

Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, the director of the Wisconsin Initiative for Science Literacy (WISL) encouraged all Ph.D. chemistry 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, state legislators, and members of the U.S. Congress.

Ten Ph.D. degree recipients have successfully completed their theses and included such a chapter, less than a year after the program was first announced; each was awarded \$500.

WISL will continue to encourage Ph.D. chemistry students to share the joy of their discoveries with non-specialists and also will assist in the public dissemination of these scholarly contributions. WISL is now seeking funding for additional awards.

Wisconsin Initiative for Science Literacy

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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NEW AXIAL REACTIVITY OF TRIMETALLIC COMPOUNDS

by

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Chapter 1

Wisconsin Initiative for Science Literacy: Introduction for a General Audience

1.1 Inorganic Chemistry

When starting out in any general chemistry class, students are first exposed to inorganic chemistry, often without their knowledge. In its most basic essence, inorganic chemistry may be defined as the study of inorganic compounds, namely, anything not containing a carbon-hydrogen bond. Although most of the building blocks of life, such as amino acids, are organic and contain carbon and carbon-hydrogen bonds, a large majority of the items we use each day to make our lives easier and more enjoyable are composed of inorganic materials.

Although most students and the public in general are more familiar with the popularized -organic compounds that are present in food, medicine, and many other products, it is important to understand inorganic chemistry and exploit it for its many uses. Inorganics comprise most of the periodic table (excluding carbon) and it is these elements that truly have the most interesting properties and reactivity. For example, the lithium batteries in cell phones and other electronics, the steel and other metals used to construct buildings and modes of transportation, and the metal impurities that give color to precious gems, among many other materials, are all inorganic materials. The study of inorganic compounds is highly relevant to the advancement of science and to the lifestyle people enjoy today.

One important and often misunderstood element of inorganic chemistry is that metals do not only exist as the bulk solid, but also as ions in solution, and this is where

most of the exciting reactivity takes place. The properties that people often associate with metals, such as high conductivity, shiny appearance, malleability and ductility, among others, are not always true for metals, especially transition metals that have reacted with other substances to form inorganic complexes.

1.2 Transition Metals

The transition metals are found in the center of the periodic table as shown in Figure 1.1. Among inorganic compounds, arguably the most interesting are those containing transition metals. The transition metals have a range of properties from highly metallic to relatively inert, so selecting the proper metal center for a given type of reaction is an important part of inorganic synthesis.

The figure shows the IUPAC Periodic Table of the Elements. The transition metals, located in the center of the table (groups 3-10 and 11-12), are highlighted in red. Other groups are color-coded: Alkali Metals (yellow), Alkaline Earths (orange), Halogens (green), Noble Gases (purple), Lanthanides (light blue), and Actinides (dark blue). The table includes element symbols, atomic numbers, and names.

IUPAC Periodic Table of the Elements																			
1		2										3						4	
H		He										Li						Be	
Li		Be										B						C	
Na		Mg										Al						Si	
K		Ca										Sc						Ti	
Rb		Sr										Y						Zr	
Cs		Ba										La						Ce	
Fr		Ra										Ac						Th	

Figure 1.1. The periodic table, with transition metals highlighted in red.¹

Transition metals are involved in a variety of reactions and processes. In order to fully make use of the capabilities of the transition metals, it is important to study them

extensively and have a fundamental understanding of their reactivity. Although the transition metals encompass all the elements highlighted in Figure 1.1, the discussion in this chapter will mostly focus on what are known as the “*d*-block” elements, or those found in the rectangle formed by Sc, La, Hg, and Zn.

1.3 Metal Oxidation States

The determination of oxidation states of atoms or ions is based on a set of rules that are taught early in general chemistry courses. Often, the property of a transition metal that determines its reactivity is its oxidation state. The oxidation state refers to the charge of the metal center and is counted based on the number of electrons at the metal center. Depending on the atoms bonded to the metal center, electrons can either be added or removed from the electron cloud surrounding the metal center and this will change the oxidation state. There are several different methods for assigning the metal oxidation state experimentally (which will be discussed in more detail later), but chemists can use their intuition and knowledge about the behavior of certain atoms and molecules to “count electrons” and assign the metal oxidation state.

