality are tabulated in Table 5.2.

Figure 5.8. Equivalent circuit used to fit impedance data of hydrated single crystal of NiL^6 ; (CPE//R-(CPE//R)).

Figure 5.9. Bode (A) and Nyquist (B) representations of impedance data for the hydrated single crystal of NiL⁶. Dots represent individual data points, while lines represent the equivalent circuit fit represented in Figure 5.8.

Table 5.2. Parameters calculated from fitting impedance data for hydrated single crystal of NiL⁶ to the equivalent circuits.

Equivalent circuit	Time Constant	$R_{ES+contact}$ (Ω)	R_{water} (Ω)	n	Q ($F s^{n-1}$)	$C_{material} (F) = \frac{R_{ES+contact}^{(1-n)/n}}{Q^{1/n}}$	$C_{water} (F) = \frac{R_{water}^{(1-n)/n}}{Q^{1/n}}$
(CPE//R-(CPE//R))	1	198000 ± 2000		0.999 ± 0.008	$9.312E-11 \pm 9.280E-12$	$9.19E-11$	
	2		1116000 ± 6400	0.637 ± 0.014	$9.666E-7 \pm 3.524E-8$		$1.01E-06$

Overall, the EIS data is consistent with the presence of two charge transfer pathways. One pathway is always present even in dehydrated state in which NiL⁶ acts as a nearly ideal capacitor, Figure 5.8.A and charge is built on electrodes but cannot be conducted between the electrodes. The other pathway is only in hydrated state and shows the occurrence of two interfacial electrochemical processes. In fact, when 17 torr P_{H_2O} is introduced to the system, structural water chains provide anchor points to adsorb water molecules and develop a subsidiary chain of water on the surface which is able to conduct charge. Due to this development, a R-R//C circuit (which is utilized when water is present

between two electrodes) is appended onto the equivalent circuit model for the dehydrated state, Figure 5.7, to form the equivalent circuit model for the hydrated state shown in Figure 5.9. Electrical properties of the crystal can be discerned by analyzing the shape of the Bode representation in Figure 5.10.A that shows at high frequency, the alternating voltage signal works to build charge across the crystal. As the frequency decreases, charge is transferred between the electrical contacts and water which has agglomerated around the contacts. As the frequency decreases further, charge propagates through the highly resistive subsidiary chain of water on the surface until the frequency is low enough that capacitive charging occurs across the surface water chain, acting as a dielectric, as per Equation 5.1 where Z_C is the impedance of a capacitor, f is the frequency, and C is the capacitance.

$$Z_C = \frac{1}{2\pi fC} \quad \text{Equation 5.1}$$

Above all, for evaluating electronic properties of NiL⁶ through abovementioned experiments and tools, quality of the surface of the crystal as well as the position of copper leads used to make contacts are significantly crucial. In other words, if the surface has significant cracks, attached fine crystals or gets covered by Paratone oil, no change in conductivity upon adsorption/desorption of moisture is observed. Furthermore, if the copper leads make contacts on the opposite sides of the crystal, charge transfer through subsidiary water chains on the surface is not recorded and accordingly EIS data show only one interfacial electrochemical process which belongs to charge propagation along the structural 1D coil water chain (in bulk) and displays a capacitance of nF scale consistent with previously reported value for the first time constant of the hydrated state of NiL⁶.

5.2.4. Thermal Studies of Water Wire

In order to prove that during desorption step in Figure 5.4, no structural water is removed and water chains remain intact, TGA studies were performed. TGA data were collected on samples of NiL^6 single crystals which were kept under vacuum for 15 minutes (10 minutes longer than the desorption stage in the experiment). Obtained results are consistent with the TGA trace of NiL^6 single crystals recorded before applying vacuum, Figure 4.13. It demonstrates that during desorption step of the experiment, water wires remain intact in the lattice and only water molecules adsorbed on the surface of NiL^6 crystal are removed by vacuum. However, if the NiL^6 crystals are kept under vacuum overnight, no water molecule will be found in the lattice, proved by elemental analysis and TGA, Figure 5.11.

Figure 5.10. TGA of the NiL^6 crystals kept under vacuum overnight.

