

# Kenyon College

## Digital Kenyon: Research, Scholarship, and Creative Exchange

---

Kenyon Summer Science Scholars Program

Summer Student Research Scholarship

---

Summer 2004

## Computational Chemistry on Metal Complexes

Emily Rains

Follow this and additional works at: <https://digital.kenyon.edu/summerscienceprogram>



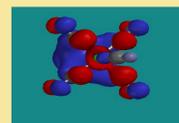
Part of the [Chemistry Commons](#)

---

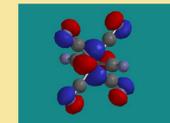
### Recommended Citation

Rains, Emily, "Computational Chemistry on Metal Complexes" (2004). *Kenyon Summer Science Scholars Program*. Paper 291.  
<https://digital.kenyon.edu/summerscienceprogram/291>

This Poster is brought to you for free and open access by the Summer Student Research Scholarship at Digital Kenyon: Research, Scholarship, and Creative Exchange. It has been accepted for inclusion in Kenyon Summer Science Scholars Program by an authorized administrator of Digital Kenyon: Research, Scholarship, and Creative Exchange. For more information, please contact [noltj@kenyon.edu](mailto:noltj@kenyon.edu).



# COMPUTATIONAL CHEMISTRY ON METAL COMPLEXES



Dr. Emily Jarvis, Dr. Rosemary Marusak, and Emily Rains

## Study #1

### Molecular Mechanics: Pt-DNA Binding

#### The Method

A **molecular mechanical approach** is typically used for large molecules and proteins. Molecular mechanics uses **charge and force constants** found through experimental studies. Electron wavefunctions are not considered, just the force effects of wavefunctions. Its strengths include being able to handle large molecules because computational time does not increase exponentially with the number of atoms, as it does with some computational approaches. The program used was Spartan 02.

#### The System

**Cis-Pt** has long been used as a cancer drug. Studies have shown that cis-Pt will bind to certain DNA sequences. Specifically, it will bind to the **N7 position of adjacent guanines** (see figure 1). There is evidence that this docking of cis-Pt onto the DNA causes a **kink in the strand**. In this study, the Pt had two ammonia ligands (see figure 1).

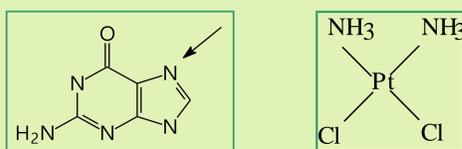


Figure 1: The N7 position of guanine, to which cis-Pt will bind (left) and square planar cis-platinum used in this study with chloride counter ions (right).

#### The Study

The sequence I studied was **CCGGATC**. I did a geometry optimization using **molecular mechanics (MMFF)** of the sequence, the sequence with Pt bound to the two adjacent guanines, and the sequence with Pt bound to the adjacent guanine and adenine. I compared the **energies of these optimized structures**. I also compared the **length from the first phosphate to the last phosphate** on each of the systems.

#### The Results

System	Energy of the system	Length from first to last P
CCGGATC DNA sequence	-764.52	31.70 A
DNA sequence with Pt at GG	-16263498	30.371 A
DNA sequence with Pt at GA	-1587.19; -1593.75	30.932 A; 31.2555 A

#### The Conclusion

Two different structures were seen for the DNA with Pt bound to the guanine and adenine. Using either structure, however, it was seen that it is **more energetically favorable for the Pt to bind to two guanines** than it is for the Pt to bind to the guanine and adenine. Also, the sequence with the **Pt at GG was the shortest and the DNA without the Pt bound was the longest**, supporting the hypothesis of DNA kinking.

#### Acknowledgements

I would like to thank Dr. Emily Jarvis and Dr. Rosemary Marusak for all of their kind and patient teaching this summer. I would also like to thank Dr. Christopher Fowler for his help with Job's plots (used in a project not shown on poster). Finally, I would like to thank Kenyon College for their generous funding of the Summer Science program.

## Study #2

### Semiempirical Calculations: Pentacyanoferrate Complexes

#### The Method

**Semiempirical calculations** are based on Hartree Fock methods; however **electron interactions, the most difficult part of Hartree Fock calculations, are handled using forces found from experimental data of similar systems**. Its advantages include being faster than Hartree Fock calculations, but has the disadvantage of relying on experimental data which may or may not be reliable for the system of interest.

#### The System

These pentacyanoferrate compounds consist of five cyanide ligands and one other ligand coordinated around a central iron (II) atom. For this study water, glycine, methionine, pyridine, pyrazine, methylpyrazine, cyanide were all tested as the sixth ligand (see figure 2).

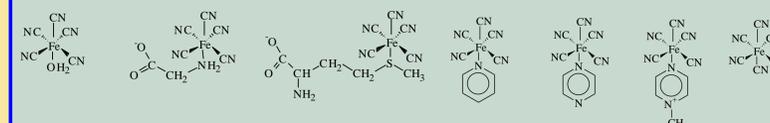


Figure 2: The various pentacyanoferrate complexes tested in this study.

