

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 20 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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**Synthetic, Spectroscopic, and Computational Studies of Bimetallic and Trimetallic
2,2'-Dipyridylamide Compounds**

by

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Chapter 1

Wisconsin Initiative for Science Literacy: Introduction for a General Audience

1.1 Inorganic Chemistry

When asked to describe inorganic chemistry, one of the easiest responses is to describe it as the opposite of organic chemistry, as the name implies, and then describe organic chemistry. However, this does an injustice to the field of inorganic chemistry, which we interact with on a daily basis and may not even realize we do. Inorganic chemistry, in simplest terms, may be defined as the study of molecules that are not carbon and hydrogen based. Inorganic materials include many of the technological advancements we rely on every day: automobiles, batteries, building materials, and certain drugs, to name a few. However, the distinction between organic and inorganic chemistry is not absolute and most often these two fields work in tandem.

One of the major themes of inorganic chemistry is the study of metals, in particular transition metals. Transition metals, highlighted in red in Figure 1.1 comprise a majority of the periodic table and can be considered the building blocks of inorganic chemistry just as carbon is considered the building block of organic chemistry. We are familiar with many of the transition metals because of their therapeutic value and presence in our bodies, such as iron, zinc, copper, and cobalt. Transition metals have a range of properties, they are conductive, reflective, malleable, ductile, and magnetic. Due to this wide range of properties it is crucial to select the appropriate transition metal for a chemical reaction or to create a new material with specific properties, and as the need for new inorganic materials grows, the study and understanding of the transition metals and their properties has become paramount. In addition to understating the properties of each transition metal on its own, many valuable materials incorporate more than one transition metal. When transition metals are combined the properties of the new material do not always mirror the properties of the constituent metals, which makes studying these systems

of great interest. The research presented in this dissertation has focused on synthesizing and studying inorganic compounds that are comprised of two or three transition metals. In the next few sections the steps necessary to synthesize, characterize, and investigate the properties of new inorganic compounds will be discussed.

Periodic Table of Elements

1 IA		Transition Metals										Nonmetals						18 VIIIA																																								
C Solid		Metals										Other nonmetals						Noble gases																																								
Hg Liquid		Alkali metals										Alkaline earth metals						Halogens	Noble gases																																							
H Gas		Lanthanoids										Actinoids						Transition metals	Post-transition metals																																							
Rf Unknown		III B										IV B						V B	VI B	VII B	VIII B	IX B	X B	XI B	XII B																																	
1	H	3	Li	4	Be	5	B	6	C	7	N	8	O	9	F	10	Ne																																									
2	He	11	Na	12	Mg	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar																																									
3	Li	19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr																					
4	Be	37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe																					
5	Na	55	Rb	56	Ba	57	La	58-71	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn																								
6	Li	87	Fr	88	Ra	89	Ac	90-103	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	101	Uut	102	Uuq	103	Uup	104	Uuq	105	Uub	106	Uuq	107	Uuq	108	Uuq	109	Uuq	110	Uuq	111	Uuq	112	Uuq	113	Uuq	114	Uuq	115	Uuq	116	Uuq	117	Uuq	118	Uuo

Key

Atomic #	Symbol	Name	Atomic Mass
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For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

Periodic Table Design and Interface Copyright © 1997 Michael Dayah. <http://www.ptable.com> Last updated Dec. 10, 2011*

Figure 1.1 Periodic table with the transition metals highlighted in red.¹

1.2 Synthesis of New Materials

When conceptualizing a new inorganic compound, it is important to consider not only what transition metal would be best, but also what ligand to use. Ligands are ions or molecules, most often carbon-, oxygen-, nitrogen-, and hydrogen-based that bond to transition metals. When transition metals bond to ligands they form a coordination complex, and one of the most important properties of a coordination complex is the oxidation state of the transition metal. The oxidation state is a number assigned to each element in a compound and represents the number of valence electrons that an atom possesses. Valence electrons are the number of electrons that the atom can gain, lose, or share when chemically bonding. The oxidation state of

transition metals can be positive, negative, or zero depending on a few factors, one of which is the charge of the ligand used to form the coordination complex. Understanding the oxidation state and in turn the number of valence electrons the transition metal possesses can help us predict the properties and reactivity of the complex. In section 1.3, characterization methods to understand the location of the electrons in a coordination complex and how they are shared between the transition metal and ligands will be discussed, but first it is important to briefly describe the different characterization methods used to characterize new compounds throughout this work.

1.3 Characterization Methods

There are numerous methods to characterize the structure and properties of coordination complexes. One of the most powerful and frequently used methods to characterize compounds is spectroscopy, which is the study of the interaction between matter and electromagnetic radiation. The electromagnetic spectrum, Figure 1.2, shows the range of frequencies and corresponding wavelengths of electromagnetic radiation. The most common types of spectroscopies for studying coordination compounds are infrared (IR), absorption (ultraviolet/visible, UV/Vis), nuclear magnetic resonance (NMR), and electron paramagnetic resonance (EPR).