5.2.5. Rate of Hydration as a Function of Pressure (P) and Temperature (T)

As shown in Figure 5.12, at room temperature, 26 °C, increasing the vapor pressure to values greater than 17 torr results in higher rate of adsorption/hydration (larger rate constants, Table 5.3) which accordingly allows the system to reach to the maximum current faster. In other words, as shown in Figure 5.13, at each hydration plot, there are two steps towards reaching saturation state (maximum current). At the first step, water molecules start to get adsorbed to the surface of the NiL^6 crystal and once enough water molecules are available at the surface to make subsidiary water chains (charge-transfer conduit), then noticeable change in current is recorded. Rate of hydration in both of the steps follows the first-order kinetics equation. As such, there is a linear correlation between $\ln I_t$ and duration of hydration and the slope of this plot equals to the rate constant for each step, Figure 5.14.

Figure 5.11. Comparison of hydration/adsorption step at different vapor pressures.

Table 5.3. Rate constant values of hydration/adsorption steps at different vapor pressures.

Rate constant (s^{-1}) - 1 st step	Rate constant (s^{-1}) - 2 nd step	Water vapor pressure (torr)
0.0306	0.0046	17
0.0324	0.0074	20
0.0358	0.0126	23
0.0382	0.0237	27

Figure 5.12. Example of the two-step hydration/adsorption process in NiL^6 single crystal.

Figure 5.13. An example of first-order rate law for the first step (A) and second step (B) of hydration/adsorption process at 27 torr vapor pressure as shown in Figure 5.13.

The observed rate constants at 26 °C for the first step shows a half-order dependence on the P_{H_2O} with a calculated $k_1 = (7.37 \pm 0.05) \times 10^{-3} \text{ torr}^{-0.5} \text{ s}^{-1}$, Figure 5.15 A. The first step is associated with adsorption of water into surface exposed sites in the crystal (O5 – O8) that dissociate under dry conditions. The observed rate constants at 26 °C for the more rapid second step are third-order dependent on the P_{H_2O} with a calculated $k_2 = (1.13 \pm 0.06) \times 10^{-6} \text{ torr}^{-3} \text{ s}^{-1}$, Figure 5.15 B. The second step is associated with formation of the organized water network and includes additional water molecules adsorbed on the crystal surface.

Figure 5.14. Linear correlation of calculated rate constants with different vapor pressures for the first step (A) and second step (B) of hydration/adsorption process.

Other environmental factor to be discussed is temperature whose effects on adsorption/desorption process, rate of charge transfer and reversibility of conductivity change upon moisture adsorption/desorption, were studied. The first experiment in this study was designed to compare maximum conductivity at 17 torr for different temperatures higher than ambient condition (26 °C), Figure 5.16. For this experiment, first the system was exposed to 17 torr vapor pressure and once the maximum current was reached, then 10 minutes were considered for maintaining the condition and calculating the average value

of maximum current at room temperature. Then, the vacuum chamber opened which followed by desorption stage and the system was maintained under vacuum for 5 minutes. At this step, furnace was set to 30 °C and the system was exposed to 17 torr vapor pressure and maintained for 10 minutes to calculate average value of maximum current at this temperature. Repeatedly, this step was followed by opening the vacuum chamber and keeping the system under vacuum for 5 minutes. This procedure repeated for 35 °C, 40 °C and 50 °C and at each temperature, the system was kept at 17 torr for 10 minutes and under vacuum for 5 minutes. As shown in Figure 5.16, while exposing the system to certain vapor pressure, increasing the temperature results in lower current values and accordingly slower charge transfer. In other word, at higher temperatures, the system requires longer time to reach to the saturation and the recorded maximum current for room temperature. It means that increasing the temperature interferes the adsorption process and formation of subsidiary water chains which slow saturation and maximum charge transfer.

Figure 5.15. Monitoring conductivity of a single crystal of NiL^6 over gradual increasing of temperature.

In order to confirm that heating does not affect the structural framework of NiL^6 and reversible change in conductivity upon adsorption/desorption is observed, another experiment was designed as shown in Figure 5.17. In this experiment (at 17 torr vapor pressure), at the beginning, the system is heated to 50 °C where the minimum conductivity of NiL^6 is recorded and by gradual decreasing of the temperature, larger values for current is observed and eventually at room temperature, the maximum current consistent with previous experiments is recorded. It means that heating only affects the rate of adsorption/desorption and since the NiL^6 frame work remains intact, subsidiary water chains at the surface are rearranged and maximum current as well as reversibility of the adsorption/desorption of the moisture is reproduced upon cooling down the system.

Figure 5.16. Monitoring the reversibility of hydration/adsorption of NiL^6 over gradual decreasing of temperature.

