

# Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of \$250 for UW-Madison chemistry Ph.D. candidates.



The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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Modifications to  $M_2M'$  **Heterometallic Chain Compounds** and their  
Spectroscopic, Magnetic, and Electronic Consequences

By  
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A dissertation submitted in partial fulfillment of  
the requirements for the degree of

Doctor of Philosophy  
(Chemistry)

at the  
UNIVERSITY OF WISCONSIN – MADISON  
2019

Date of final oral examination: 7/24/2019

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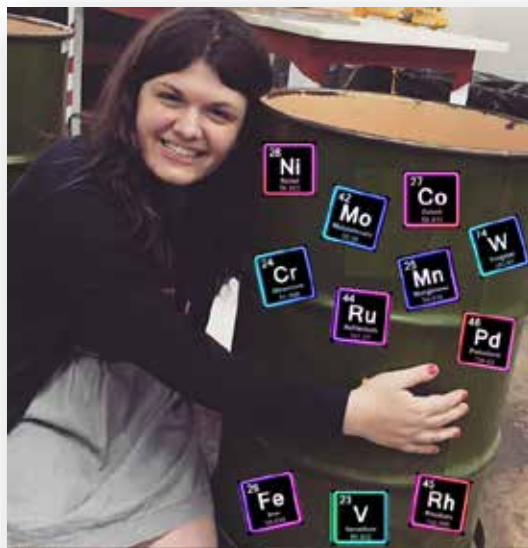
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## Chapter One

### Dr. Chipman or: How I Learned to Stop Worrying and Love Transition Metals

*Wisconsin Initiative for Science Literacy: Introduction for a General Audience*



*This chapter begins with a reflection on my education in Inorganic Chemistry followed by a description of the field and what I've accomplished in my doctoral research.*

As any student is told in their high school chemistry course, inorganic chemistry involves the science of “that short stubby rectangle” in the middle of the periodic table. I was no different. Figure 1.1 shows the same periodic table that I learned from when I took my first chemistry course in 2007. While a large portion of inorganic chemistry is centered on that rectangle, inorganic chemistry encompasses so much more! Nonetheless, I was told I would learn more about that magical rectangle in college.

I entered college in August of 2010 and sat through General Chemistry, Organic Chemistry, and then Biochemistry before I was finally able to take a course on “that short stubby rectangle.” To my dismay, I was placed in “Advanced Inorganic Materials” because the introductory course didn’t fit my schedule. This meant two things: 1) I waited until my junior year of *college* (Fall 2012) before I could learn anything substantive about inorganic chemistry, and 2) I would graduate college in 2014, seven years after I started taking chemistry courses, without taking a fundamental inorganic chemistry basics course. Logically, this meant I enrolled at UW–Madison in Fall 2014 for grad school and joined John Berry’s *inorganic* chemistry

research group. I nervously informed John that “I have never taken a formal inorganic chemistry course.” This turned out to be ok in his eyes and five years later in 2019, I’m defending the research I did in inorganic chemistry to become Dr. Jill Ann Chipman.

**Periodic Table of the Elements**

**KEY**

Atomic Mass → 12.011      Oxidation States → -4, -2, +2, +4

Symbol → C      Regular atomic masses are based on  $^{12}\text{C} = 12$  exactly

Atomic Number → 6      Note: Numbers in parentheses are mass numbers of the most stable or common isotope.

Electron Configuration → 2-4

Source: CRC Handbook of Chemistry and Physics, 91<sup>st</sup> ed., 2013-2017, CRC Press

**Figure 1.1** The New York State Reference Tables Periodic Table of the Elements. This is the periodic table I used while learning chemistry in high school. "That short stubby rectangle" is highlighted in orange.<sup>1</sup>

I’ve really found my space in the field of inorganic chemistry, but it took twelve years to get here! It took about half that time to even begin to understand inorganic chemistry. For a field that supports life as we know it, inorganic chemistry shouldn’t be a mysterious black box to society. It needs a better introduction than “the short stubby rectangle” or “*not* organic.” I’ve therefore written this introductory chapter as means to answer two questions:

- 1.) What *is* Inorganic Chemistry?
- 2.) How did my research *contribute* to Inorganic Chemistry?

