

## Bo Research Group



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### Abstract

Our research deals with the application of computational chemistry methods to a variety of subjects. In most cases, we work in close collaboration with experimental groups both at ICIQ and at other institutions. Research topics fall into three main categories:

-Structure and reactivity of organometallic compounds and homogeneous catalysis-related issues, such as characterisation in-silico of reactive intermediates, elucidation of reaction

mechanisms, origin of the chemo-, regio- and enantioselectivity, ligand effects, ligand design and structure-selectivity relationships.

-Supramolecular Chemistry: structure of host-guest systems, assessment of non-bonding interactions and supramolecular catalysis.

-Polyoxometalates (POMs): electronic structure, mechanisms of catalytic oxidation reactions, dynamic structure of cations and solvent water molecules around and inside POMs.

### Polyoxometalates

Understanding solution and solid-state chemistry of uranium is imperative for implementation of all stages of the cradle-to-grave nuclear fuel cycle, as well as monitoring contamination in the environment and treating nuclear wastes. A new class of uranium compounds was discovered by Prof. Burns (Notre Dame, IN, USA) in 2005, which are nanoscale uranyl peroxide clusters containing  $\text{UO}_2^+$  groups bonded through peroxide bridges to form polynuclear molecular species (polyoxometalates). Recently, our group demonstrated computationally the important roles of alkali cations on growth and stabilization of that anionic uranyl-peroxide species. This year, in collaboration with Prof. Nyman (U. Oregon, USA) and Prof. Navrotsky (U.C. Davis, USA) groups, we carried out computational studies of two crystalline uranyl peroxide U28 polyoxometalate cluster compounds with different encapsulated species, and provided detail to the delineation of the stability landscape of uranyl-peroxide materials. This study [1] reached the cover of a Journal as shown in Figure 1.



Fig. 1 - Hand-drawn art cover. *An antique scale, thermometers and an abacus inspired the theme of antiquity or classic tools for scientific measurements, combining experiments and computation.*

The activation of molecular oxygen by metal complexes for green and selective chemical oxidations remains a formidable challenge and a major goal of the current research activity

dedicated to oxidative transformations. In this light, the use of a totally inorganic ligand system derived from molecular polyoxometalates (POMs), is emerging as a rewarding strategy to the design of innovative catalysts with improved stability for recycling aims. Indeed, POMs provide a wide range of structures and coordination geometries to include one or more multi-redox active transition metal centers, enabling catalysis.



Fig. 2 – Art cover inspired in the COST Action PoCheMoN (Polyoxometalates Chemistry for Molecular Nanoscience).

In collaboration with Prof. Bonchio (U. Padova, Italy) we investigated, using a combined kinetic spectroscopic and computational approach, the catalytic oxygen transfer to dimethylsulfoxide (DMSO) yielding the corresponding sulfone ( $\text{DMSO}_2$ ) mediated by molecular polyoxometalates with one embedded ruthenium center, with general formula  $[\text{Ru}^{\text{II/III}}(\text{DMSO})\text{XW}_{11}\text{O}_{39}]^{\text{n-}}$  ( $\text{X}=\text{P}, \text{Si}; \text{n}=4-6$ ). [2] This study addressed: (i) the  $\text{Ru}^{\text{III}}$  catalyst resting state; (ii) the bimolecular event dictating its transformation in the rate-determining step; (iii) its aerobic evolution to a high-valent ruthenium oxene species; (iv) the terminal fate to diamagnetic dimers. This work reached the back-cover cover of a Journal as shown in Figure 1.

The last topic regarding polyoxometalates in which the group is actively working deals with giant quasi-spherical capsules known as

Keplerates, with general formula  $[(\text{Mo}^{\text{VI}})_5\text{O}_{21}(\text{H}_2\text{O})_6]_{12}\{(\text{Mo}^{\text{V}}_2\text{O}_4)_{30}\text{L}_{30}\}^{\text{n-}}$ . Continuing the collaboration we started some years ago with (Prof. Bonet, URV), we studied the dynamic properties of water encapsulated inside Keplerates. [3] Molecular dynamics simulations allow studying the collective behavior of encapsulated water, and provide information on the time-averaged structure as shown in a spatial distribution function in Figure 3.