To understand how temperature can affect the rate of hydration or moisture adsorption of NiL⁶ and in order to verify the consistency with the previously obtained results and conclusions, another experiment was designed to study kinetically this system at different temperatures. As shown in Figure 5.18, adsorption/desorption cycle was monitored at different temperatures. In other word, during adsorption stage of each cycle, the system was exposed to 17 torr to reach to the maximum conductivity and after stabilization, the vacuum chamber got opened and desorption occurred. Based on obtained results, increasing the temperature extends the time period for reaching to maximum conductivity. As explained before, heating interferes in adsorption process and accordingly it takes longer for water molecules on the surface to get arranged and form subsidiary water chains for complete charge transfer (maximum conductivity).

Figure 5.17. Monitoring conductivity change during adsorption/desorption process at different temperatures.

Figure 5.19 compares the hydration step of each cycle at different temperatures to provide a comprehensive understanding on the role of temperature in rate of hydration (required time for reaching to maximum conductivity). As it shows here and also was observed before, hydration stage consists of two steps and by increasing temperature, these two steps take longer to be completed. In other words, higher temperatures agitate the normal adsorption of water molecules (first step) and accordingly formation of subsidiary water chains (second step) is postponed so it takes longer for the system to reach to saturation state (maximum conductivity). As an example, Figure 5.20 shows that each of the hydration steps follows the first order kinetics equation which demonstrates a linear correlation between $\ln I_t$ and duration of hydration. The slope of this plot equals to the rate constant for each step. For other temperatures as plotted in Figure 5.19, rate constants for two hydration steps were calculated and all trends were consistent with first order rate law. The related data are tabulated in Table 5.4.

Figure 5.18. Comparison of hydration step of NiL^6 at different temperatures under 17 torr vapor pressure.

Figure 5.19. An example of first-order rate law for the first step (A) and second step (B) of hydration/adsorption process at 26 °C as shown in Figure 5.19.

Table 5.4. Rate constant values of hydration/adsorption steps at different temperatures.

Rate constant (s^{-1}) - 1 st step	Rate constant (s^{-1}) - 2 nd step	Temperature (°C)
0.0307	0.004	26
0.0018	0.0018	28
0.0012	0.0012	30
0.0011	0.0005	32

Figure 5.21 shows that calculated rate constants (same procedure that was explained for 26 °C) have negatively exponential relationship with temperatures. As such, the higher temperature results in exponential decrease of the rate constant. In other word, at higher temperatures, the hydration/adsorption processes and accordingly charge transfer are slower, Figure 5.21.

Figure 5.20. Exponential correlation of calculated rate constants with different temperatures for the first step (A) and second step (B) of hydration/adsorption process.

5.2.6. Proposed Mechanism

Modulation of the crystal environment between dry and wet conditions tunes the conductivity of the crystal surface via a two-step process. Under dry conditions (Fig. 4A) the surface exposed 1D water chains are isolated due to vacancies of the water, O8, sites on the surface. Under these dry conditions, the crystal acts as a capacitor. Upon exposure to water vapor, the volatile sites are slowly populated (Fig. 4B) resulting in a slight increase in conductivity. Once the volatile sites are occupied, additional water molecules begin to assemble on the surface connecting the 1D water wires through the structural and volatile water sites (Fig. 4C). This loosely held network provides a pathway for charge transfer between the electrodes. Finally, an organized, extended network is achieved resulting in current saturation associated with wet conditions (Fig. 4D).

Figure 5.21. Illustration of the changes in the 001 surface of $\text{NiL} \cdot \text{H}_2\text{O}$ (NiL = grey, O5-O6 water channel = red, O7 structural water = dark blue, O8 volatile water = purple, surface adhered water = light blue) under dry conditions (A) upon exposure to wet conditions over time (B – D). Contact points (not shown) are located near the 100 edge. Charge propagation occurs along the b -direction on the 001 surface. A) Under dry conditions, volatile water is absent and the crystal acts like a capacitor. B) Exposure to wet conditions populates volatile water positions leading to a small increase in conductivity. C) The accumulation of surface water upon longer exposure to wet conditions provides charge propagation pathways and larger increases in conductivity. D) Saturation with surface water results in an extended charge propagation network pathways with maximum conductivity.