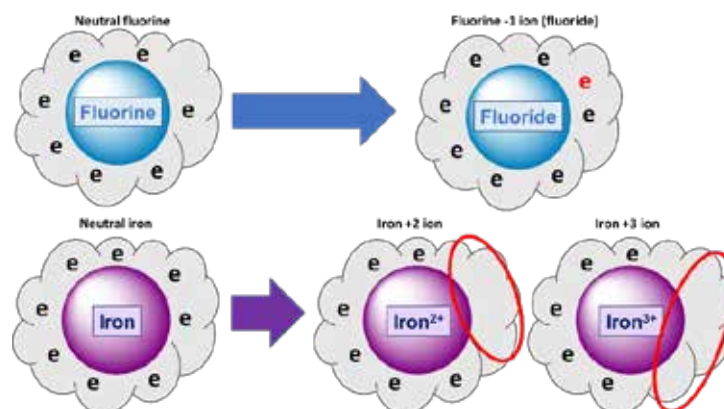
## 1.1 What *is* Inorganic Chemistry?

The American Chemical Society defines inorganic chemistry by stating “Inorganic chemistry is concerned with the properties and behavior of inorganic compounds, which include metals, minerals, and

organometallic (defined below) compounds.”<sup>2</sup> Whereas organic compounds *must* contain a carbon–hydrogen bond, inorganic compounds are largely centered on compounds that do not contain carbon. Organometallics are a special mix of organic and inorganic chemistry and they contain a metal bonded to a carbon. Generally speaking, many inorganic compounds include a metal; more specifically, a transition metal. As mentioned above, the transition metals are “that short stubby block” in the middle of the periodic table. That block makes up about 1/3 of the periodic table.

In contrast to the other 2/3 of the elements, the transition metals contain two key properties. Many non-transition metals have one of these two properties, but *not* both! Transition metals are conductive, lustrous, malleable, and ductile, just like the other elements of the periodic table classified as metals. Conductive means that the material can allow electricity (aka a current) to flow through. For example, the electrical wires in many homes are made of copper, a transition metal. Transition metals are also lustrous, meaning they’re shiny. The remaining two properties, malleability and ductility are very similar. We can think about them by thinking of a large block of any transition metal. We may want a sheet of our metal; transition metals are malleable and are easily flattened into sheets. Maybe we don’t want a sheet, we instead want to make our block a wire; transition metals are ductile and can be drawn into thin wires. These are all properties of transition metals that we can see with our naked eyes. The property that interests me about transition metals, however, is one we *can’t* see with the naked eye.

The other distinctive property of transition metals is that they can house different numbers of electrons and still be stable. Most elements can exist in two states; neutral (atom) or charged (ion). Transition metals are no different in this way, but they are different in that they can exist in multiple charged states. That is, they can hold different numbers of electrons and still be stable. In comparison to the other elements of the periodic table, this is a relatively unique property. For example, the element fluorine (F) which is not a transition metal, can exist in a neutral form, or as an ion, with a  $-1$  charge, by housing an additional electron. Meanwhile, the element iron (Fe), which is a transition metal, can exist in a neutral form, but it can also exist with  $+2$  or  $+3$  charge, by losing two or three of its electrons, respectively. Figure 1.2 illustrates these differences. Not very many other elements outside the transition metals are capable of doing this. It is only the transition metals that have both of these properties.



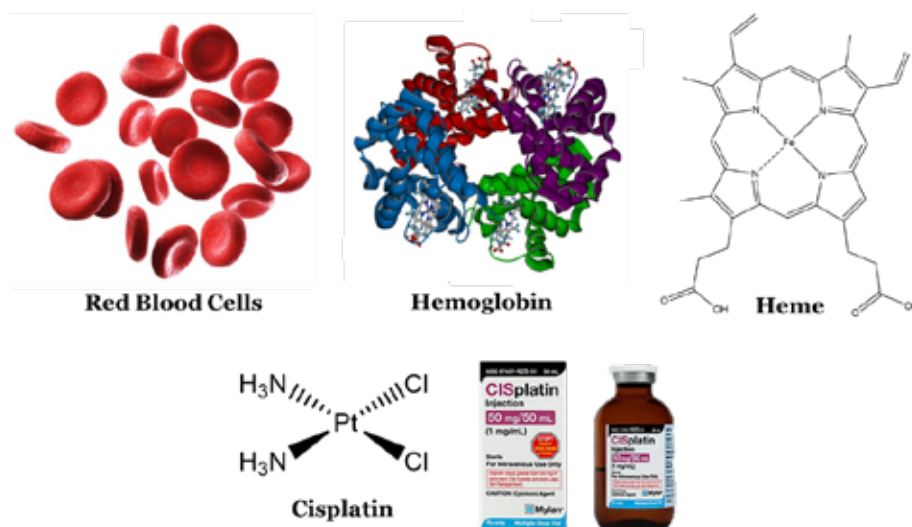
**Figure 1.2** Fluorine can house one additional electron when it is an ion (top); Iron can lose either two or three electrons when it is an ion (bottom). Electrons are denoted by the letter “e”

