

# Computational calculations of tris(bipyridine)nickel molecules, using Density Functional Theory.

Zinhle Mtshali, Jeanet Conradie

*Department of Chemistry, University of the Free State, Nelson Mandela street 205, 9301,  
South Africa, 2011036460@ufs4life.ac.za*

**Centre for High Performance Computing, 2022  
National Conference, 30 Nov to 2 Dec 2022**

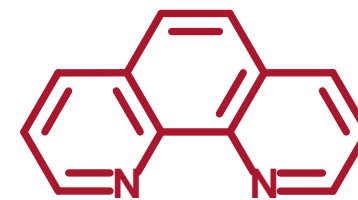
**Acknowledgements:** The South African National Research Foundation.  
The CHPC of South Africa and the High Performance Computing facility of the UFS

# Introduction

- Polypyridine complexes are molecules in which a metal core is covalently bonded to a polypyridyl, such as bipyridine or phenanthroline.
- Polypyridine complexes like bipyridine and phenanthroline have been frequently used as metal chelating ligands due to their great thermal and redox stability and simplicity of functionalization.
- Knowledge of the Ni(II/III) redox potential is necessary
- Knowledge of the electronic structure of Ni(II) and Ni(III) is necessary



2,2'-bipyridine  
(bpy)



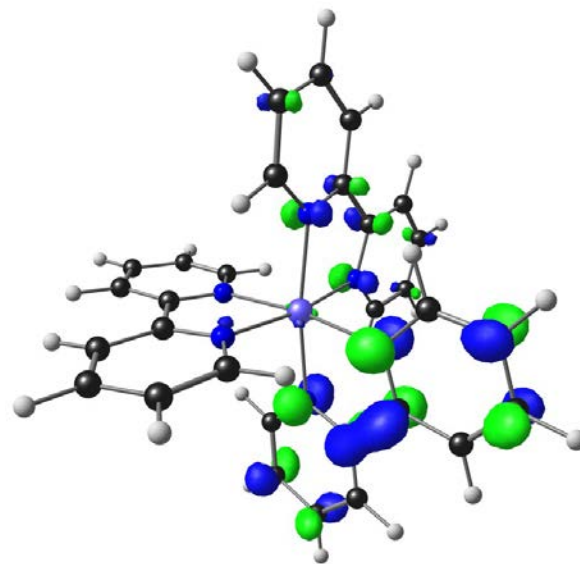
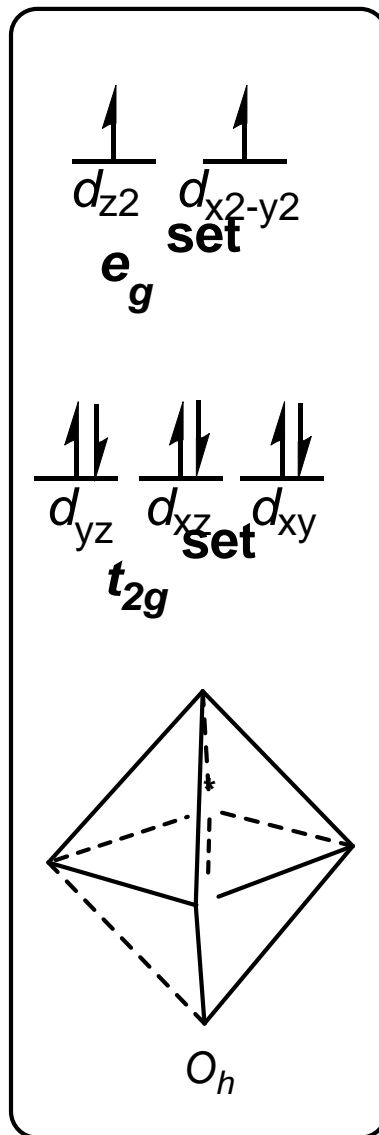
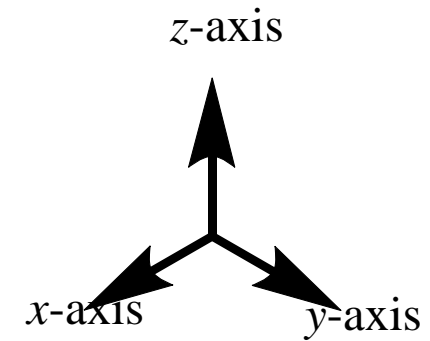
1,10-phenanthroline  
(phen)

**Reference :** H. Hadadzadeh, G. Mansouri, A. Rezvani, H.R. Khavasi, B.W. Skelton, M. Makha, F.R.Charati, Mononuclear nickel(II) complexes coordinated by polypyridyl ligands, Polyhedron. 30 (2011) 2535–2543..

