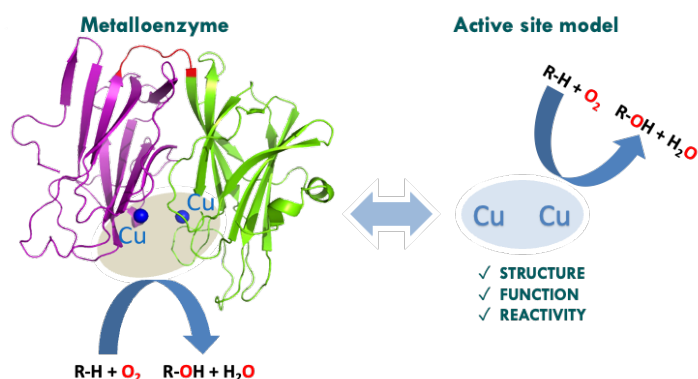


BIOINSPIRED TRANSITION METAL COMPLEXES: MAGNETISM, SPECTROSCOPY, REACTIVITY

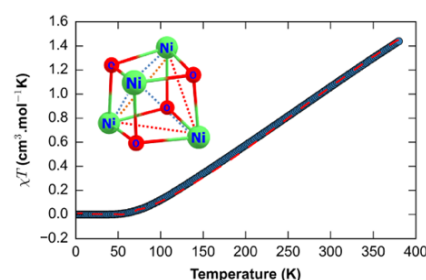


I did my PhD thesis in the BiosCiencs team at Aix-Marseille University. BiosCiencs is a multidisciplinary team focused on understanding complex biological systems through bio-inspired models. My research involved computational modelling of molecular architectures in bioinorganic chemistry for spectroscopic,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

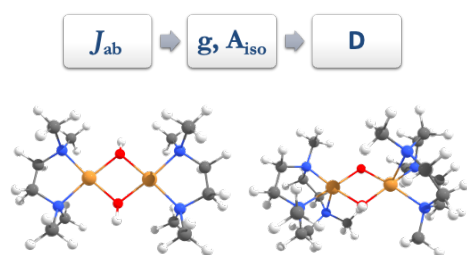
Polynuclear magnetically coupled systems

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

Gurjot Singh, **Stefani Gamboa**, Maylis Orio, Dimitrios A. Pantazis and Michael Roemelt. *Theoretical Chemistry Accounts*, **2021**, 140:139.



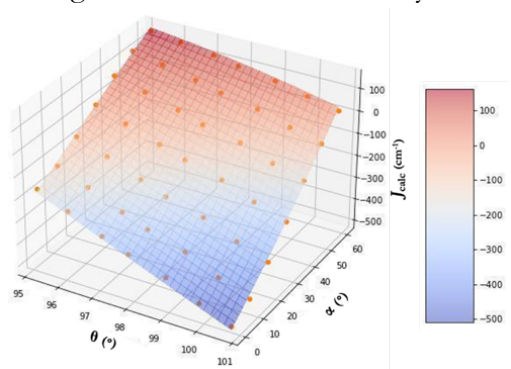
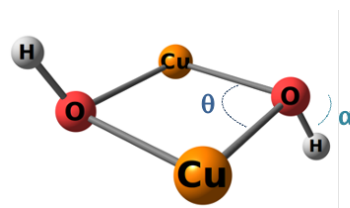
Accurately predicting the spectroscopic and magnetic properties using computational methods is challenging due to the intrinsic multi-determinantal character of electronic states. Therefore, in collaboration with the Max Planck Institute and the Bochum University in Germany, we assessed theoretical methods 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 *i*) Broken-Symmetry density functional theory (BS-DFT)¹, *ii*) Complete Active Space Self-Consistent Field (CASSCF) coupled with n-Electron Valence State second-order Perturbation Theory (NEVPT2)², *iii*) Density Matrix Renormalization Group method (DMRG)³, *iv*) Difference-Dedicated Configuration Interaction (DDCI)⁴ and *v*) Coupled-Cluster Broken Symmetry (CC-BS)⁵. Unfortunately, no method provided accurate results for both complexes, either due to the method's intrinsic limitations or high computational costs. For example, while the well-established Broken-Symmetry density functional theory (BS-DFT) yielded moderately accurate results, it is highly dependent on the functional, the system, and spin contamination. On the other hand, while the Difference-Dedicated Configuration Interaction (DDCI) method provided accurate results, it is not practical for larger systems due to high computational costs. Overall, these findings emphasize the importance of carefully evaluating computational tools before use to accurately describe magnetic properties. 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 bis- μ -hydroxo Cu dimers

Stefani Gamboa-Ramirez, Michel Giorgi, Sylvain Bertaina, A. Jalila Simaan, and Maylis Orio. “*Magneto-structural correlation in polynuclear copper complexes: counterion effect*” Manuscript in preparation.

Understanding the underlying mechanism that governs the magnetic interaction in paramagnetic complexes is tightly connected with their intrinsic geometrical parameters. Many factors tune the magnetic interaction of two or more paramagnetic centers in close vicinity. However, the structural parameters and the exchange interaction are strongly correlated.⁶ 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



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¹ Noodleman, L. *J. Chem. Phys.* **1981**, 74 (10), 5737–5743.