5.2.7. Monitoring Conductivity as a Function of Pressure (P)

In order to monitor the gradual change in conductivity of NiL^6 single crystal at different vapor pressures, following experiment was proceeded for more precise evaluation of the process. As shown in Figure 5.23, the system was maintained at 17 torr (maximum current) for 10 minutes and the average current of 56 nA was recorded. The vacuum chamber got slightly opened to decrease the vapor pressure to 16 torr and the system was kept at this pressure for another 10 minutes. The average current at this step is 38.3 nA. This trend is repeated at lower water pressures and at each step, average current is calculated, Table 5.5. Comparing the recorded current values at different vapor pressures

demonstrates two concepts. First, increasing the vapor pressure from vacuum condition (8 torr) to 12 torr is not associated with significant change (couple of order of magnitude) in current. This indicates that adsorption of water molecules at this pressure, 12 torr, is not sufficient to complete the surface water network for charge propagation. Second, the greatest change in current is from 15 torr (14.1 nA) to 16 torr (38.3 nA) which means more than half of the surface water network is formed at 16 torr.

Figure 5.22. Monitoring conductivity over gradual desorption on a single crystal of NiL⁶.

Table 5.5. Average values of conductivity over gradual desorption on a single crystal of NiL⁶ presented in Figure 5.23.

Water vapor pressure, (torr)	I (nA)	R (MΩ)
17	56 ± 0.8507	0.179
16	38.3 ± 1.4148	0.262
15	14.1 ± 2.4848	0.729
14	3.43 ± 0.1949	3.23
13	0.496 ± 0.1487	22.1
12	0.0836 ± 0.2008	163

In order to verify that the recorded current at 17 torr is the maximum value for NiL⁶ and increasing the vapor pressure does not change the maximum current, the system was exposed to higher vapor pressures and as shown in Figure 5.24, the maximum current is consistent with the recorded average value of 56 nA at 17 torr. These results demonstrate that increasing vapor pressure accelerates the adsorption/hydration process which results in reaching faster to the maximum current (saturation state) but does not affect or increase the maximum value of the current.

Figure 5.23. Monitoring conductivity of NiL⁶ during hydration/adsorption stage at different vapor pressures.

5.3. Conclusion

Electronic properties of NiL⁶ were investigated using two-probe resistance measurement as well as electrochemical impedance spectroscopy (EIS). The results demonstrated that due to the presence of π - π stacking between adjacent imidazole rings along the *b*-axis, a robust framework is formed through which water molecules make hydrogen bonds with carboxamide oxygens (anchor spots) and get arranged as the single file water wires in the lattice. This robust framework does not collapse under vacuum and

remains intact even after numerous cycles of adsorption/desorption, therefore water chains maintain integrated during desorption stage of the experiment (proved by TGA). Accordingly, it confirms that reversible conductivity change in the single crystal of NiL^6 upon adsorption/desorption of water molecules. In other words, exposing the system to the 17 torr water vapor pressure results in adsorption of water molecules and formation of subsidiary water chains which are responsible for charge propagation. In fact, the recorded conductivity for NiL^6 is associated with the presence of the subsidiary water chains on the surface and charge transfer through structural (in bulk) 1D water coils is insignificant. Additionally, EIS proved that the dehydrated NiL^6 behaves as a nearly ideal capacitor and stores the charges around the electrodes but does not involve in any charge transfer process while hydrated NiL^6 due to adsorbing water molecules behaves as a capacitor that involves in transferring charges between electrodes. In fact, the first electrochemical process is associated with agglomeration of charge at contacts (capacitance is within nF scale) and second process is the result of transferring charge between contacts (capacitance is within μF scale, three order of magnitude greater than the first process) through subsidiary chain on the surface of NiL^6 . Above all, since the equivalent circuits used for fitting EIS data and calculating capacitance and other related parameters have been previously reported for failure evaluation of organic coatings, it demonstrates that the hydrated system of NiL^6 can also be considered as a potential tool to evaluate the protective performance of coatings.

CHAPTER VI

CONCLUSIONS

In this dissertation a series of studies on structurally similar hydrated complexes were reported with H-bonding motifs that vary as a function of the crystal packing of the host molecules. The presence or absence of interlayer H-bonding interactions in these complexes results in different stacking arrangements, which positions the carbonyl O atoms to interact water molecules confined in various motifs such as 1D channels (as stream or coiled chains), 2D cascades and isolated pools. The thermal properties of the hydrated structures correlate with the differences in the H-bonding motifs and the H-bonding motifs facilitate orientation of the metal stacks to support propagation of the charge carriers. As such, electronic properties of NiL^6 (confining 1D coiled water chains) were investigated in both hydrated and dehydrated states and significant change in charge transfer was observed due to adsorption of water molecules through anchor points provided by stacking pattern of NiL^6 complexes.