Most transition metals have oxidation states that are more commonly accessible, and for this reason, chemists can predict how certain molecules will react with these metals. For example, chromium (Cr) often exists in the +2 or +3 oxidation state (meaning the metal electron cloud has given up two or three electrons, respectively, to form a bond) and easily forms compounds such as CrCl_2 or CrCl_3 . Although simple compounds of this type are useful, it is of great interest to chemists to test the limits of metal oxidation states

and study how this affects the reactions these metal compounds are capable of carrying out.

1.4 Gaining Fundamental Understanding

The chemistry of a transition metal is dramatically affected by its ligand environment. Ligands are simply ions or molecules that bond to the transition metal. The metal and ligands can form single, double, or triple bonds. When a metal bonds to any number of ligands, the result is known as a coordination complex, and coordination complexes of the same metal often have very different properties, including the observed color of the complex, which is one of the most exciting aspects for students entering the field of inorganic chemistry. Several examples of well-known transition metal complexes and their corresponding colors are given in Figure 1.2.

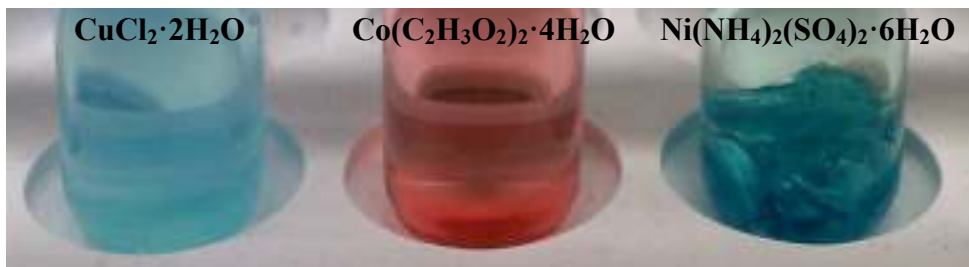


Figure 1.2. Colorful transition metal complexes in water.²

The colors of the compounds shown in Figure 1.2 appear because of the structures of the compounds, depending mainly on the identity of the metal center and its ligands. It is important to understand the structure and properties of coordination compounds to predict their behavior and make compounds that will have useful applications, as catalysts, pigments, and therapeutic agents, among others.

1.5 Characterization Methods

There are numerous ways to probe the structure and properties of coordination compounds. One very powerful and diverse tool to study chemical structure is spectroscopy, which is the study of the interaction of matter and radiated energy. The electromagnetic spectrum (Figure 1.3) shows the relationship between the different types of energy in terms of wavelength and frequency, as well as common sources of these types of energies. There are numerous types of spectroscopies, including infrared (IR), absorption (UV/Vis), nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and X-ray crystallography, which are all used extensively in the Berry group to probe coordination compounds. Although the physics behind each technique will not be described here, a brief overview of each method will be given so that the reader will understand how we use these powerful tools.