Given these two properties, chemists can tailor the environment around a transition metal in order to give it desired behaviors. As chemists, we must carefully design our compounds to have them behave in ways that we would like. However, nature has been able to harness the power of transition metals too. They are found in minerals, plants, and animals. For example, many of the precious gemstones we value come from some of the most common minerals in the world. However, with a small amount of a transition metal “impurity” these common minerals skyrocket in value. For example, the ruby is formed when a chromium impurity is present in the mineral corundum.<sup>3</sup> Figure 1.3 below shows the mineral corundum in comparison to both a rough and a cut ruby.



**Figure 1.3** The mineral corundum is composed of aluminum and oxygen. Upon introduction of a chromium impurity, a ruby can be formed. Both a rough ruby and cut ruby are shown for contrast.<sup>4</sup>

Our bodies are full of red blood cells, which get their distinctive red color from the iron center in a complex called heme, which lives in a protein called hemoglobin (Figure 1.4 top). Heme has more responsibilities than just binding oxygen and making our blood red. It helps promote a variety of chemical reactions in our bodies that allow us to live.<sup>5</sup> Our bodies do not just contain iron however and many of the medications that help humans to overcome health complications contain a transition metal. One of the most well-known cancer drugs, cisplatin, was initially discovered in 1845 (Figure 1.4 bottom). It remains in use today and contains platinum.<sup>6</sup> Moving outside of our bodies, we can also find platinum in the catalytic converter of the cars that we drive. We might also find rhodium, cobalt, zinc, and copper, which are all transition metals.<sup>7</sup> Moving to smaller items, metals including copper, nickel, silver, gold, and lead, are also found in our cell phones, computers, and tablets. It would be negligent to disregard the point that many of these metals do come from non-renewable sources.<sup>8</sup> This means we are responsible for recycling our used electronics and car parts in a way that allow us to sustain our way our life without damaging the world around us!



**Figure 1.4** (Top) the iron center in heme gives red blood cells their distinctive red color. Heme is a part of the protein known as hemoglobin. (Bottom) cisplatin is one of the most well-known and used cancer drugs.<sup>9</sup>

For inorganic chemists, nature provides an amazing inspiration source. A great deal of inorganic research is focused on understanding how metals in living things do what they do. Other chemists marry the field of inorganic chemistry with organic chemistry (the chemistry of the element carbon) to form a hybrid field called organometallic chemistry. Organometallic complexes contain at least one metal-carbon bond. While both of these topics are studied in the Chemistry department at UW-Madison, neither one

represents my research. My research remains in understanding some of the most fundamental aspects of inorganic chemistry and finding applications for some of the complexes that I make.

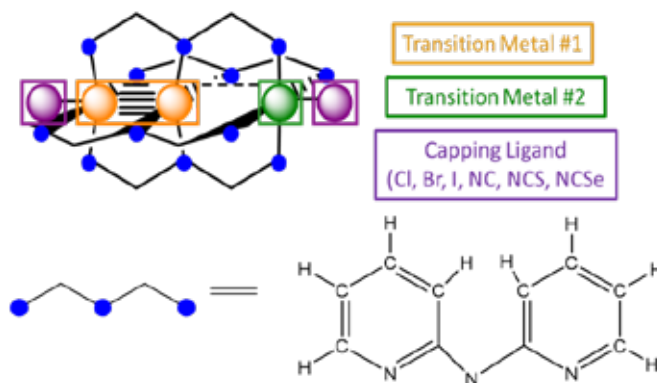
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## 1.2 How did my research contribute to Inorganic Chemistry?

