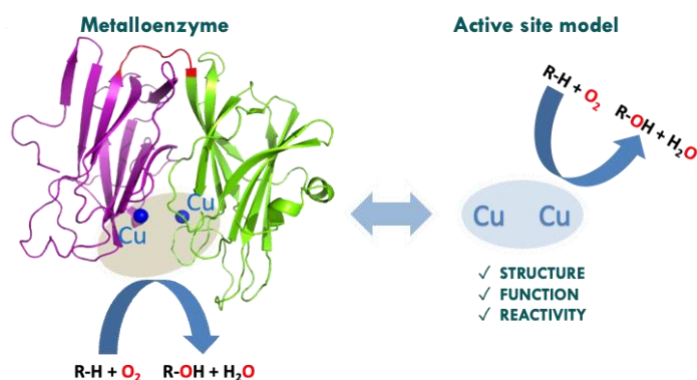


Bioinspired transition metal complexes: magnetism, spectroscopy, reactivity

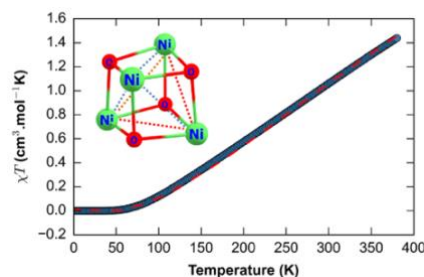


I did my PhD thesis in the BiosCiencs team at Aix-Marseille University. BiosCiencs is a multidisciplinary team focused on understanding complex biological systems through bio-inspired models. My research involved computational modelling of molecular architectures in bioinorganic chemistry for spectroscopic,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

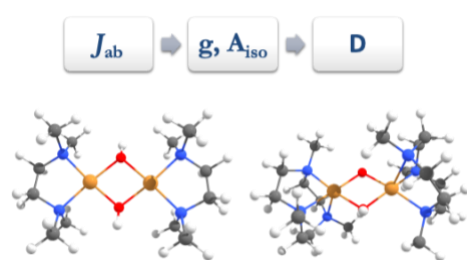
was related to quantum chemistry tools for studying magnetic properties, reaction mechanisms, catalytic performance, and synthetic target development.

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

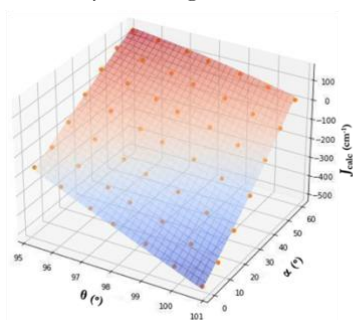
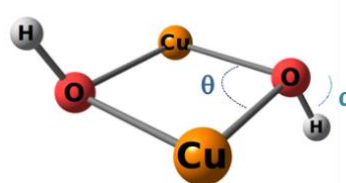


Accurately predicting the spectroscopic and magnetic properties using computational methods is challenging due to the intrinsic multi-determinantal character of electronic states. Therefore, in collaboration with the Max Planck Institute and the Bochum University in Germany, we assessed theoretical methods 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

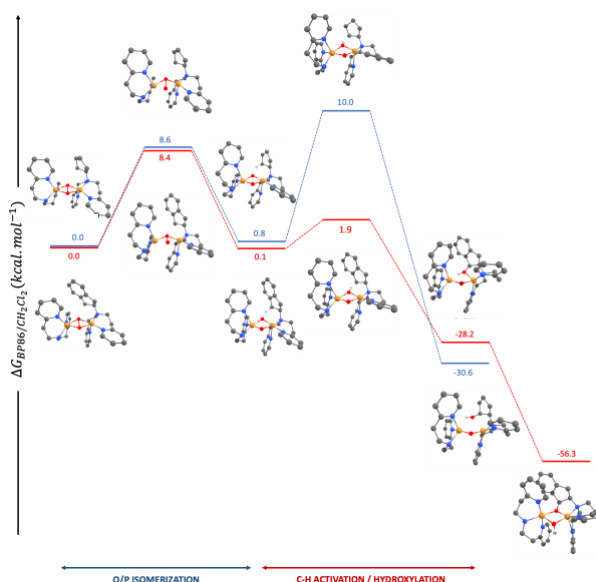
Understanding the underlying mechanism that governs the magnetic interaction in paramagnetic complexes is tightly connected with their intrinsic geometrical parameters. Specifically, we found that the out-of-plane angle (α) of the hydroxo bridging ligand in a family of dinuclear copper complexes is as crucial as the Cu-O-Cu angle (θ) 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 μ -hydroxo bridging ligands requires accounting for the out-of-plane angle (α) 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 α , θ , and J , which improved the prediction of J values for 20 copper complexes when α was corrected in the crystal structure. This emphasises the importance of considering geometrical parameters for accurately predicting magnetic properties in paramagnetic systems, providing insights for designing and optimising magnetic materials.