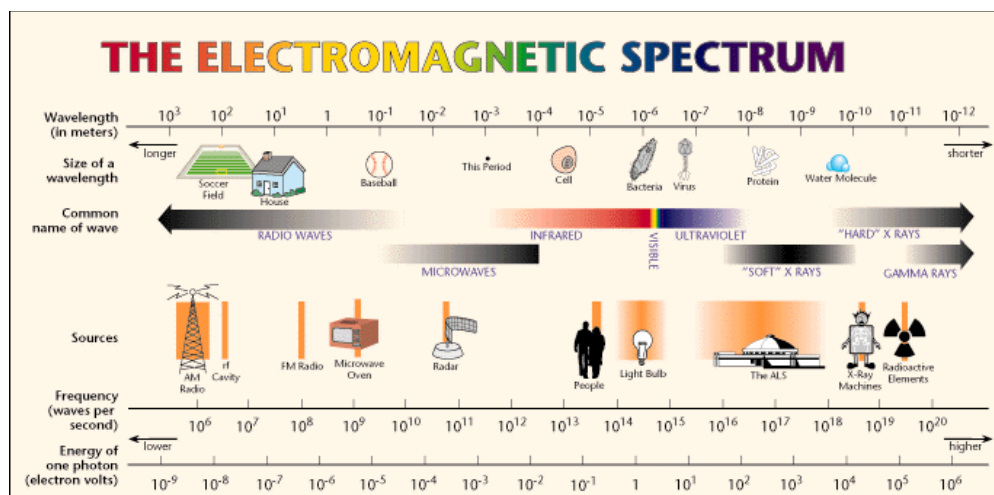


Figure 1.2. The electromagnetic spectrum.²

X-ray diffraction (XRD) has also played a vital role in this work and plays a significant role in the discovery of a new compounds. XRD and the subsequent data analysis is used to identify the molecular structure of a crystalline material. XRD relies on the atoms in a molecule to diffract incident X-ray beams. Measuring the angles and intensities of the diffracted beams allows you to determine the identity and position of the atoms that make up a molecule. In general terms, XRD provides a valuable three-dimensional picture of the molecule, which you can use to determine atom to atom distances and angles between different atoms in the molecule, and the overall charge of the molecule. An example of a crystal structure characterized by XRD is shown in Figure 1.3. This structure contains two different transition metals, Mo and Ru, and four ligands that are represented by the blue and black spheres. What this crystal structure does not provide is a description and the location of the electrons, known as the electronic structure. Computational methods are employed, in a separate experiment, to determine the electronic structure.

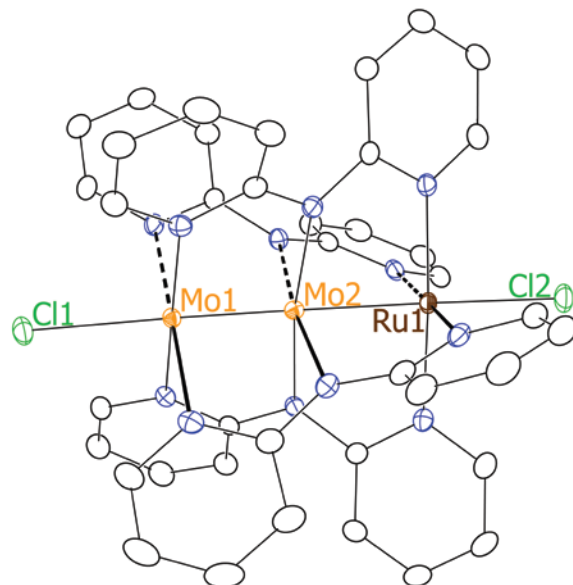


Figure 1.3. X-ray crystal structure of $\text{MoMoRu}(\text{dpa})_4\text{Cl}_2$. Blue spheres represent nitrogen atoms and black spheres represent carbon atoms. Hydrogen atoms have been omitted for clarity.

1.4 Computational Chemistry

Chemists have utilized computational chemistry much more in the past decade as the speed and processing power of computers has advanced. Computational chemistry relies on the laws and theories of physical chemistry to predict the structure, spectroscopic properties, and electronic structure of molecules. Chemists compare computer-predicted values to experimental results for validation, and the computer predictions help to explain the reason why certain experimental features are observed, in ways that spectroscopic methods alone cannot. To start a computational simulation you must first input a set of structural coordinates, which can be obtained from the X-ray crystal structure. After you set the appropriate operating procedures, which tell the computer how and what to calculate, the computer very efficiently (within hours or days) calculates a prediction of the molecule's electronic structure and any other properties you set the computer to calculate.

