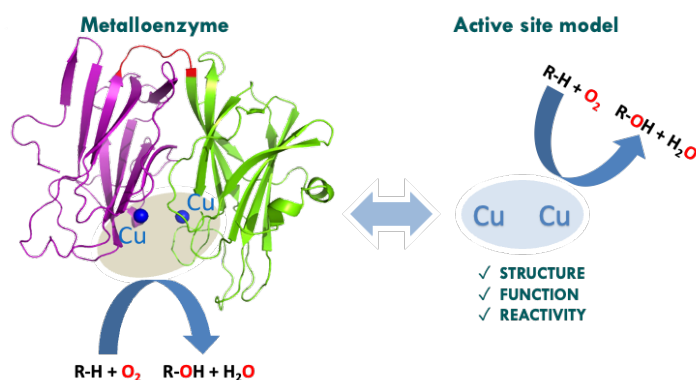


## Bioinspired transition metal complexes: magnetism, spectroscopy, reactivity

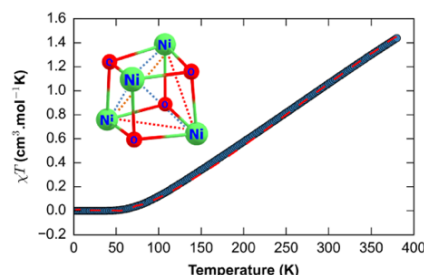


I did my PhD thesis in the Biosciences team at Aix-Marseille University. Biosciences is a multidisciplinary team focused on understanding complex biological systems through bio-inspired models. My research involved computational modelling of molecular architectures in bioinorganic chemistry for spectroscopic, magnetic and catalytic applications. My main focus

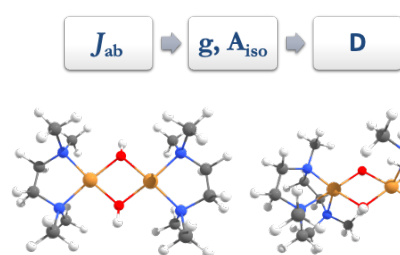
was related to quantum chemistry tools for studying magnetic properties, reaction mechanisms, catalytic performance, and synthetic target development.

### Polynuclear magnetically coupled systems

Polynuclear transition metal complexes containing paramagnetic cations have been thoroughly studied since they represent the crossroad to important research fields, *e.g.*, magnetic, electronic, and optical materials and biomimetic and catalytic systems. Unique electronic and chemical properties arise when the unpaired electrons of two or more open-shell centres interact. Understanding the electronic configuration of these magnetically coupled systems has been crucial in investigating essential areas such as the oxygen-evolving complex, bioinspired synthetic metal complexes, and single-molecule magnets. Our expertise in handling such systems spans various theoretical approaches and computational methodologies, including Broken-Symmetry DFT (BS-DFT) and Density Matrix Renormalization Group method (DMRG).



### Methodologies for theoretical spectroscopy and magnetic properties calculation

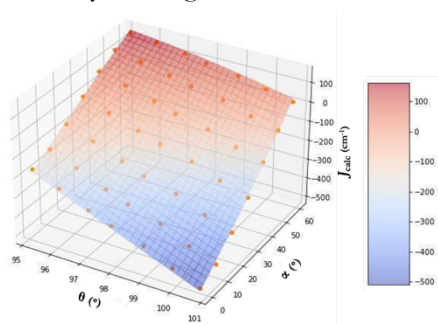
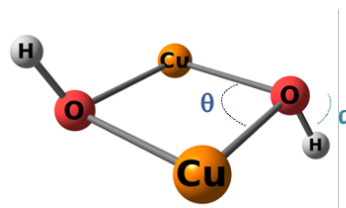


Accurately predicting the spectroscopic and magnetic properties using computational methods is challenging due to the intrinsic multi-determinantal character of electronic states. Therefore, in collaboration with the Max Planck Institute and the Bochum University in Germany, we assessed theoretical methods for calculating magnetic parameters ( $J_{ab}$ ) in transition metal complexes. These

methodologies are critical in interpreting complex experimental data and developing models that elucidate the structure and function of inorganic and bioinorganic catalysts. Examples of such approaches include BS-DFT, Complete Active Space Self-Consistent Field (CASSCF), n-Electron Valence State second-order Perturbation Theory (NEVPT2), DMRG, Difference-Dedicated Configuration Interaction (DDCI) and Coupled-Cluster Broken Symmetry (CC-BS). Furthermore, spin-projection and *ab-initio* methods were used to calculate the g-tensor ( $g$ ), isotropic hyperfine coupling constant ( $A_{iso}$ ) and zero-field splitting ( $D$ ).

## Magneto-structural correlation in polynuclear bioinspired copper complexes

Understanding the underlying mechanism that governs the magnetic interaction in paramagnetic complexes is tightly connected with their intrinsic geometrical parameters. Specifically, we found that the out-of-plane angle ( $\alpha$ ) of the hydroxo bridging ligand in a family of dinuclear copper complexes is as crucial as the Cu-O-Cu angle ( $\theta$ ) in determining the magnetic coupling. This, in turn, is tightly correlated to the ability of the counterion to form hydrogen bonding. We found that accurately describing the magnetic properties of copper complexes with  $\mu$ -hydroxo bridging ligands requires accounting for the out-of-plane angle ( $\alpha$ ) and the counterion. We developed a protocol to position the hydroxo hydrogen more reliably and used spin projection methods to model the magnetic properties of different crystal structures with diverse counterions. We successfully modified the experimental  $J$  values by tuning the counterion, highlighting its role in influencing the magnetic coupling.



Furthermore, by combining experimental and computational inputs, we constructed a three-dimensional correlation between  $\alpha$ ,  $\theta$ , and  $J$ , which improved the prediction of  $J$  values for 20 copper complexes when  $\alpha$  was corrected in the crystal structure. This emphasizes the importance of considering geometrical parameters for accurately predicting magnetic properties in paramagnetic systems, providing insights for designing and optimizing magnetic materials.

## Reactive copper-oxygen species for C-H activation

Molecular magnetism is important for understanding magnetic and electron transport in bioinspired compounds, which can help elucidate their reactivity. Copper-containing enzymes, specifically monooxygenases, are crucial for oxidation reactions and have potential applications in alternative energy sources. We aimed to re-investigate the Cu-mediated hydroxylation of intramolecular C-H bonds using bioinspired copper complexes. However, computational challenges arise due to the multideterminal nature of the  $\text{Cu}_2/\text{O}_2$  adducts. To overcome this, we developed a computational protocol to provide the correct electronic structure of the reaction intermediates before proceeding with mechanistic studies. Our analysis provides insights into the C-H hydroxylation's mechanism, regio-, and stereoselectivity using ligands with activated or non-activated C-H bonds. Computational tools such as Nudge Elastic Band (NEB), time-dependent DFT (TD-DFT) and spin-projection methods were utilized to calculate the reaction mechanism pathway, spectroscopic and optical properties such as g-tensor ( $g$ ), isotropic hyperfine coupling constant ( $A_{\text{iso}}$ ) and UV/Vis spectra.