In Chapter 3, subtle modification of the ligand framework resulted in formation of various H-bonding networks that can affect and tune related electronic properties. These results offer promise for the rational design of HB motifs based on small changes in the host framework with predictable physical properties. In Chapter 4, using identical ligand framework resulted in formation of isostructural complexes of NiL^6 and CuL^6 with similar H-bonding motifs which results in analogous thermal stabilities and phase transition at

elevated temperature. As such, the subsequent efforts were fulfilled to analyze conductivity change in the hydrated structures and investigate the potential application of the synthesized material based on its charge transfer pattern. Chapter 5 reports the changes in conductivity of NiL⁶ crystals in both hydrated and dehydrated states. The obtained results demonstrate significant and reversible change in conductivity associated with surface bound water molecules on the 001 crystal face.

Overall, the results in this dissertation demonstrate the importance of crystal engineering to vary H-bonding motifs and tune electronic properties. The formation of isostructural complexes of Ni(II) and Cu(II) with similar H-bonding networks from an identical ligand framework provided a means to investigate significant changes in the charge transfer process and electronic properties of the hydrated and dehydrated states of a Ni(II) complex with structural coiled water chains and providing the most probable mechanism for charge propagation. The remainder of this Chapter will summarize the main findings of each chapter followed by a discussion of areas for future research in this area.

In Chapter 3, variations in water HB motifs for a group of structurally related hydrated Ni(II) complexes containing N₃X (X = S or O) donors were reported. X-ray crystallography was used to demonstrate how small changes in the ligand framework lead to different orientations of the carboxamido oxygens, which influences the solid state packing and related HB patterns. As a result, three different HB networks were observed including 1D water chains (streams), 2D tapes of infused rings (cascades), and isolated water dimers (pools).¹²⁷ In fact, HB motifs in this series of related planar Ni(II) complexes vary as a function of the crystal packing of the host molecules, Scheme 3.2. The interlayer HB interactions in NiL² and NiL³ results in an AAAA stacking arrangement, which

positions the carbonyl O atoms to interact water molecules confined in 1D channels. The absence of HB stacking interactions between the layers of NiL⁴ result in an ABAB stacking arrangement with large void spaces between alternating layers. The –OCH₃ group in NiL⁵ act as a gate to generate isolated void spaces resulting in pools of water as a result of the ABBA stacking arrangement. The mass quantity of water stored per volume of crystal is dependent on the packing arrangement. The pools of NiL⁵ contain the least amount of water at 10.96 mg cm⁻³. The streams of NiL² and NiL³ hold approximately twice as much water as NiL⁵ with values of 20.72 and 23.97 mg cm⁻³, respectively. The cascades of NiL⁴ retain 116.7 mg cm⁻³, which is 10 times the water of NiL⁵. Analysis of the Nyquist representation (Z' and $-Z''$) for the complexes shows that Z'' changes with frequency, in the high frequency domain, while Z' remains relatively constant. This indicates that the vast majority of the system impedance is caused by capacitive elements, rather than resistive elements. The similarities in measured capacitances and system resistances for NiL², NiL⁴, and NiL⁵ are attributed to the nearly identical π -stacking distances of the metal complexes of ~ 3.4 Å. Charge transfer appears to propagate through the metal complex stacks with the water of hydration serving a structural role. In fact, the HB motifs facilitate orientation of the metal stacks to support propagation of the charge carriers, but do not appear to be directly involved in charge propagation. The thermal properties of the hydrated structures correlate with the differences in the HB motifs.

These results offer promise for the rational design of HB motifs based on small changes in the host framework with predictable physical properties. It is also envisioned that the water structure could serve as a conduit for proton conduction, which is a focus of continued efforts. As such, subsequent efforts were fulfilled to design new materials by

engineering of these reported structures to form 1D water wires and study charge transfer mechanism in these structures under various environmental conditions.

In Chapter 4, new complexes containing 1D water wires were reported. Isostructural Cu(II) and Ni(II) complexes based on N,N'-(ethane-1,2-diyl)bis(1-methyl-1H-imidazole-2-carboxamide) (H₂L) were synthesized and fully characterized by single crystal X-ray diffraction, spectroscopic methods, and thermal analysis. The hydrogen bonding motifs in isostructural planar CuL⁶ and NiL⁶ complexes are identical due to similar crystal packing of the host molecules. The interlayer HB interactions in CuL⁶ and NiL⁶ result in a twisted AAAA stacking arrangement, which positions the carbonyl O atoms to be in interaction with water molecules confined in coiled 1D chains. The thermal properties of the hydrated structures correlate with the identical HB motifs and in both structures, the 1D coiled chains require a higher temperature to break the strong HB interactions within the channel and between the water and structural O atoms. Also, decomposition of the ligand framework of CuL⁶ and NiL⁶, both occurs above 250 °C and 300 °C and is accompanied by a phase transition as indicated by the endothermic process.