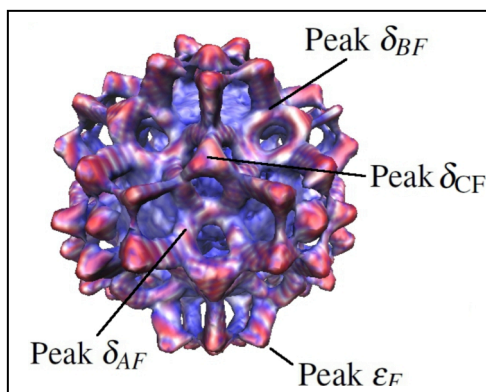


Fig. 3 - Probability of finding oxygen atoms of water molecules inside a Keplerate

### Catalysis and Reactivity

The collaboration with Prof. Fernández (URV) on the metal-free activation of boranes, which started years ago, has continued. By applying the same concepts we developed for activating diboranes without metals, we discovered that seleno-boranes can be directly activated by  $\alpha,\beta$ -unsaturated carbonyl substrates, without the need to use a base. Indeed, using the reactant phenylselenium borane, this new reaction provides high yields and selectivity towards the 1,4 addition product for a number of substrates. Our theoretical studies enabled proposing a mechanism (Figure 4), which fully justifies the reactivity and the selectivity. Also, our results predicted similar reactivity for analogous sulphur-boranes. This establishes an useful method for creating C–Se and C–S bonds.[4]

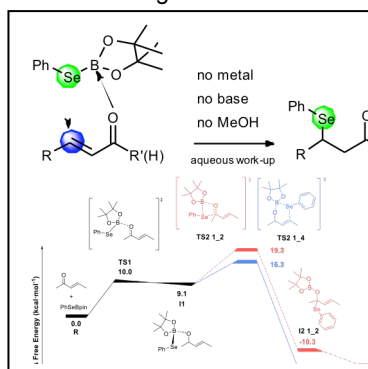


Fig. 4 - Proposed reaction pathway for the reaction of PhSeBpin with 3-penten-2-one.

In the framework of a long-term collaborative project with Prof. Kleij's group at ICIQ, we studied the mechanism of a new aluminium-based catalyst for the reaction of  $\text{CO}_2$  with epoxides to produce cyclic carbonates. The new aluminium-amino-tris-phenolate complex is much more efficient than a Zn(Salen) complex that we studied last year. The reaction mechanism is equivalent for both complexes, as it is delineated Figure 5. Our DFT based computational studies revealed activation energy barriers much lower for the aluminium based catalyst than for the zinc complex, in complete agreement with experimental outcome.[5]

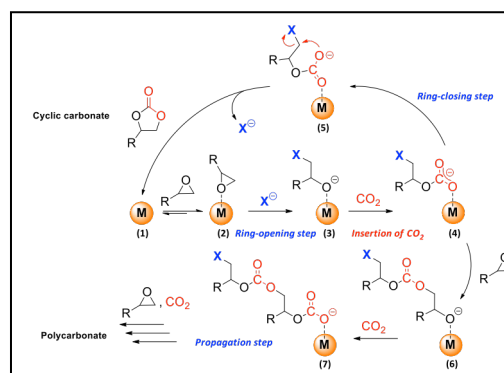


Fig. 5 - Reaction mechanism for the chemical fixation of  $\text{CO}_2$  into epoxides leading to formation of polycarbonates and cyclic carbonates.

It is worth mentioning that this aluminium-amino-tris-phenolate complex (Figure 6) is more versatile than the previous Zn catalyst, since by tuning reaction conditions polycarbonates can also be formed. We plan to continue working on this topic, both qualitatively (explaining mechanisms) and quantitatively (computing TOFs).