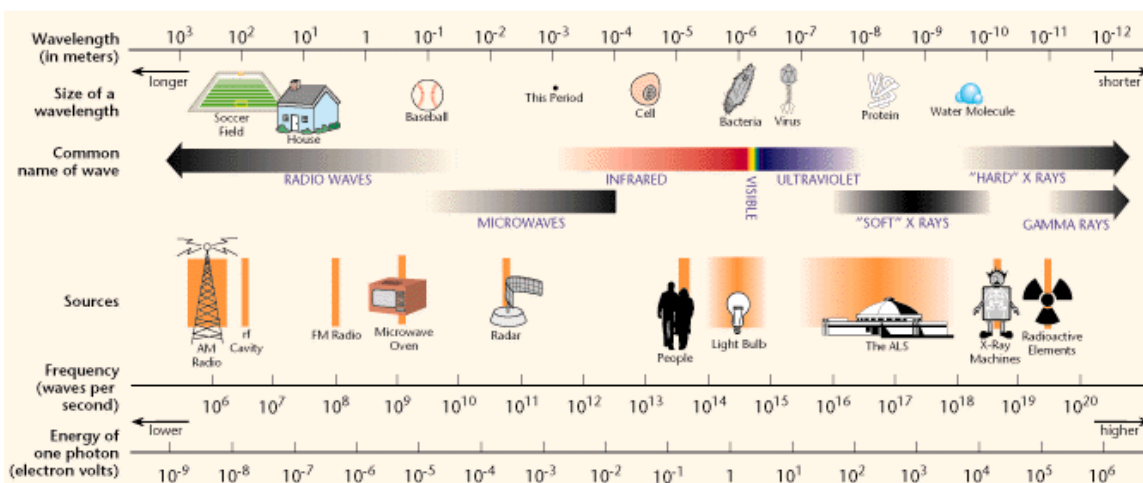


Figure 1.3. The electromagnetic spectrum.³

1.5.1 Infrared Spectroscopy

Infrared (IR) spectroscopy relies on the principle that molecules are in constant motion. The types of atoms and bonds in a molecule determine the type of motion that will be present in the molecule, such as stretching and bending, as well as the energy of this motion. IR spectroscopy studies these vibrations of molecules and their energies. Passing infrared light over a small sample allows molecules to absorb this light energy based on the strength of the bonds in the molecule. This information is depicted by peaks of certain shape and size that correspond to the identity of the bonds in the molecule and help to determine a structure.⁴ An example of an experimental IR spectrum is shown in Figure 1.4, and the peak at 2051 cm^{-1} is a signature for the presence of an N_3^- group in the molecule. The absence of peaks between 4000 and 2100 cm^{-1} indicates that this compound has no bonds that respond (stretch or bend) to this energy range.

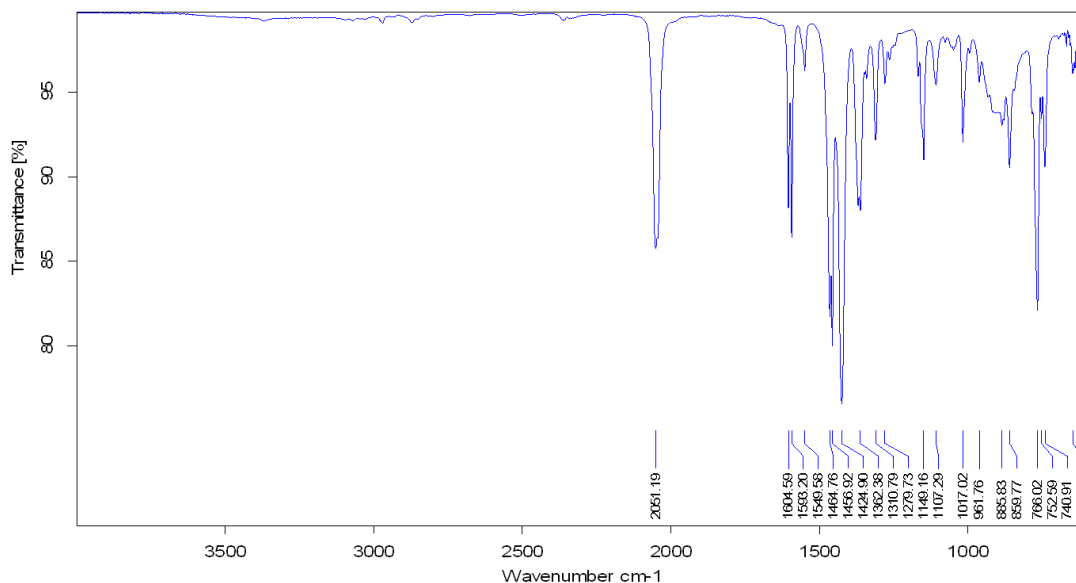


Figure 1.4. IR spectrum of $\text{Cr}_2(\text{dpa})_4(\text{N}_3)_2$.