#### The Study

In this study I looked at the **HOMO/LUMO energy gap** for each compound using semiempirical calculations (I also tested these gaps using Hartree Fock calculations, but found the semiempirical data to be more interesting). In addition to the energy gap, I looked at **which atomic orbitals contributed most to the HOMO and LUMO molecular orbitals**. The program used (Spartan 02) allowed the actual **visualization of these orbitals**. In addition, the **vibrational modes** of the carboxyl group in the amino acid ligands were studied.

#### The Results and Conclusions

Homo/ Lumo Character

Complex	Homo Character	Lumo Character
Gly	d	p
Met	d	p
Aqua	d	p
Hexocyano	d	p
Pyridine	d and p mix	d and p mix
Pyrazine	d and p mix	d and p mix
Methylpyrazine	d and p mix	d and p mix

Energy Gaps (For Amino Acid Ligands)

Complex	Homo Energy	Lumo Energy	Lumo-Homo
Gly-Fe	5.93401 eV	14.76035 eV	8.82634 eV
Met-Fe	4.6197 eV	11.72312 eV	7.10342 eV
Aqua-Fe	2.75056 eV	12.27082 eV	9.52026 eV
Hexocyano	6.70736 eV	16.97212 eV	10.26476 eV

Vibrational Modes of Carboxyl Group (Amino Acids)

Met: Change in Freq. (bound-free)		
Bend		4.19
Stretch		159.1
Assym Stretch		-141.35
Gly: Change in Freq. (bound-free)		
Bend 1		13.54
Stretch		187.5
Assym Stretch		-167.7

#### The Conclusions

We found that for the **Gly, Met, water, and cyanide**, the **HOMO** orbital was mostly **d** in character, whereas the **LUMO** orbital was mostly **p** in character. For the nitrogen rings, the HOMO and LUMO were a **mix of d and p** character. Also of interest was the **hexacyanoferrate**, in which the HOMO, HOMO (-1) and HOMO (-2) were all **degenerate** in energy (which you would expect since all orbital orientations have identical electronic environments). The **Gly-complex** carboxyl group's vibrational modes had **greater shifts in frequency** when bound than did the Met-complex. The **energy gaps** we found were **much larger than those expected** from experimental data, although this is not surprising considering the level of computation.

## Study #3:

### Hartree Fock: Ni Complexes

#### The Method

Hartree Fock is a computational approach based upon **Schrodinger's equation,  $\hat{H}\Psi=E\Psi$** . The Hamilton contains terms for the kinetic energy, potential energy between the nucleus and the electrons, and electron-electron interactions. The **wavefunction is iteratively refined** through many cycles called SCF cycles, or self-consistency cycles, until the **lowest energy wavefunction** is found. Hartree Fock calculations have the strength of very clear theory and sometimes they provide a good reproduction of experimental results, esp. for the **ground state molecules**. These calculations, however, become impractically slow for very large systems. For this study I used unrestricted Hartree Fock calculations (critical for open shell systems) using the 3-12G\* basis set.

#### The System

The two nickel complexes **C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Ni** and **C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Ni** differ by only one water molecule yet have very different properties. The former is **brown, diamagnetic, and square planar**; the latter is **green, paramagnetic, and tetrahedral**. The brown complex, due to molecular orbital splitting, should be in the **singlet state**. The green complex, due to different molecular orbital splitting, should be in the **triplet state**. The exact structure for these compounds is not known, although several have been proposed. Instead of dealing with the entire molecule, which would have been too time intensive using the computer power available, the **system was restricted to a simple Ni atom with a few ligands**. The molecules tested are given in figure 3.

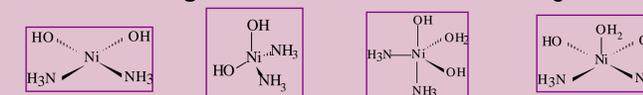


Figure 3: The four and five coordinate Ni complexes tested in this study.

#### The Study

Since experimental studies show that the **tetrahedral should be paramagnetic, we expect the triplet state to be most stable**, whereas the **other structures should be diamagnetic and most stable in the singlet state**. I tested each of these structures in both the singlet and triplet states to determine which state was more energetically favorable. For all the structures I did a single point energy calculations using UHF (3-12G\*) and a core starting guess. I also did a geometry optimization using UHF (3-12G\*) with the default starting guess.

#### The Results

Structure	Singlet Energy (AU)	Triplet Energy (AU)
Tetrahedral	-1761.3448	-1761.4769
Sq. Planar	-1761.3398	-1761.2862
Bipyr.B	-1836.9433	-1836.7897
Sq. Pyr	-1836.9559	-1836.3900 to -1836.8496

#### The Conclusions

Using the unrestricted HF single point energy calculations, the **tetrahedral** structure showed an **energetic preference for the triplet state**, whereas the **other three structures** preferred the **singlet state**. Also, the geometry optimization would convert the **tetrahedral to square planar** in the **singlet state** but would retain a **distorted tetrahedral geometry** in the **triplet state**.