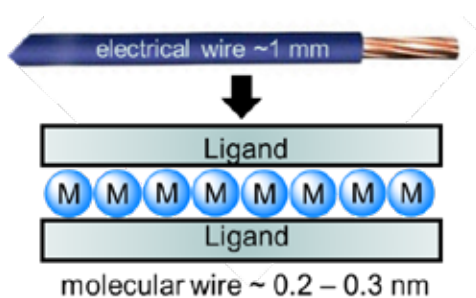
One of the characteristics of a transition metal is the ability to conduct electricity. The big picture goal of my research is take that ability, fine tune it, and make small-scale single molecule electronic pieces. In order to make smaller electronics that have the same (or more) strength as their larger versions, we need smaller building blocks. The smallest possible building block? A molecule! My research has involved making **Heterometallic Extended Metal Atom Chains**, or HEMACs, for short. The chains I work with are three metal atoms long, with two different metals arranged asymmetrically. The metal chain is surrounded by four paddlewheel supports, called ligands. A ligand is most generally defined as something that is bound to a metal. A ligand can be as simple as one atom or it can be part of group of atoms. The ligand used in this work is dpa (or 2, 2' dipyridylamine). There are an additional two capping ligands on either end of the chain. Our group has a well-established method for building these chains, and much of my work has focused on the effects of changing the capping ligands on the ends of the chains.<sup>10-16</sup>

Scheme 1.1 shows the general HEMAC structure as well as the places I have made modifications as part of my research. If we look at a HEMAC and compare it to a normal electronic wire, there's a similarity! A wire contains a core that carries current and it is surrounded by an insulating blanket. A HEMAC contains a three-metal atom long chain (the core) and surrounds it with insulating ligand! Of course, my research goes a little bit further than just a visual similarity, shown in Figure 1.5. I've chosen to focus this section on the two contributions I've made that are closest to molecular electronics.



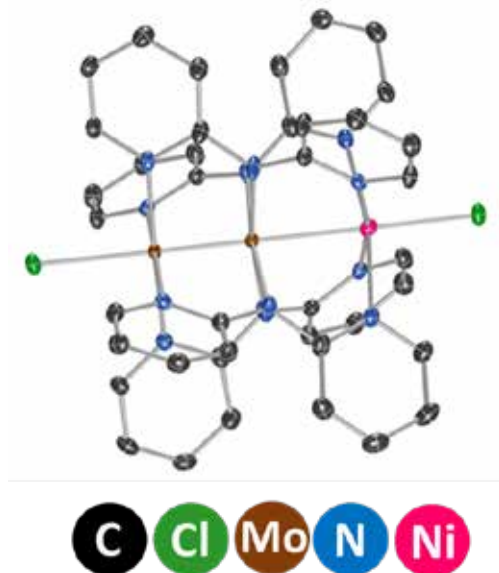


**Scheme 1.1** The general structure of one of my HEMAC compounds supported by the dpa ligand. Different spheres represent different portions of the HEMAC that I have modified.



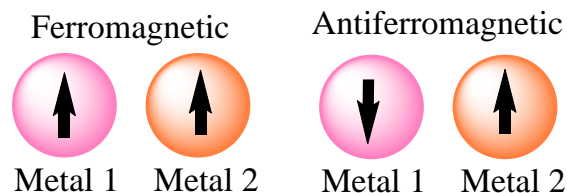
**Figure 1.5** The visual comparison between an electric wire and a molecular wire. The molecular wire is much smaller than a normal electric wire but shares the same design.

My first major success in research used molybdenum (Mo) and nickel (Ni) to form a Mo–Mo–Ni chain that didn't behave like any other previously made chain.<sup>17</sup> The compound I started with was  $\text{Mo}_2\text{Ni}(\text{dpa})_4\text{Cl}_2$ . Our group had not yet made this compound, so this in itself is a new advancement. A structure of this chain is shown below (Figure 1.6).



**Figure 1.6** A structural representation of  $\text{Mo}_2\text{Ni}(\text{dpa})_4\text{Cl}_2$ . Different color spheres represent different atoms. Hydrogen atoms have been removed for clarity.

This chain consists of a  $\text{Mo}_2$  species that is bound together and contains no unpaired electrons in addition to a  $\text{Ni}^{2+}$  ion that contains two unpaired electrons. When I remove an electron from the overall chain, it can come from either  $\text{Ni}^{2+}$  or  $\text{Mo}_2$ , for this chain, it came from  $\text{Mo}_2$ . This means that in total I have three electrons each with a preferred spin (think clockwise or counterclockwise). Two spins can pair (couple) together with the same spin (ferromagnetically) or with opposing spins (antiferromagnetically). This is illustrated in Figure 1.7.



**Figure 1.7** Electrons in different metals can pair together with spins that are in the same direction (ferromagnetic: left) or opposite (antiferromagnetic: right).