1.5.2 UV/Visible Absorption Spectroscopy

UV/Visible (UV/Vis) absorption spectroscopy measures the amount of ultraviolet or visible light that passes through a solution of a compound. This technique is only useful if a solution is colored, as colorless solutions will allow all of the light to pass through and no information will be collected. At certain energies, more or less light will pass through the sample depending on the identity of the compound, and this gives insight into the structure of the compound. This technique works on the premise that ultraviolet and visible light have enough energy to push an electron into a higher energy orbital.⁵ The amount of energy needed for this process to occur in a certain molecule gives insight about the energy of the orbitals in the compound, which is very important for understanding chemical reactivity. This method is also useful to monitor a reaction, since the starting material and product will usually have quite different spectra. A sample spectrum is given in Figure 1.5.

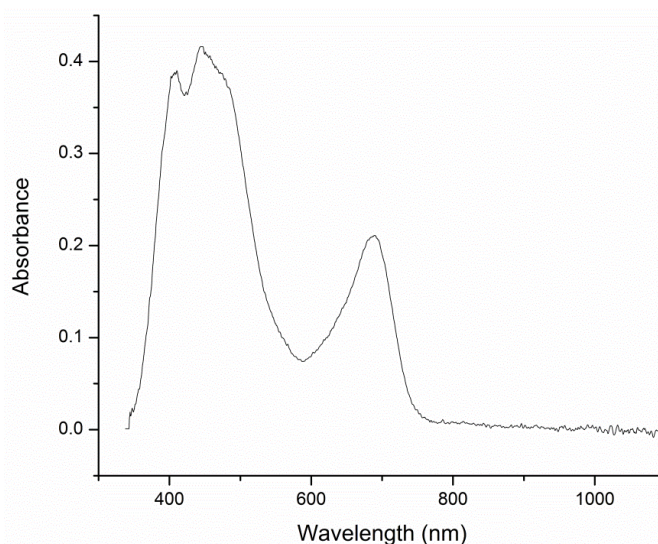


Figure 1.5. UV/Vis spectrum of $\text{Cr}_2\text{Fe}(\text{dpa})_4(\text{SO}_3\text{CF}_3)_2$ in acetonitrile.

To analyze a UV/Vis spectrum, it is useful to consider a color wheel (Figure 1.6). The spectrum above shows that the compound absorbs color at around 700 nm (in the red region of the visible light spectrum). This means that the observed color of the solution is actually green. Since the compound also absorbs at 450 nm, we should also observe orange color in the solution, so the resulting color is actually a mixture of both orange and green. Indeed, the color of the solution depicted in Figure 1.4 is dark brown.

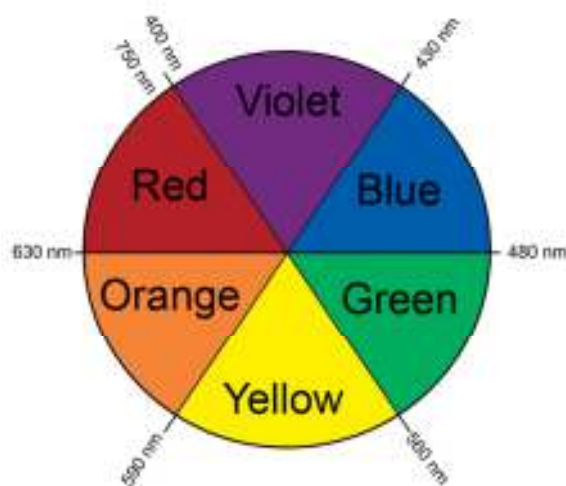


Figure 1.6. Color wheel depicting the relationship between absorbed color and observed color.