The HB motifs facilitate orientation of the metal stacks to support propagation of the charge carriers. As such, EIS studies were performed to analyze the charge transfer in NiL⁶. Based on EIS, the presence of two time constants in NiL⁶ suggests the presence of two different types of domains within the structure of the material. Introducing additional water as a dielectric into a capacitive system decreases the electric field strength, which decreases the voltage and in turn increases the capacitance. Because the capacitance of time constant 2 is several orders of magnitude higher than that of time constant 1, we postulate

that the domain corresponding to time constant 2 is significantly more water-permeable and amenable to charge conduction.¹⁵⁴

In Chapter 5, the electrical properties of NiL⁶ complex reported in Chapter 4 were examined using two-probe resistance measurements and EIS. The results demonstrated that due to the presence of π - π stacking between adjacent imidazole rings along the *b*-axis, a robust framework is formed through which water molecules make hydrogen bonds with carboxamide oxygens (anchor spots) and get arranged as the single file water wires in the lattice. This robust framework does not collapse under vacuum and remains intact even after numerous cycles of adsorption/desorption, therefore water chains maintain integrated during desorption stage of the experiment (proved by TGA). Accordingly, it confirms that reversible conductivity change in the single crystal of NiL⁶ upon adsorption/desorption of water molecules at the crystal surface. In other words, exposing the system to the 17 torr water vapor pressure results in adsorption of water molecules and formation of subsidiary water chains (as a dielectric) which are responsible for charge propagation. In fact, the recorded conductivity for NiL⁶ is associated with the presence of the subsidiary water chains on the surface supported by EIS data that proved charge transfer through structural (in bulk) 1D water coils is insignificant. The rate of hydration at different temperatures and under various water vapor pressures were monitored and results demonstrated that at higher vapor pressures the rate of hydration and accordingly charge transfer is faster while increasing temperature lowers the rate of charge transfer. In fact, considering an equilibrium between adsorption – desorption process explains that at higher vapor pressures, adsorption gets dominant and at higher temperatures desorption happens faster.

Additionally, EIS proved that the hydrated NiL⁶ behaves as a capacitor through two interfacial electrochemical processes with 3 order of magnitude difference. The first process is associated with the charge transfer through structural 1D water coils (in bulk) and its capacitance is within nF range while the second process belongs to charge propagation through subsidiary water chains formed on the surface and its capacitance is within μ F scale, three order of magnitude greater than the first process as well as the dehydrated state. Above all, since the equivalent circuit models used for fitting EIS data and calculating capacitance and other related parameters have been previously reported for failure evaluation of organic coatings¹⁰⁰⁻¹¹², it demonstrates that the hydrated system of NiL⁶ can also be considered as a potential tool to evaluate the protective performance of coatings.

Future studies based on this dissertation include measuring conductivity for CuL⁶ crystals or for NiL² and NiL³ confining 1D water wire (stream) in their crystal lattice. For these crystals, other than similar experiments, a different series of studies can be done such as monitoring the rate of charge transfer at lower than room temperature, recording the minimum required water vapor pressure for maximum conductivity at lower temperatures and finding the optimum condition for each crystal in which maximum conductivity can be reached. Eventually, by comparing the maximum conductivity, rate of charge transfer and structural features of each crystal, it can be understood how to modify the structure to reach the maximum current at shortest time and with minimum applied energy (regarding temperature and vapor pressure)

From a design standpoint, the N,N'-(ethane-1,2-diyl)bis(1-methyl-1*H*-imidazole-2-carboxamide) ligand (organic framework) can be modified by varying the ligand backbone

and the steric bulk around the carboxamido-O can be used to modulate the spacing and orientation between complexes in the stack. Accordingly, this would modify the HB motifs, dehydration temperatures, and tune the conductivity. The combination of effects could be used to design materials that undergo structural changes upon dehydration with quantifiable effects on the charge transfer properties of the materials.