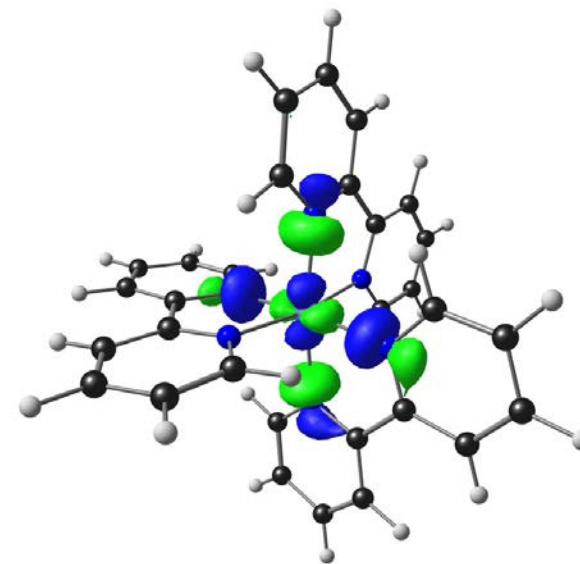
# DFT methods

- **DFT code:** Gaussian 16
- **Functional:** B3LYP
- **Basis set:** triple- $\zeta$  basis set 6-311G(d,p) for the lighter atoms (C, H, O) and the def2-TZVPP basis set for both the core and valence electrons of Ni.
- **Gas phase calculations**
- **HPC Content:**
  - Nodes Requested: 2
  - Cores Requested: 16 - 32 (per Node)
  - Memory Requested: 4200 MB (per Node)
  - Run time ca 30 - 60 h for geometry optimization and frequency calculations
  - Output file size: 60 - 120 MB (chk file 1 – 3 GB)

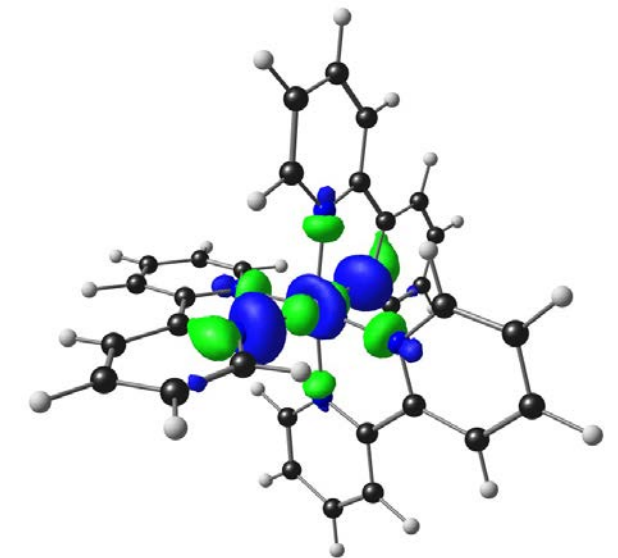
# DFT results Ni(II) d<sup>8</sup>



LUMO:  
ligand based

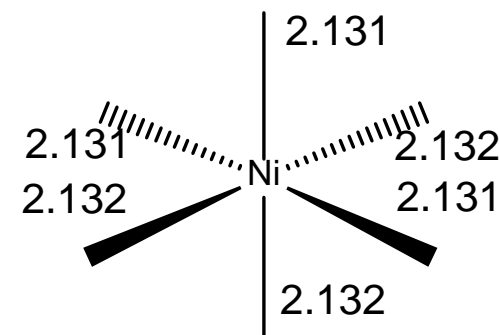


HOMO:  
mainly  $d_{z^2}$



HOMO-1:  
mainly  $d_{x^2-y^2}$

*tris(bipyridine)nickel(II)*:  
octahedral







# Summary

- The octahedral optimized geometry for the lowest energy state for  $q = 2$  ( $S = 1$ ) differs from the Jahn- Teller distortion-exhibiting geometry for  $q = 3$  ( $S = \frac{1}{2}$ )
- The optimized geometry for  $q = 2$  and 3 are in agreement with experimental electron spin resonance studies
- DFT also showed that the  $q = 1, 0$  and  $-1$  all contain a nickel(II) central ion ferromagnetically coupled to one, two or three bipyridine radicals, respectively