1.5.3 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool that can often be used exclusively to confirm a structure because it gives information about how different atoms are bonded to one another. In NMR spectroscopy, it is important to know that atomic nuclei can spin around and generate a magnetic field. When atomic nuclei are in solution, they can spin at random; however, when they are placed near a larger magnetic field, they will become aligned either with or against the field.⁵ (A helpful analogy is swimming fish: in a lake (absence of magnetic field), they can swim any

which way they please, but if they are placed in a river (a magnetic field), they must either swim with or against the current.) When a magnetic field is applied, all of the nuclei flip to the same orientation, but in the absence of magnetic field, the nuclei can return to either the “with” or “against” state they were originally in. At that point, the nuclei generate a signal related to the difference in energy between the “with” and “against” state. A portion of a sample spectrum is shown in Figure 1.7.

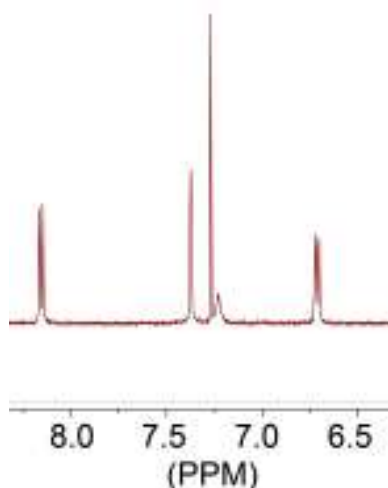


Figure 1.7. Sample NMR spectrum in CD_2Cl_2 .

These signals give clear information about the structure of the compound.⁵ The shape and location of the peaks indicate the type of bonds and functional groups near a given nucleus. In Figure 1.7, we can look at the peak at 7.3 ppm and see a tall singlet peak. This region tells us that we likely have a phenyl proton. The absence of any divisions in the peak tells us that there are no hydrogen nuclei nearby to interact with this group. Thus, from one peak, we have a great deal of information that we can combine with some knowledge of the reactions we perform to determine the structure of the compounds we make.

1.5.4 Electron Paramagnetic Resonance Spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy is similar to NMR, but is used to study structures that are paramagnetic, i.e. have unpaired electrons, and relies on electron spin rather than nuclear spin. Electrons have two possible spin states, either up or down, and EPR makes use of this property. Microwave radiation has enough energy to flip the spin of an electron in the presence of a magnetic field. The difference between the number of electrons in the up and down spin states generates a signal and the larger the difference, the higher the signal.⁶ The magnetic field at which a signal appears gives information about which atom the electron is located on and which orbitals are occupied by these electrons. This technique is especially useful for transition metal compounds, as they often have unpaired electrons, an example of which is given in Figure 1.8.

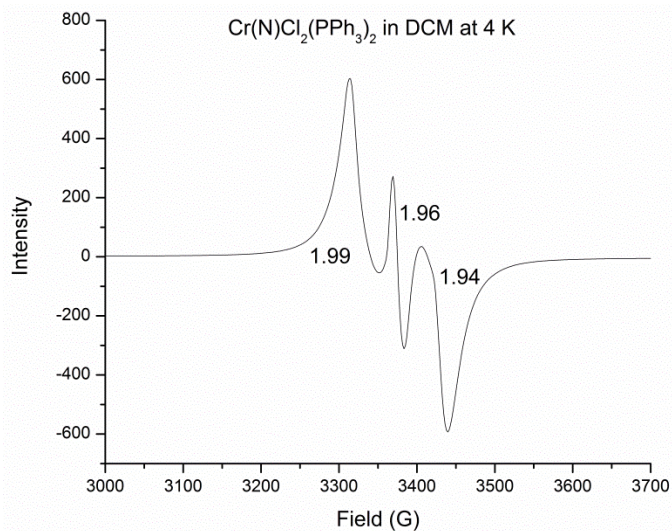


Figure 1.8. EPR spectrum of $\text{Cr(N)(PPh}_3)_2\text{Cl}_2$ in dichloromethane, including g values that help determine the location of the unpaired electron.

