Exploration of the Impact of Metal Identity and Ligand Field Strength on the Electronic Structures of Metal Ions

LAKE FOREST COLLEGE

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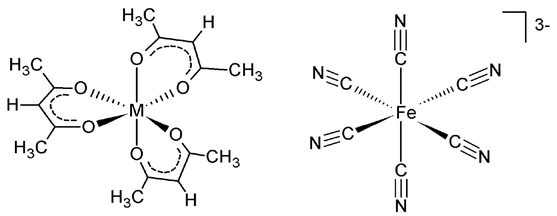
Introduction



M = Fe, Ru

Figure 1. Metal complexes M(acac)3 and [Fe(CN)6]3- explored in this exercise (acac⁻ = acetylacetonate, K⁺ cations omitted in K3[Fe(CN)6]).[1]

In this experiment, crystal field theory, electronic structure calculations and magnetic susceptibility will be used to examine the impact of metal identity and ligand field strength on the electronic structures of metal ions. Three metal complexes were chosen for investigation and are shown in figure 1. The properties and reactivities (color, redox potential, ligand exchange rates and paramagnetism) of iron and ruthenium can be dramatically changed by their *d*-electron configurations. Color is one apparent property that changes based on the d-orbital configuration in this experiment. Through crystal field theory, electronic structure calculations and magnetic susceptibility the d-electron configurations of the three metal complexes can be determined. The d-electron configurations can be influenced by the metal and the identity of the ligand, therefore both will be varied in this experiment.

Crystal Field Theory

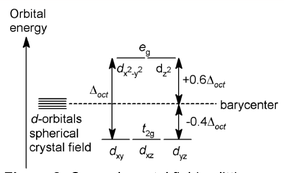


Figure 2. General crystal field splitting diagram for an octahedral metal complex.[1]

The placement of electrons in a metal's *d*-orbitals is most strongly influenced by the coordination geometry of the ligands around the metal. Crystal field theory can be used to determine what impact ligands may have on the energies of the various *d*-orbitals. This theory assumes that ligands may be treated as electron densities. These ligands destabilize the orbitals to higher energies by repelling the electrons in the metal *d*-orbitals. The electrostatic charge of the ligands is known as the crystal field. The ligands are attached to the metals in definitive coordination geometries, therefore the ligands interact with some *d*-orbitals more than others, repelling them to higher energy relative to the barycenter. While the ligands interact less with some *d*-orbitals; these *d*-orbitals are actually stabilized to lower energies relative to the barycenter. If the metal was not interacting with any ligands then all *d*-orbitals would have equal energy, described by the barycenter. The amount of stabilization and destabilization is different for different geometries. All of the metal complexes investigated have a six-coordinate ligand coordination environment with an *pseudo*-octahedral geometry. With this arrangement, the $d_{x^2-y^2}$ and the d_{z^2} orbitals are repelled to higher energy relative to the barycenter. While the d_{xy}, d_{xz}, and d_{yz} are stabilized to a lower energy relative to the barycenter. These groups of orbitals are referred to as having e_g and t_{2g} symmetries, respectively. The energy difference between these two sets is referred to as Δ_{oct}.

Filling the *d*-orbitals

The placement of the electrons in the *d*-orbitals will be determined by the configuration that gives the lowest energy. Principles of Crystal Field Theory can be applied to determine how the electrons will fill the d-orbitals. The e_g orbitals is higher energy than the t_{2g} orbitals therefore one might expect that the electrons will fill the e_g orbitals firt. However pairing electrons is also high energy because they tend to repel each other. The energy to pair two electrons is known as the pairing energy. If more energy is required to pair up two electrons than is needed to move one electron to the e_g orbitals then the configuration is high-spin. If more energy is needed to move the electron to the e_g orbitals than is needed to pair the electrons then it is low spin. The variation in electron configurations among metal complexes results in different properties.

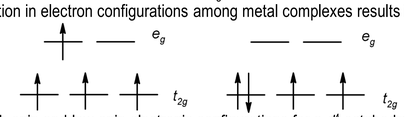


Figure 3. High-spin and low-spin electronic configurations for a d^4 octahedral metal complex.[1]

The electron configuration are effected by the identity of the metal center, the charge of the metal ion, and the identity of the ligands. Experimental observations have determined trends in the d-block metals. The Δ_{oct} values for various transition metals are ranked below in a spectrochemical series of metals.[1]

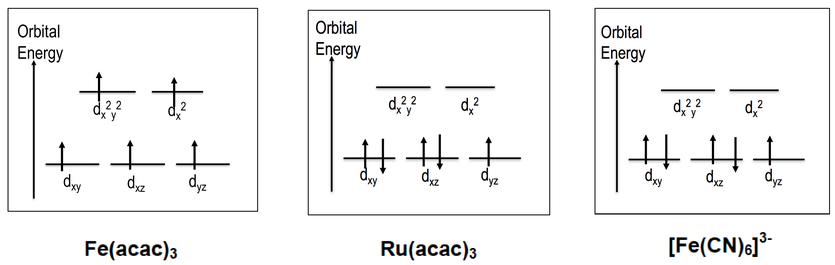
$$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Co^{3+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$$