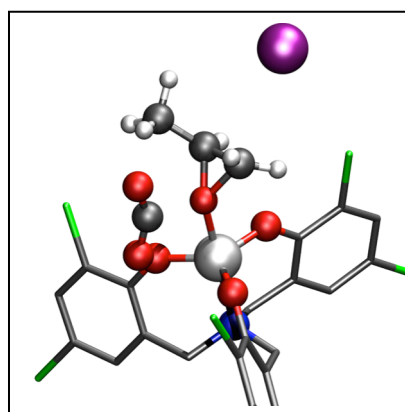


Fig. 6 - Al(amino-tris(phenolate)) +  $\text{CO}_2$  + epoxide

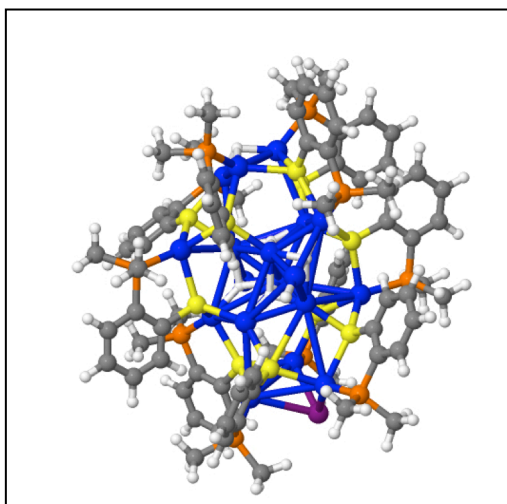


Fig. 7 – Copper nano cluster containing 18 metal atoms (blue), ten phosphino-thiolate ligands (P :orange ; S :yellow), one iodine atom (violet) and seven hydrogen atoms ligands (white).

Finally, the last two articles published in 2014 are related to punctual collaborations with other ICIQ research groups. Llobet's group synthesized a trinuclear Ru–Zn heteropolynuclear complexes featuring bridging N-donor ligands. Isomerism regarding open and closed forms was observed and studied by DFT methods.

## Articles

1- “The Energy Landscape of Uranyl–Peroxide Species”

*Chem. Eur. J.* (2014) 20, 3646 – 3651

E. Tiferet, A. Gil, C. Bo, T. Y. Shvareva, M. Nyman, A. Navrotsky

2- “Oxygenation by Ruthenium Monosubstituted Polyoxotungstates in Aqueous Solution: Experimental and Computational Dissection of a Ru(III)–Ru(V) Catalytic Cycle”

*Chem. Eur. J.* (2014) 20, 10932 – 10943

A. Sartorel, P. Miró, M. Carraro, S. Berardi, O. Bortolini, A. Bagno, C. Bo, M. Bonchio

3- “Encapsulated Water Inside Mo132 Capsules: The Role of Long-Range Correlations of about 1 nm”

*J. Phys. Chem. C* (2014) 118, 5545 – 5555

M. García-Ratés, P. Miró, A. Müller, C. Bo, J. B. Ávalos

4- “Face to face activation of phenylselenium boranes with  $\alpha,\beta$ -unsaturated carbonyl substrates: facile synthesis of C–Se bonds”

*Chem. Comm.* (2014) 50, 8420 – 8423

Van Leeuwen's group succeeded in crystallizing a copper nanocluster from a complex mixture of copper nanoparticles. Phosphino thiolate ligands have not been used before in the synthesis of nanoparticles, and resulted particularly suited in templating the formation of small nanoparticles. Indeed, for the first time the formation of an unprecedented eighteen copper atoms nanocluster was reported. The X-Ray crystal structure was incomplete since hydrogen atoms ligands were not located. We used DFT methods to analyze the spatial shape of the lowest empty energy levels of a model cluster, and that provided information about the regions of space where additional electron density should be allocated. Then we designed a strategy consisting in adding progressively hydrogen atoms and electrons to the system and optimizing partially the geometric structure. Indeed, seven hydrogen atoms and seven additional electrons were added to the system until achieving the greatest stability, thus obtaining a satisfactory geometry of the nanocluster as displayed in Figure 7. It was finally formulated as  $[\text{Cu}_{18}\text{H}_7\text{L}_{10}]$ , wherein L is the ligand  $[\text{SC}_6\text{H}_4\text{PPh}_2]^-$ . This paper [7] also reached the cover page of *Chem. Eur. J.*

X. Sanz, C. M. Vogels, A. Decken, C. Bo, S. A. Westcott, E. Fernández

5- “Highly Active Aluminium Catalysts for the Formation of Organic Carbonates from  $\text{CO}_2$  and Oxiranes”

*Chem. Eur. J.* (2014) 20, 2264 – 2275

C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo, A. W. Kleij

6- “Ru–Zn Heteropolynuclear Complexes Containing a Dinucleating Bridging Ligand: Synthesis, Structure, and Isomerism”

*Inorg. Chem.* (2014) 53, 12407 – 12415

L. Mognon, J. Benet-Buchholz, S. M. Wahidur Rahaman, C. Bo, A. Llobet

7- “Phosphinothiolates as Ligands for Polyhydrido Copper Nanoclusters”

*Chem. Eur. J.* (2014) 20, 16121 – 16127

M. A. Huertos, I. Cano, N. A. G. Bandeira, J. Benet-Buchholz, C. Bo, P. W. N. M. van Leeuwen