1.5.5 X-Ray Crystallography

X-ray crystallography is the process of determining the structure of a crystalline compound using X-ray diffraction patterns. With some luck, pure compounds crystallize out of solutions and it is possible to obtain a picture of the composition and connectivity of atoms in a molecule. It is important to note that a crystal “consists of atoms arranged in a pattern that repeats periodically in three dimensions”⁷ and sometimes compounds appear crystalline but are actually fine powders or are not well-ordered. As a result, it is not typically easy to obtain nice, diffraction-quality crystals, which explains why this technique is usually not a first resource even though it is very powerful. When quality crystals are available, X-ray diffraction is very helpful for solving transition metal coordination structures that are difficult to analyze by other methods (due to paramagnetism or small quantities). A diffractometer is used to analyze the crystals. A source shoots X-rays at a single crystal, and detectors collect the diffraction pattern that results. Based on the composition of a crystal, there will be different angles and strengths with which the X-rays are diffracted. After some complicated computations, it is possible to assign the peaks as molecule and understand how all the atoms are bonded to one another. An example crystal structure is shown in Figure 1.9.

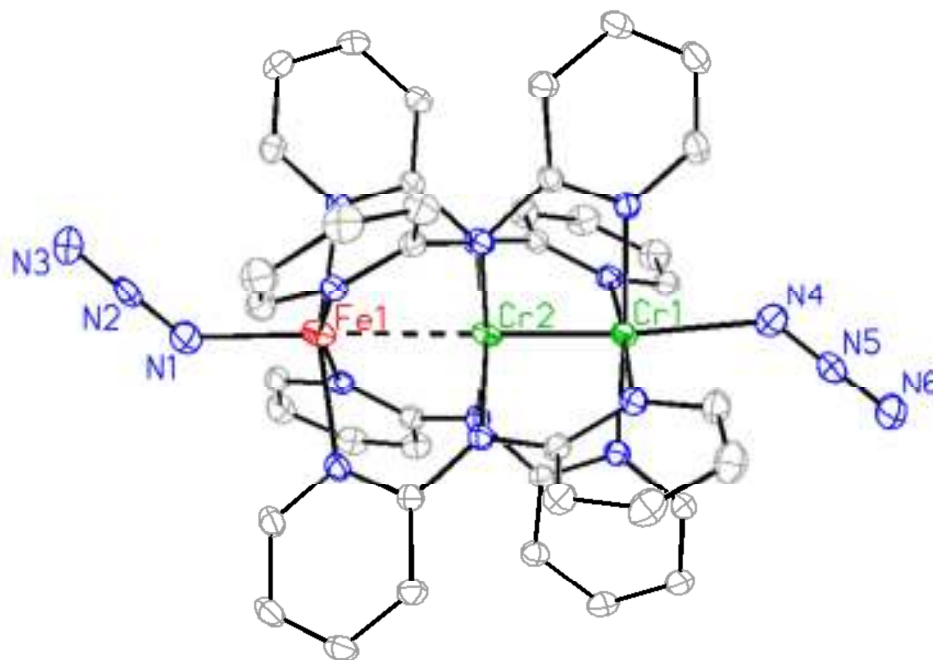


Figure 1.9. X-ray crystal structure of $\text{Cr}_2\text{Fe}(\text{dpa})_4(\text{N}_3)_2$ (blue = nitrogen, gray = carbon and hydrogen atoms are not shown to help visualize the molecule).