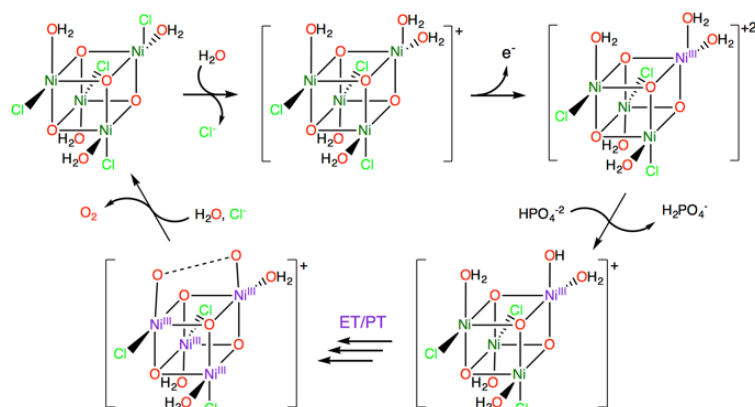
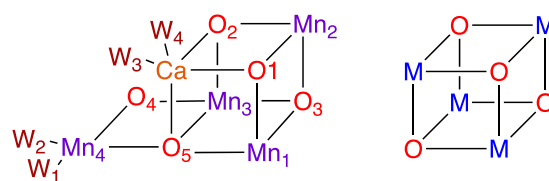
Reactive copper-oxygen species for C-H activation

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 Cu_2/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 utilised to calculate the reaction mechanism pathway, spectroscopic and optical properties such as g-tensor (g), isotropic hyperfine coupling constant (A_{iso}) and UV/Vis spectra.



Oxygen evolution catalyst design

Transforming solar energy into chemical energy is one of the most critical processes sustaining life on Earth. In the case of photosynthesis, it involves the four-electron oxidation of dioxygen into water driven by solar light. Organisms that are able to convert light into fuel rely on a membrane protein called Photosystem II (PSII). The active site of PSII, where the water oxidation occurs, is known as the oxygen-evolution complex (OEC), comprised of a $\text{Mn}_4\text{O}_5\text{Ca}$ cluster. Hence, catalytic water oxidation, as part of water splitting strategies, could provide abundant fuels from renewable sources, which is much needed judging from the current energetic crisis. Unfortunately, catalytic water oxidation is a global challenge representing the bottleneck for water splitting, and much remains to be done. Taking inspiration from the OEC topology where PSII can accumulate four electrons within a tetrametallic-oxo cluster, one can imagine a bioinspired model featuring metal-oxo subunits, leading to “cubane”-type M_4O_4 complexes. Two robust nickel cubanes were prepared in good yields from readily available starting materials under ambient conditions. These tetranuclear complexes are active for electrocatalytic water oxidation at neutral pH, as proven by combining experimental and theoretical approaches. The BS-DFT approach was successfully employed in the study of the magnetic properties of the Ni-cubanes, as well as to elucidate their ground-state electronic structure. Using the HDvV Hamiltonian within the BS-DFT framework, we provided the computed magnetic sublevels that allow the assignment of both ground and first excited states. Furthermore, theoretical reactivity studies confirmed the feasibility of the



oxygen evolution carried out by both Ni-cubanes. Extension of this self-assembly strategy for preparing other water oxidation catalysts with benzimidazole-based ligands and earth-abundant metals (Co and Fe) is currently underway using both experimental and theoretical tools.