Modeling of Transition Metal Complexes

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Abstract - Environmentally harmful heavy metals can come from industrial catalysts, which make use of heavy and expensive metals in their production processes. A replacement for any one of these catalysts would diminish the risks of catalyst disposal and the harmful effects on the environment. This project investigates the binding mode between the reaction of a transition metal ion and amino acids, particularly histidine. It aims to facilitate the design of an alternative catalyst through computational chemistry. Histidine was chosen for the amino acid because it is a commonly occurring amino acid that has favorable crosslink element: sulfur. Nickel (II) ion was chosen because it is cheaper and lighter than the metals currently in use. Different carboxyl group configurations yielded different bonding modes between the histidine and the metal ions. The objective is to calculate the different binding/interaction energies, which would provide the insight of how the interaction occur and which binding structure might be the best interaction. The higher the binding energy, the more stable the complex will be.

Keywords: nickel, histidine, complexes, catalyst, computational chemistry, metal

1 Introduction

Computational chemistry is a field of chemistry dedicated to predicting properties of particles and how particles will react to each other through computational algorithms. By giving the computer the means to calculate the positions of the atoms or ions, and how they will react to changes over time, the computer simulation can test for different scenarios that would be cost and time prohibitive or effective to synthesize and characterize in a laboratory setting. Because the actions of electrons in their orbitals are what dictate intramolecular and intermolecular interactions, such as different binding angles, π-π interaction, intermolecular forces and bonding sites, this allows simulations to give important information on how particles will react to changes in their environment, to other particles, and what physical and chemical properties of a proposed geometry might contain.

The Schrödinger equations were developed in 1926 by Irwin Schrödinger and allowed orbitals to be modeled for a hydrogen-like atom. Subsequent work on these equations gave scientists the shapes for electron orbital clouds.¹ The quantum mechanic (QM) modeling has been successful in many field in predicting the binding mode, interaction energies, and electronic properties such as infrared (IR), and UV-vis spectra. QM model uses these electron clouds to determine the shape and geometry of composition and help determine how atoms would bond and interact. For example, when atoms of ligand approach the central metal ion to form a complex, the electron-electron repulsion between the electron from the atoms of ligand and electrons from the metal ion will force five d-orbitals of metal ion to split according to the approaching direction of ligand and orientation of the d-orbitals. QM calculation will be able to predict such splitting to determine the suitable/final stable geometry should such complex represent. On the other hand, we can visualize the final geometry of the modeling results and derive what electron-electron repulsion would have occurred and how the d-orbital would be split. All this splitting pattern are based on the amount of “imaginary” collision between the electrons of the central metal ion and electrons of the incoming ligand when the complex is formed. However, such “imaginary” collision shall not be confused with the coordination bond formed in the complex.

2 Experiment Design

The way that the computer is able to calculate the positions of the atomic orbitals and the movement of electrons and other particles is by using a set of basis set (a mathematical expression) to describe the electrons. These electrons expression will then follow the basic physical rules such as Hund's Rule, the Aufbau Principle, and the Pauli Exclusion Principle, which help us define how electrons fill the orbitals within any given atomic and geometric structures. Most popular functionals used are either Hartree-Fock or Density Functional Theory (DFT). In our study, we will use DFT’s B3LYP functional and LANL2DZ basis set for metal ions and 6-31G* for rest of elements in the structure. Certain approximations are employed in order to achieve the relative accurate modeling results within the reasonable time frame. For example, because the electrons are so light compared with the nuclei. Therefore, the motion of atomic nuclei and electrons in a molecule can be separated, which is the heart of the Born–Oppenheimer (BO) approximation.² Also the electrons are moving at the speed of light, there would be no way of tracking the electron movements and their accurate position within the sensitivity of our instruments. The
exchange and correlation functions in the Schrödinger equations will be approximated. These mathematical approximations were developed in the 1990's, and allowed reasonably accurate molecular modeling simulation results to be run without a massive amount of computing power and time. These simplifications mean that these functionals and basis sets work very well for most of geometry optimization and electronic property calculations. Though the validation of these different functionals and basis set for particular problems are still yet to be tested and validated. For this project, the combination of B3LYP functional with LANL2DZ/6-31G* basis set is a particularly well-balanced basis set by other studies.\[3][4]