Experimental observations have also determined trends in the ability of ligands to influence the spin-state of metal complexes. Ligands that have a lot of influence on the splitting of the *d*-orbitals resulting in large Δ_{oct} values are known as strong-field ligands. Low-spin metal complexes are often formed with strong-field ligands. Ligands that don't have a lot of influence on the splitting of the *d*-orbitals resulting in smaller values of Δ_{oct} are known as weak-field ligands. Experimental observations have determined trends in the ability of ligands to split *d*-orbitals of a metal complex and are displayed in a spectrochemical series of ligands below.

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^- < CH_3CN < py\ (pyridine) < NH_3 < en\ (ethylenediamine) < bipy\ (2,2'\text{-}bipyridine) < phen\ (1,10\text{-}phenanthroline) < NO_2^- < PPh_3 < CN^- \approx CO$$

Predicting the Spin-State of M^{3+} Complexes Using Crystal Field Theory

Crystal Field Theory was applied to predict the most likely spin-state of the metal complexes investigated in this experiment. Although $Acac^-$ is not on the common list of ligands, literature has revealed that it has similar ligand field strength to oxalate ($C_2O_4^{2-}$) or hydroxide (OH^-) which are listed.[1] The effect of charge will not be considered since both metal ions being investigated in this experiment have a 3+ charge. The following predictions were made as to the spin states of the metal complexes investigated in this experiment. Known properties indicates that Fe^{3+} has a low Δ_{oct} value, and $Acac^-$ is a weak field ligand, so it would be expected that $Fe(acac)_3$ will have a high-spin electron configuration. When the metal ion is changed to Ru^{3+}, the Δ_{oct} values increase changing the electron configuration to low-spin. When the ligand is changed to CN^-, a strong firld ligand, the Δ_{oct} values increase changing the electron configuration to low-spin.



$Fe(acac)_3$ **$Ru(acac)_3$** **$[Fe(CN)_6]^{3-}$**

Figure 4. *d*-orbital splitting diagrams for $Fe(acac)_3$, $Ru(acac)_3$, and $[Fe(CN)_6]^{3-}$. High-spin, low-spin and low-spin states are shown, respectively. The diagrams show one, five and one unpaired electrons, respectively.

Predicting the Spin-State Using Electronic Structure Calculations

Gaussian electronic structure program was used to model the metal complexes investigated in this experiment in order to determine the relative energies of the high-spin and low-spin electronic configurations of each metal complex. Gaussian allows for input the charge and spin multiplicity for each molecule, therefore it is possible to perform calculations on models that are specified as having a high-spin states or low-spin states. An important part of using this software is to choose a computational model. Literature indicated that density functional theory (DFT) calculation would be the best method.[1] It is also important to select a functional, which is the specific DFT method the calculation will use.[1] It was also indicated that the best functional would be B3LYP.[1] Then LANL2DZ was selected as the basis set which is the specific mathematical functions that the calculations will use. For the purposes of this experiment geometry optimization and frequency calculations were performed. The favored electron configuration will have lower energy than the unfavored electron configuration. Therefore, the relative energies obtained from the calculations will indicate which electron configuration is most likely.

Table 1. DFT-Calculated Energies (all values in Hartrees).[1]

Complex	Spin State	Electronic Energy	Electronic + Zero-point Energy
$Fe(acac)_3$	low	-1159.04812135	N/A
$Fe(acac)_3$	high	-1159.05994543	-1159.059945
$Ru(acac)_3$	low	-1129.47237471	-1129.472374
$Ru(acac)_3$	high	-1129.39301212	-1129.393912
$[Fe(CN)_6]^{3-}$	low	-680.32157239	N/A
$[Fe(CN)_6]^{3-}$	high	-680.27118667	-680.271186700

The optimization energy of the molecule was used to compare the lowest energy values. The total energy, optimization energy plus the frequency energy would have been ideal but the frequency energy was not determined for all molecules. The optimization energy for each molecule was compared, high spin against low spin. The lowest energy would be the most thermodynamically favorable so predictions were made based on which spin state had the lowest energy. Iron acetylacetonate was a high spin state while the other two had a low spin state.