1.5.6 Thermogravimetric Analysis and Differential Scanning Calorimetry

In this thesis, we discuss the formation of azide compounds (as shown in Figure 1.9 and described in Section 1.7), which are able to lose dinitrogen when heated or in the presence of light. There are two useful techniques that help quantify the changes occurring in the azide compounds upon heating, which should result in the loss of dinitrogen. One of which is thermogravimetric analysis (TGA), which is essentially just a measurement of the mass of a sample as it is heated. The other useful technique is differential scanning calorimetry (DSC), which measures heat loss from a sealed sample as it is heated. Often, when there is a physical change, such as melting or gas loss, there is a huge spike in the DSC curve, which indicates the energy of the change. Figure 1.10

shows both TGA and DSC plots that indicate the loss of two molecules of dinitrogen from the overall molecule, and the energy of this process.

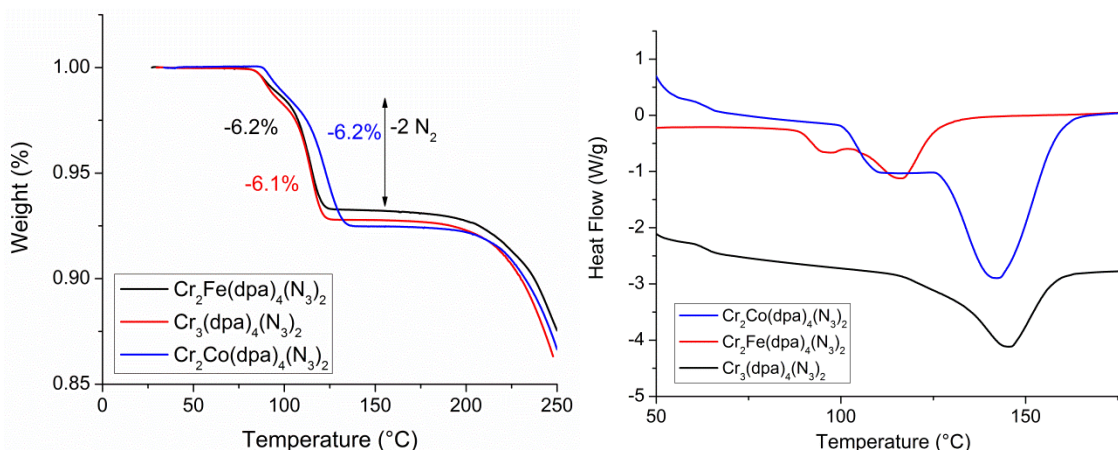


Figure 1.10. TGA data for three trimetallic azide compounds (left), showing a mass loss corresponding to loss of two dinitrogen molecules. DSC data (right), showing that energy is required for the system to lose N_2 .

1.6 Metal-Metal and Metal-Ligand Multiple Bonding

In the Berry group, we are very interested in studying reactions of transition metals. We believe that if one metal center has many interesting properties, then a compound containing two or three metal centers has that many times more interesting properties. Bimetallic (complexes with two metal centers) and trimetallic (three metal centers) are those most often studied in our group, especially if two of the metal centers are interacting with each other through a bond. Most transition metals can form compounds wherein there are two of the same metal center bonded to one another, with different bond orders - single bonds, double bonds, triple bonds, quadruple bonds,⁸ or even quintuple bonds (though these are quite rare).⁹

Since the early 1960s, metal-metal bonded compounds have been actively studied, especially with the help of X-ray crystallography, which confirmed the (previously unknown) presence of metal-metal bonds.⁸ A wealth of compounds has been made since that time, but because the properties of these compounds span such a large range of reactivity (including catalytic properties), there are many more yet to be prepared. One relatively unexplored area in this field is the preparation of complexes with both metal-metal multiple bonds and metal-ligand multiple bonds. There are many compounds that have metal-ligand multiple bonds and these are often useful for transferring atoms or understanding the steps in catalytic cycles. However, there is a scarcity of compounds containing both metal-ligand and metal-metal multiple bonds and we believe these would be of great interest for making reactive metal-ligand multiply bonded species, as well as for understanding the interactions responsible for the proposed enhanced reactivity.