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CURRICULUM VITA

Nina Saraei

Summary

- 8+ years of research experience in Inorganic chemistry including rational design & crystal engineering, synthesis, X-ray characterization, spectroscopy, TGA/DSC, kinetic studies, resistance & electrochemical impedance measurements
- Accomplished to integrate inorganic materials into moisture sensors by monitoring conductivity via hydrogen bonds
- Demonstrated quantitative & analytical skills with interdisciplinary educational & practical background in physics, chemical engineering and pharmaceutical sciences
- Independent researcher and strong team member experienced in collaborating cross-functionally with physicists and chemical engineers in various research labs
- Proficient in Office, Mercury, Corel draw, Mestrenova and skilled in Origin, SHELX and EndNote
- Fluent in written and oral communications for clear & effective exchange of information at wide diversity of disciplines and level of sophistication
- Adroit at scientific writing, data analysis and presentations

Research and Work Experience

PhD Candidate | University of LouisvilleAugust 2014 – Present.....Louisville, Ky

- Conducted kinetic, structural and spectroscopic studies on reversible primary alcohol addition to transition metal complexes via Single-crystal XRD, UV-Vis, FT-IR, ESI-MS, Elemental analysis: A series of Cu(II) complexes were designed, synthesized and purified. Single crystals were grown and characterized by SXRd and verified by FT-IR, ESI-MS and EA. Kinetic studies were performed by using UV-Vis, calculation of rate constants, order of reactions and derivation of rate law for each methanol addition/elimination equilibrium. A possible mechanism of the addition /elimination was proposed based on obtained results. The results were featured on cover of *Dalton Transactions*, Volume 45, 2016.
- Investigated the impact of secondary sorption of hydrocarbons on the interlayer morphology of organic surfactant modified montmorillonites: Related experiments were designed to systematically quantify: 1. The interactions between mineral phase (alluminosilicates), surfactants and hydrocarbon sorbates; 2. The interlayer expansion of montmorillonite due to consecutive intercalation of surfactant and hydrocarbons; and 3. The surfactant arrangement and re-arrangement before and after hydrocarbon sorption. Accordingly, I managed to clarify 1. The impact of hydrocarbon sorbates on the interlayer surfactant re-arrangement; 2. Ease of sorbate intercalation and the magnitude of interlayer expansion due to the secondary sorption; and 3. The modified engineering behaviors of organoclay when facing non-polar fluids, fuels and non-aqueous phase liquids (NAPLs). The results were published in *Colloids and Surfaces A: Physicochemical & Engineering Aspects*, Volume 520, 2017.

- Evaluated conductivity, thermal behavior, stability and structural features of various water cluster motifs in structurally similar Ni (II) complexes via Single-crystal XRD, TGA/DSC, Electrochemical impedance spectroscopy (EIS): A series of similar organic frameworks were designed to be used in preparation of Ni(II) complexes. Single crystals were grown and proved the presence of various hydrogen bond motifs within crystal lattice. The variation of water cluster motifs was correlated to thermal stability and conductivity of each complex. The results were featured on cover of *Crystal Engineering Communications*, Volume 20, 2018.
- Investigated reversible resistance and impedance change upon dehydration/rehydration of a group of hydrated Ni (II) and Cu(II) complexes in forms of single crystals, pellets and thin films for developing potential applications as moisture sensors via 2-probe resistance measurement, EIS, SDT, Raman: Two hydrated Ni(II) and Cu(II) complexes were synthesized, structurally characterized and showed reversible and drastic change in resistance and impedance under hydrated and dehydrated conditions which the potential application of this unprecedented observation is proposed as moisture sensors/switch. Synthesis, thermal analysis and electrochemical impedance spectroscopy of these complexes were published in *Inorganica Chimica Acta*, Volume 492, 2019 and the main results are at the process of being published and filed as patent.

Calibration Intern | Micro Precision Calibration.....*June 2019 – August 2019*.....San Jose, Ca

- Applied validated metrology methods and standards for maintaining, testing, troubleshooting and calibrating a variety of analytical instrumentation for laboratory and clinical equipments
- Modified calibration procedures as needed and developed new methodologies for constantly changing materials and equipments used at the laboratory
- Identified and utilized appropriate measurement procedures for electrical, dimensional, chemical and thermodynamic calibration
- Performed related statistical calculations, corrective and preventive actions to address identified measurement problems for each instrument
- Validated and issued calibration certificates for in tolerance electrical, mechanical devices and analytical assortments

Scientific Assistant | Department of Active Pharmaceutical Ingredients (API) - Akbarieh Co.
June 2013 – June 2014