This research project is to investigate the different binding modes of the histidine amino acid with Ni(II) ion. The previous study in this group investigated the binding mode using the N-atoms in the R-group of histidine. The bond lengths and bond angles of those binding modes were sought between the metal ion and the oxygen atoms in the carboxyl group, as well as the binding energy (shown in Table 1). For comparison, we investigate what if the N-terminal and C-terminus were to be used to bind the metal in this study. Total of five experiments were designed to run the simulation under computational chemistry.

| Table 1 Binding Energy of N-atoms in the R-group of histidine |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Charge/mu 0  | 0 hist      | -1 hist     | -2 hist     | Figure 2    | Figure 4    | Figure 6    | Figure 8    |
| 1           | 1.114000    | 1.114000    | 1.114000    | 1.114000    | 1.114000    | 1.114000    | 1.114000    |
| 2           | 1.221000    | 1.221000    | 1.221000    | 1.221000    | 1.221000    | 1.221000    | 1.221000    |
| 3           | 1.328000    | 1.328000    | 1.328000    | 1.328000    | 1.328000    | 1.328000    | 1.328000    |
| 4           | 1.435000    | 1.435000    | 1.435000    | 1.435000    | 1.435000    | 1.435000    | 1.435000    |
| 5           | 1.542000    | 1.542000    | 1.542000    | 1.542000    | 1.542000    | 1.542000    | 1.542000    |
| 6           | 1.649000    | 1.649000    | 1.649000    | 1.649000    | 1.649000    | 1.649000    | 1.649000    |
| 7           | 1.756000    | 1.756000    | 1.756000    | 1.756000    | 1.756000    | 1.756000    | 1.756000    |
| 8           | 1.863000    | 1.863000    | 1.863000    | 1.863000    | 1.863000    | 1.863000    | 1.863000    |

\[BE = \text{binding energy}\]

The calculation results would then be viewed and analyzed on the workstation again for electronic, vibrational, absorption and optical properties.

**Experiment 1.** Our first attempt is to bind the metal with neutral histidine amino acid. Figure 1 shows model constructed before the simulation. The after results were a bit surprising because even though metal Ni did bind to the N atom and one of O atom of carboxylate group, it broke one of C-C bond (Figure 2). The C-C bond length in the optimized neutral histidine was 1.54815, and the same bonds in the complex were 4.45892 and 4.26724. This shows that the Ni(II) is unlikely to bind to a neutral histidine amino acid. This is rather trivial since COOH functional group on the neutral histidine would be much less likely to have an electron density available to be used for binding to the metal.

![Figure 1 Simulation before experiment 1](image)

**Experiment 2.** Therefore, our second attempt investigates the binding the metal ion with ionized histidine by removing the proton from the C-terminus (COOH group). This results in the histidine carrying a (-1) charge. Figure 3 illustrates the model constructed with overall neutral charge, and Figure 4 illustrates the binding mode after the reaction, respectively. Unlike the previous experiment, this experiment successfully bind the metal ion to the (-1) charged histidine ion without breaking histidine into fragments. The simulation results suggest that the metal ion situate in a square planar binding mode with two histidine amino acids. Furthermore, the C-terminus from each histidine amino acid is transfer to each other. In experiment 4 we shall investigate the cis conformation of similar binding mode where the C-terminus of each histidine would be on the opposite of nitrogen of N-terminus of other histidine. The purpose of experiments 2 and 4 is to study the trans effect of binding atoms to the electronic and geometric properties. Furthermore, the subtle change in the electronic and/or geometric parameters would be very well reflected in the optical measurements such as the infrared and Ultra Violet visible spectra.

3 Computational Results

All calculations were carried out on a Computing cluster in the department of chemistry at Prairie View A&M University. The model was constructed using GaussView software on a standalone workstation. When the possible binding geometry was designed, the computations were sent to the G09 modeling software on the cluster to be calculated. The calculation results would then be viewed and analyzed on
By examining the bond lengths of C-C, C-N, C-O, and C=O (in table) before binding and after binding, it can be seen that the O-C bond in the carboxyl group weakens and lengthens to allow the O-Ni bond to take place (Table 1), whereas the opposite O=C bond on the carboxyl group shortens to accommodate the changing electron densities. Compared to the optimized -1 histidine (Figure 4), the O-C bond in the carboxyl group lengthened from 1.25793 to 1.30896, and the O=C bond shortened from 1.26177 to 1.22110.