² a) Angeli, C.; Cimiraglia, R.; Evangelisti, S.; Leininger, T.; Malrieu, J.-P. *J. Chem. Phys.* **2001**, 114 (23). b) Angeli, C.; Cimiraglia, R.; Malrieu, J.-P. *J. Chem. Phys.* **2002**, 117 (20), 9138–9153. c) Angeli, C.; Cimiraglia, R.; Malrieu, J.-P. *Chem. Phys. Lett.* **2001**, 350 (3–4), 297–305.

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⁵ Schurkus, H. F.; Chen, D.-T.; Cheng, H.-P.; Chan, G. K.-L.; Stanton, J. F. *J. Chem. Phys.* **2020**, 152 (23), 234115.

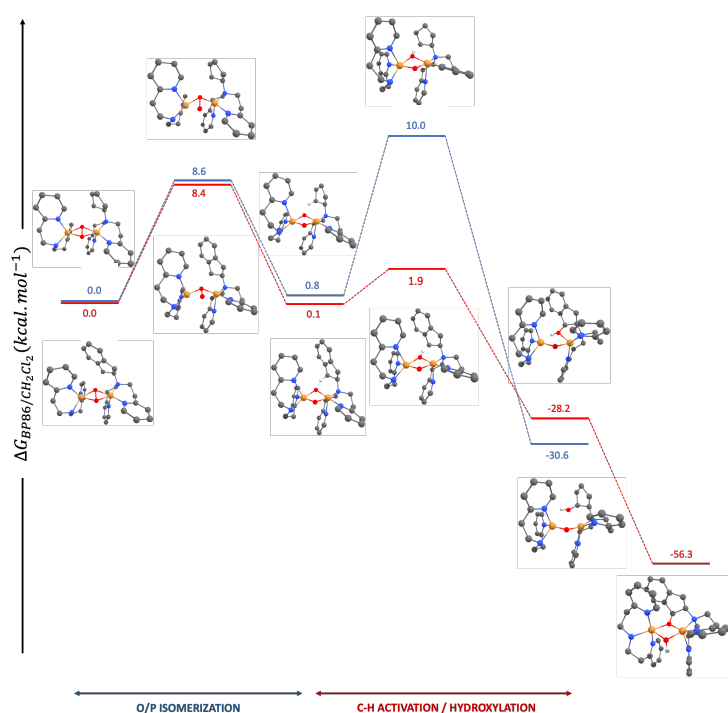
⁶ a) Kahn, O. VCH: New York, NY, **1993**. b) Ruiz, E. Springer: Berlin, Heidelberg, **2004**; pp 71–102.

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.

Computational insights of selective intramolecular O-atom transfer mediated by bioinspired copper complexes

Stefani Gamboa-Ramirez, Bruno Faure, Marius Réglier, A. Jalila Simaan, and Maylis Orio. *Chem. Eur. J.* **2022**, e202202206.

Molecular magnetism is closely related to the study of magnetic and electron transport in bioinspired model compounds. Understanding the electronic and magnetic properties of these compounds can lead to a better understanding of their reactivity. Copper-containing enzymes are involved in many essential biological processes and play a key role in oxidation reactions. In particular, monooxygenases that catalyze the activation and hydroxylation of C-H bonds under mild conditions are of great interest for potential applications in alternative energy sources. In this study, we aimed to reinvestigate the stereoselective Cu-mediated hydroxylation of intramolecular C-H bonds from tridentate ligands using DFT calculations. However, computational investigation of dinuclear copper species presents a major challenge due to the nature of the Cu_2/O_2 adducts. The **O** intermediate is a closed-shell system, while the **P** isomer is in an open-shell arrangement. Therefore, the isomerization equilibrium between **P** and **O** presents a bottleneck for computational methods, as single determinant methods cannot properly



describe the singlet ground spin state, while multiconfigurational approaches remain rather costly for medium-to-big sized systems.⁷ 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.

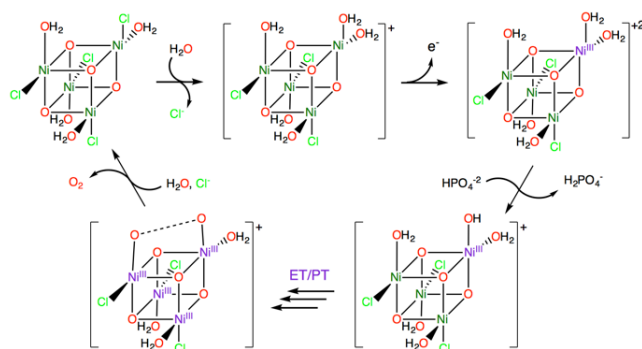
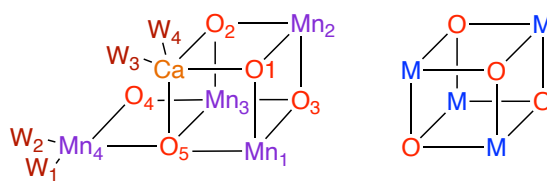
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Oxygen evolution catalyst design

Ana C. García-Álvarez, **Stefani Gamboa-Ramírez**, Diego Martínez-Otero, Maylis Orio and Ivan Castillo. *Chem. Commun.*, **2021**, 57, 8608.

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).⁸ 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.

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