Title : Metal complexes in constraint environments

Institute : iSm2, UMR-CNRS-7313

Team: CTOM

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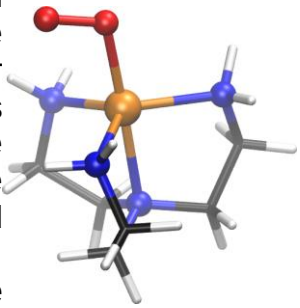
Application to Dr. Nava:
- Before April 26, 2024
- 1st semester M2 Average must be >= 60 / 100
- Provide
  - o Cover letter
  - o Letter of recommendation
  - o CV

Context

The development of 4th period metal chemistry is strategical for reducing the use of less available, more polluting and more expensive 5th or 6th period metals in catalysis. Chemists are inspired by nature to design synthetic molecular systems with specific reactivity properties, as in enzymes. The inclusion of transition metals in complex molecular structures, such as molecular cages, is one way of controlling the metal's environment and enabling specific catalytic activity. The complexes thus obtained are often characterized by UV-vis spectroscopy, but band assignment is often empirical.

Project

In this project we propose to computationally study 4th period metal complexes in constrained environments: by varying the nature of the ligands, we aim at understanding the influence of the molecular environment on the properties of the systems. Ab-initio calculations will be carried out to validate the TD-DFT methods used and to delve deeperinto the nature of the excited states responsible of the absorption spectra of certain complexes with non-standard properties, such as copper azido or superoxido complexes. Depending on progress, the reactivity of these complexes will be investigated: their ability to oxidize small molecules or the molecular environment will be explored theoretically. Cage effects (deformation or electronic effects) will be decomposed using various known approaches.



Exemple of a copper(II) superoxido complex

This project is part of our team's recent studies on the analysis of the properties and reactivity of metal complexes, in interaction with our laboratory's experimentalists. It will enable the candidate to use and master a wide range of methods and manipulate several calculation programs (Gaussian, TURBOMOLE, Molpro, Orca, OpenMolcas, etc.).

Références Bibliographiques

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2. G. Qiu, D. Diao, L. Chaussy, S. Michaud-Chevallier, A. J. Simaan, P. Nava, A. Martinez, C. Colomban, *Dalton Trans.*, **51**, 10702-10706, 2022. DOI: 10.1039/D2DT00607C
3. L. Chaussy, M. Delorme, A. Punter, Y. Carissan, J.-L. Parrain, M. Amatore*, P. Nava*, L. Commeiras*, *Dalton Trans.*, **52**, 14123-14131, 2023. DOI: 10.1039/d3dt02291a.
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