Synthesis of Iron Acetylacetonate

In a 100 mL beaker, 3.3 grams of $FeCl_3 \cdot 6H_2O$ was dissolved in 25mL of distilled water. In a 20 mL beaker, 3.8 grams of acetylacetone was mixed with 10 mL of methanol. A stir bar was added to the $FeCl_3 \cdot 6H_2O$ and stirring began over a stirrer/hot plate. Over a 15 minute timeframe, the acetylacetone solutions solution was slowly added to the $FeCl_3 \cdot 6H_2O$ solution. The solution turned dark red. In a separate beaker, 5.1 grams of sodium acetate was dissolved in 15mL if distilled water. Over a 5 minute period, the sodium acetate solution was added to the dark red solution while stirring. A red solid began to precipitate. The mixture was heated to 80°C and was kept at temperature for 15 minutes while stirring. The mixture was cooled to room temperature slowly to allow crystals to form, then chilled in an ice bath. The solid was filtered off using vacuum filtration and then dried on filter paper then left in an open petri dish for one week.

Figure 5. $FeCl_3$ ground with mortar and pestle

Figure 6. Acetylacetone and $FeCl_3$ solution.

Determining the Number of Unpaired Electrons Using a Magnetic Susceptibility Balance

The spin-states of the metal complexes were predicted using crystal field theory. The d-orbital splitting diagrams were drawn for each metal complex. The electrons were drawn in the appropriate places based on crystal field theory. Iron acetylacetonate was synthesized in the laboratory for later measurements on the Johnson-Mattey Magnetic Susceptibility balance. Once the compound dried, the magentic susceptability balance was used to determine the number of unpaired electrons. The balance was turned on and warmed up for 10 minutes. An empty sample tube was placed in the balance to find R_0. Then the sample was transferred into the sample tube and R was directly measured.

$$X_g = \frac{CL(R - R_o)}{10^9 * M}$$
$$X_m = X_g * MW$$
$$X_A = X_m + Cor(10^{-6})$$
$$U_{eff} = \left(\frac{3KTX_A)}{NB^2}\right)^{1/2} = 2.828(X_AT)^{1/2}$$

C: Calibration Constand found to be 1.255
L: Length of sample in tube in cm. Min of 1.5cm
M: Mass of Sample
MW: Molecular weight
Cor: Correction value found in the magnetic susceptability instruction manual
T= Temperature of room at time of measure

These magnetic susceptibility balance and the calculations were also used for iron cyanide and ruthenium acetylacetonate. Computational chemistry used Gaussian to determine the energy of each complex, in turn finding whether the complex was high spin or low spin so the d-orbitals could be determined.

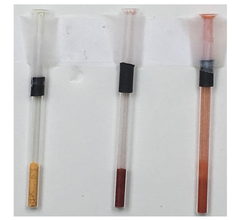


Figure 7. Magnetic Susceptibility Tubes

Table 2. Magnetic Susceptibility Balance Data.

Complex	R_0	Sample Mass (g)	Sample Length (cm)	R	Temperature (K)	Correction Value
$Fe(acac)_3$	-44	.0853	1.9	1784	297.15	178
$Ru(acac)_3$	-35	.0945	1.6	90	297.15	178
$K_3[Fe(CN)_6]$	-30	.1631	1.8	402	297.15	136

Table 3. Magnetic Susceptibility Balance Calculation Results.

Complex	X_g	X_m	X_A	μ_{eff}	Unpaired electrons (spin-only)	Unpaired electrons (actual)	Spin-State
$Fe(acac)_3$	5.11004E-05	0.018047136	0.018225136	6.58116322	5	5	High
$Ru(acac)_3$	2.65608E-06	0.001058158	0.001236158	1.713973836	1	1	Low
$K_3[Fe(CN)_6]$	5.98337E-06	0.001969965	0.002105965	2.237138612	1	1	Low

Conclusions

The spin state of three metal complexes was determined using three different methods during this experiment. Crystal field theory, DFT, and magnetic susceptibility were all used to help determine the spin state and the number of unpaired electrons in the metal complexes. Knowing the spin state can help determine the number of unpaired electrons in the d-orbital of the complex. The number of unpaired electrons in the d-orbital can greatly impact how the complex interacts and reacts. All three methods gave similar results. Knowledge of crystal field theory and ligands is necessary to predict the number of unpaired electrons and the spin state for the first method to work. Magnetic susceptibility is a very quick and easy way to find the number of unpaired electrons in a complex, but figuring out if it is high spin or low spin would require some knowledge of crystal field theory or another experimental method like computational chemistry because the magnetic susceptibility balance will only give calculation for number of unpaired electrons. Using Gaussian and computation chemistry theoretical energies can be determined, keeping in mind that the lowest energy is the most thermodynamically stable, the spin state can easily be determined. It was found that Iron Cyanide and Ruthenium acetylacetonate were both low spin state. The iron cyanide complex had 1 unpaired electron (magnetic susceptibility) and the ruthenium complex had 5 unpaired electrons. Iron acetylacetonate was found to be high spin state (Gaussian) and It had 1 unpaired electron (magnetic susceptibility).

Acknowledgements

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