1.7 Exploring New Reactivity

Bimetallic and trimetallic linear compounds have been made by our group and by others for several years, and the methodology is well-established. However, the methods for preparing systems containing both metal-metal and metal-ligand bonds had to be developed. In my research, I sought to expand on this idea by adding a third metal to the mix. Trimetallic compounds of the type shown in Figure 1.11 are well-studied, and usually feature three metals of the same type (homometallic), but can also have different metals (heterometallic), where two of the metals are quadruply bonded and the third metal has some interaction without a formal bond. In these compounds, the metals centers are almost all held in place by bridging ligands. One limitation in these

compounds is the choice for the ligand at the axial (end) site, which are primarily chloride ions or solvent molecules, with little variation.

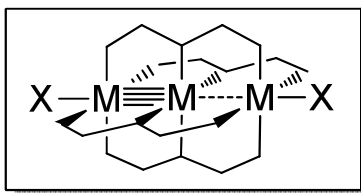


Figure 1.11. A trimetallic complex where X is an axial ligand such as chloride and the ligands surrounding the metal are shaped in paddlewheel formation.

The main goal of this thesis is to prepare trimetallic compounds with more variation at the axial site, with the hope of accessing metal-ligand bonding. The most straightforward way to approach this problem is to isolate a compound with an axial ligand that is able to react in such a way that it forms multiple bonds under some reaction conditions, such as oxidation, heating, or exposure to light. One useful starting point is the azide ligand, N_3^- , which easily loses nitrogen (N_2) upon heating or irradiation (Figure 1.12).

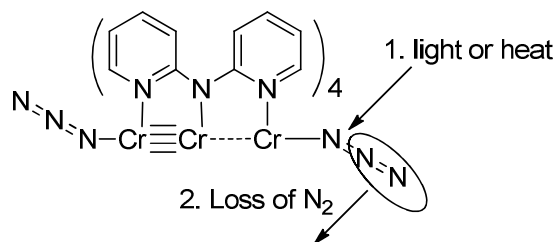


Figure 1.12. Loss of N_2 from azide (may occur on either or both sides of the molecule).

The trimetallic azide compound is very interesting because it could, in principle, lose a dinitrogen molecule from either side of the compound or from both sides, resulting in the formation of a chromium-nitrogen multiple bond. These compounds are also useful because it is easy to prepare analogues containing a different metal, such as manganese,

cobalt, or iron in the third site while the chromium-chromium quadruply bonded unit remains intact. This allows us to study the effect of both changing axial ligands and seeing how the metal choice affects the reactivity of the compound.

We also studied the starting materials and products by a variety of spectroscopic methods, and gained insight into the structure and reactivity of these compounds. Clearly, the use of azide ligands is a very useful way to make trimetallic compounds with new axial ligands.

Another method for making trimetallic compounds with new axial ligands is by simple switching. This thesis describes the use of triflate (an SO_3CF_3 group that is bonded to the metal atom through oxygen), thiocyanate (SCN), or chloride groups in varying arrangements on the trimetallic chain. The preparation of these compounds is straightforward, and usually forms crystals that can be analyzed by X-ray crystallography (see above) to determine their structure. Interestingly, the ligands on one side of the molecule have an impact on the bond lengths and angles on the other side of the molecule. This result was somewhat unexpected because the metal centers are fairly far apart, but it also corroborates the idea that the metal centers are very sensitive to changes in the ligands.

1.8 Conclusions

To conclude, the main goals of this project are three-fold: 1. to determine strategic ways to prepare trimetallic compounds with new axial ligands; 2. to analyze these materials with various spectroscopic techniques to learn about their structures; and 3. to understand how the reactivity of the compounds changes with changes in the structure. I

hope that this chapter has given the reader a glimpse into the logic (and sometimes luck) that goes into preparing new compounds and exploring the depths to which we can push our understanding of fundamental chemical interactions. Thank you for reading!

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