**Experiment 3.** Our third run focuses on the binding mode of Ni(II) to two histidine by removing additional proton from N-terminus (Figure 5 shows the model constructed before the simulation). Because of additional loss of proton, the histidine now carries (-2) charge (one from the C-terminus and the other from the N-terminus). The overall charge of this binding mode would be (-2) charge. Figure 6 shows the results after the simulation where this histidine would indeed bond to the metal and formed a planar structure similar to those of experiment 2 in Figure 4. However, there are fundamental differences between the Figure 4 and Figure 6.

Namely, because the nitrogen is more basic and more electronegative than the carbon atoms, the nitrogen “grabbed” a hydrogen from the adjacent β-carbon of the histidine where a double bond is formed. As a result, it shortens this C3-C4 bond on the complex in order to remain stable. This experiment suggests that such mode would be unlikely in the solution and would not be a viable binding mode. The complexes formed with the -2 charged histidine had very different bonding energies from the complexes with the -1 charged histidine, and had a binding energy of -889.000767754 kcal/mol instead of the others, which were ~-730 kcal/mol.

**Experiment 4.** In the fourth attempt, we positioned the histidine so that they were both facing the same direction (Figure 7 illustrates before the simulation). By doing so, the C-terminus of each histidine would be opposite of N-terminus of the other histidine. The simulation results would be similar to that in experiment 2 but in the cis binding mode.

As shown in Figure 8, the bonding mode of deprotonated histidine (-1 charge) with the Ni(II) ion demonstrated a weaker binding. The calculated interaction energy by subtracting the summation of total energy of Ni(II) and histidine ion from that of complex for this cis form is -
733.48 kcal/mol, compared to that of trans form -743.19 kcal/mol. The 9.71 kcal/mol higher in the interaction energy of the cis form than those in the transfer form can be due to the trans effect in experiment 2.

**Experiment 5.** Since all previous four experiments resulted in a square planar geometry at the nickel ion site, in the fifth attempt, a tetrahedral structure for this complex was proposed and constructed as shown in Figure 9 before the simulation.

The simulation result in Figure 10 indicated that a Ni(II)-histidine complex will not support a tetrahedral geometry. Interestingly, its final simulation result settled into a cis form as experiment 4, rather than a more stable trans form. Nevertheless, the square planar geometry was “chosen” by all of these various simulation attempts because only the square planar geometry would result in a diamagnetic complex with the eight (8) d-electrons. All other splitting such as octahedral or tetrahedral would result in uneven occupation of d-orbital as shown in Figure 11. The left is a tetrahedral geometry, where d-orbital splits into two groups: dxz, dyz, dxy are in higher energy and the other two d orbitals in lower energy. Per the Hund’s Rule and the Aufbau Principle, these eight d-electrons from Ni(II) would be occupied in a mixed mode of pair and single electrons on the top level of splitting. This would cause the disparity in the electron pairing and would require further splitting. Otherwise, the Ni(II) would be paramagnetic. However, if the Ni(II) is in square planar geometry as shown on the right of Figure 11, then there is no problem of pairing these electrons in pair and have diamagnetic property, which consists with the experimental observation. The bond lengths of the these complexes in various binding modes are summarized in Table 1. Two histidine groups faced opposite directions, and the complex was formed successfully in a planar geometry.

**4 Conclusions**

Nickel(II) could bind with (-1) negative charged histidine amino acids on the N-terminus and C-terminus, but will not bond with neutral histidine or (-2) charged histidine. When the neutral histidine was used, it did not bond with the Ni(II) and instead broke apart and the (-2) charged histidine would re-arrange H by “robbing” the adjacent H from carbon to maintain the proper N-terminus. All of other binding mode would form a planar structure, and it was confirmed that tetrahedral bonding would not be supported by the Ni(II).

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**6 References**