In order to figure out which situation was occurring, I turned to a new instrument in our department called a SQUID magnetometer (Figure 1.8). A magnetometer is a great instrument in that it allows the user to determine what the electrons in their compound are doing. It can also be used to

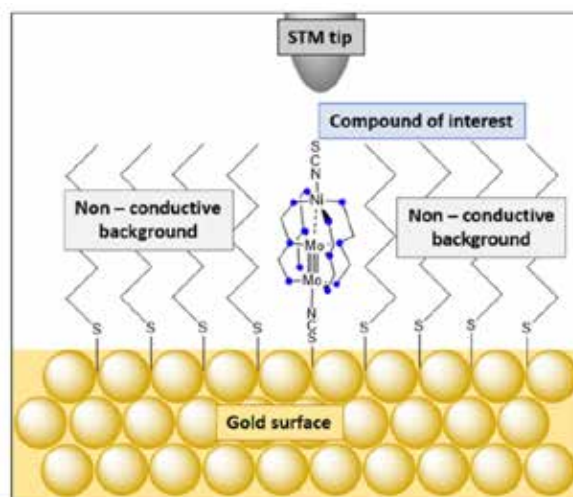
determine if the compound of study is behaving like a single molecule magnet. When I conducted SQUID measurements on my  $\text{MoNi}(\text{dpa})_4\text{Cl}_2$  chain, I determined the electrons are coupled in the same direction, meaning they are coupled ferromagnetically. This was a surprising result as all the other chains prior to this one have electrons that couple in the opposite direction; meaning they couple antiferromagnetically.<sup>18-22</sup> Using other methods, including computations, I was able to learn why this occurred and make a generalized statement for future work. As I leave this project to our younger students, they can apply the same methods to our other chains as I did to my  $\text{Mo}_2\text{Ni}(\text{dpa})_4\text{Cl}_2$  HEMAC. We would like to see one of the HEMACs behave like a small magnet, called a single molecule magnet. These are especially valuable in computers and other electronics, which continue to be made smaller and smaller (meaning they need smaller and smaller parts).



**Figure 1.8** The SQUID magnetometer at UW–Madison.<sup>23</sup>

Most of our chains are made with chlorine (Cl) capping ligands bound to the terminal ends. However, one of the long-term goals of this project is to bind our chains to gold surfaces and determine if our HEMACs can act like tiny wires. Past work from other labs have determined that homometallic extended metal atoms can act like small wires.<sup>24</sup> Computational chemists have suggested that HEMACs would do the same.<sup>25-26</sup> This testing occurs by using an instrument called a scanning tunneling microscope (STM) to measure the current response across one molecule (Figure 1.9).<sup>27</sup> The molecules of interest are bound to a gold surface and separated by other molecules that do not have a response. This is where the challenge lies for HEMACs. All of the HEMACs up until 2018 were made using chlorine capping ligands

and chlorine does not bind to gold. The ligand of choice for chain compounds is the thiocyanate ligand. This ligand is made of a nitrogen (N), a carbon (C), and a sulfur (S) atom all in a line; N–C–S. The important part of this ligand is a sulfur atom, which can bind very strongly to gold, although there are other options.



**Figure 1.9** An STM is used to measure the current properties of HEMACs. HEMACs are bound to a gold surface and may be isolated from one another by other species that do not have a current response.

Our group has tried in the past to switch the chlorine out for one of these ligands, but it has been quite challenging.<sup>28-29</sup> My second major project made this transformation simpler. I've developed a way to swap the capping ligands on the ends of the HEMACs out for whatever capping ligand we would like.<sup>30</sup> I've made a small library of HEMACs based on the same Mo<sub>2</sub>Ni chain in my first project with different capping ligands, some of which contain sulfur. They are currently being tested as wires by another research group. These different capping ligands will likely affect how well each HEMAC behaves as a wire. We're especially excited about this work because we're using two different metals instead of one. This means we might have current flow in one direction over another. This is called a diode. Just as with a single molecule magnet, these potential single molecule wires or diodes would be valuable in electronic devices as we continue to make smaller and smaller electronics!

These two pieces of my research don't cover all of the work that I've done over the past five years. Instead, they're the two pieces that are closest to molecular wires *and* have solidified my understanding of inorganic chemistry the most. Further, even though my work represents only a small section of the field, I hope that you, the reader have a better understanding of the field of inorganic chemistry as a whole and if

someone asks you what inorganic chemistry is you don't need to say "that small stubby rectangle" or "not organic."

Thank you for reading. I hope you enjoy the rest of this dissertation.

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