The electronic structure of a complex is the arrangement of the electrons in orbitals which are, in theory, the houses for the electrons. Each orbital has a specific shape and characteristics. For the sake of this discussion we will only discuss the d orbitals, which are shown in Figure 1.4. Each of these orbitals can, at maximum, hold two electrons. The oxidation state of the transition metal or metals present in the molecule determine the total number of valence electrons that will be housed in the five d orbitals. Chemists aim to know what orbitals are filled and with how many electrons. This information provides rationale to describe the molecule's properties and helps chemists systematically design new materials.

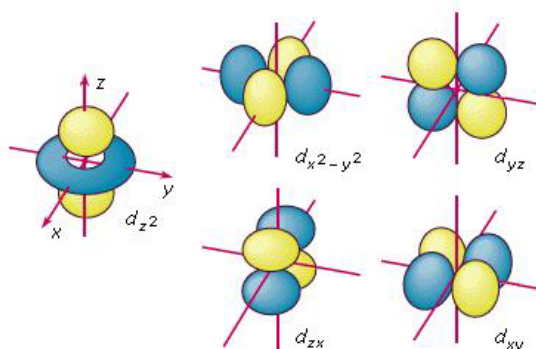


Figure 1.4. The five d-orbitals. The blue and yellow colors represent different phases.³

1.5 Conclusions and Overview of Thesis Work

In the work presented herein, I synthesize and characterize molecules that possess two and three transition metals. My goal is to understand how the metals in the systems interact with each other and use that information to eventually design new inorganic materials. The second chapter provides a review of the ligand, 2,2'-dipyridylamine ligand (dpaH), that I worked with during my Ph.D. studies. Chapters 3 – 5 detail molecules that contain just two transition metals. Chapter 3 is a purely computational study on dichromium (Cr_2), dimolybdenum (Mo_2), and ditungsten (W_2) compounds that provide an introduction into how transition metals interact and form bonds. Bonds are simply the sharing of valence electrons between two atoms. Chapters 4

and 5 more thoroughly detail the synthesis and characterization of molecules that contain two transition metals, namely, Cr, Mo, and W. In these molecules an oxygen (O) atom is also incorporated, see Figure 1.5. In Figure 1.5, I show a molecule which possess two W atoms (purple spheres) with one W atom forming a bond to an O atom (red sphere). Computational chemistry is also used to characterize the electronic structure of these systems.

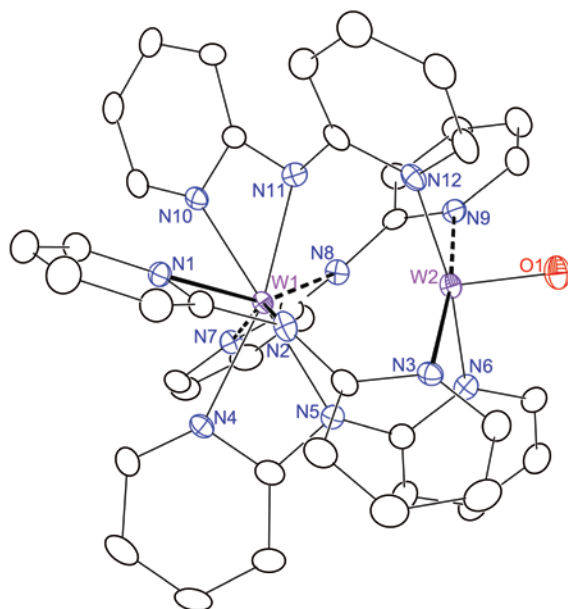


Figure 1.5. X-ray crystal structure of $[W_2O(dpa)_4]^{2+}$. Black spheres represent carbon atoms. Hydrogen atoms have been omitted for clarity.

In chapters 6 – 9 the focus is shifted from systems with just two transition metals to systems that have three transition metals, see Figure 1.3. The X-ray crystal structure in Figure 1.3 shows a compound that has two Mo atoms (orange spheres) and a ruthenium (Ru) atom (brown sphere). In these chapters my goal is to understand how the molecules' electronic structure and in turn physical properties change when a third transition metal is added to the system. The synthetic procedures that I discovered are thoroughly described, along with the physical characteristics of the molecules. From this work, I was able to draw conclusions about

the nature of interactions between the three transition metals and their effect on the overall system properties.

Overall, the work I describe in this thesis details the synthetic methods to make novel compounds that possess multiple transition metal interactions, and the experimental and computational characterization methods used to fully understand the molecule's properties. From this work I was able to establish a foundation to understand how transition metals interact in systems that incorporate two and three transition metals. I hope this chapter has been beneficial to you, and helped you understand the processes and techniques that are used by inorganic chemists, and chemists as a whole, that drive chemical research. I thank you for reading.

References

- (1) Periodic table of elements taken from <http://www.doccasagrande.net/>.
- (2) Electromagnetic spectrum taken from www2.lbl.gov.
- (3) d-orbitals taken from www.britannica.com.