- Resolved the possible issues on Assay, Loss of drying, Solubility, Microbial limits, etc. in Certificate of Analysis (COA) based on USP tests
- Investigated GMP of potential API suppliers based on international standards as well as regulations issued by Ministry of Health such as hygienic manufacturing area, controlled environmental conditions of manufacturing facilities, Well-written instructions and procedures, etc.
- Followed-up with customers from purchasing till launching the product to market
- Attended in several CPHIs & evaluated new ideas for developing cooperation with other potential API suppliers on recently launched products based on current supply & demand trends in pharmaceutical industry

MSc Researcher | University of Tabriz.....*August 2010 - December 2012*

- Integrated synthesis, characterization, spectroscopic & microbial studies on a series of 1st row transition metal complexes of N₂O₄ and N₄O₂ Schiff base ligands via Powder XRD, NMR, Cyclic Voltammetry, Immunoassay

Quality Control Intern | Aburaihan Pharmaceutical Co..... *March 2008 - August 2008*

- Conducted COA essential tests for each product based on MOA & USP procedures
- Applied chromatography techniques GC-MS, HPLC for quality control and routine analysis of final products
- Assessed bioequivalence tests to assess the expected in vivo biological equivalence in preparation of a drug

Education

University of Louisville *Louisville, KY ...PhD in Inorganic chemistry....August 2014 - Present*

- Graduate School Council (GSC) Travel Award for presentation in ACS Great Lakes Regional meeting 2019
- Student Department Travel Fund for presentation in ACS Great Lakes Regional meeting 2019
- Graduate School Council (GSC) Travel Award for participation in 256th ACS meeting
- Art & Sciences Research & Creative Activities Grant Award for research proposal
- Graduate School Council (GSC) Travel Award for presentation in 255th ACS meeting
- Graduate Network in Arts & Sciences (GNAS) Research Fund Award

University of Tabriz *Tabriz, Iran ...MSc in Inorganic chemistry...August 2010 - December 2012*

- Certificate of presentation in 20th Symposium of Crystallography & Mineralogy of Iran
- Certificate of presentation in 14th Iranian Inorganic Chemistry Conference

Islamic Azad University *Tehran, Iran BSc, Applied chemistry August 2004 - February 2009*

Technical Skills

Computer | Proficient in Office, Mercury, Origin, Mestrenova, Corel draw

Language | English (fluent), Persian (native)

Publications

- Nina Saraei; Alexander J Gupta.; Oleksandr Hietsoi; Brian C Frye; Gamini Sumanasekera; Gautam Gupta; Mark S Mashuta; Robert M Buchanan; Craig A Grapperhaus, Small molecule crystals with 1D water wires modulate electronic properties of surface water networks, *Materials Today*, **2020. Submitted**

- Nina Saraei, Oleksandr Hietsoi, Brian C Frye, Alexander J Gupta, Mark S Mashuta, Gautam Gupta, Robert M Buchanan, Craig A Grapperhaus, Water wire clusters in isostructural Cu (II) and Ni (II) complexes: Synthesis, characterization, and thermal analyses, *Inorganica Chimica Acta*, **2019**.
- Nina Saraei, Oleksandr Hietsoi, Christopher S Mullins, Alexander J Gupta, Brian C Frye, Mark S Mashuta, Robert M Buchanan, Craig A Grapperhaus, Streams, cascades, and pools: various water cluster motifs in structurally similar Ni (II) complexes, *CrystEngComm*, **2018**. (Featured on the cover of journal)
- Mohammad Ghavami, Qian Zhao, Sadra Javadi, John Samuel Dilip Jangam, Jacek B Jasinski, Nina Saraei, Change of organobentonite interlayer microstructure induced by sorption of aromatic and petroleum hydrocarbons—A combined study of laboratory characterization and molecular dynamics simulations, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2017**.
- Wuyu Zhang, Nina Saraei, Hanlin Nie, John R Vaughn, Alexis S Jones, Mark S Mashuta, Robert M Buchanan, Craig A Grapperhaus, Reversible methanol addition to copper Schiff base complexes: a kinetic, structural and spectroscopic study of reactions at azomethine C = N bonds, *Dalton Transactions*, **2016**. (Featured on the cover of journal)
- Younes Hanifehpour, Nina Saraei, Sanaz Mokhtari Asl, Sang Woo Joo, Synthesis and Structural Characterization of Two New Nano-Coordination Compounds Based on Mercury (II) NN Donor Schiff Base, *Journal of Inorganic and Organometallic Polymers and Materials*, **2012**.