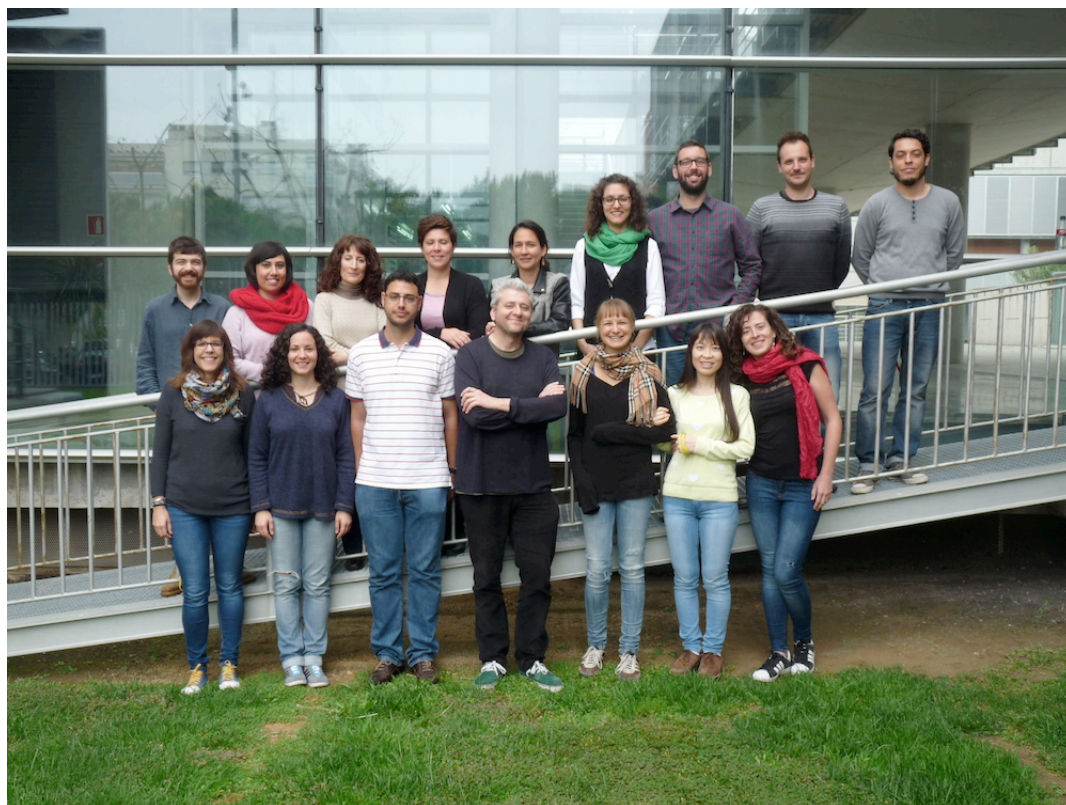


Galán-Mascarós Research Group



Group Leader: José Ramón Galán-Mascarós

Postdoctoral researchers: Yong Sung Koo, Neus Corella, Cristina Sáenz de Piapón, Felipe Andrés Garcés (since February), Jordi Aguilera (since September), Jesús González (since October)

PhD students: Joaquín Soriano, Nelson Giménez, Bárbara Rodríguez, Pilar Maldonado, Marta Blasco, Franziska Hegner, Lijuan Han (since April)

Laboratory technician: Vanesa Lillo

Summer fellows: Otilia-Violeta Stoica

Administrative support: Paula Segovia

Abstract

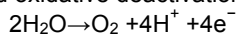
Our research team is devoted to the development of new molecule-based materials for applications in the fields of Renewable Energies and Materials Sciences. On the former, we are developing efficient and stable redox catalysts from Earth abundant metals, with special interest in water splitting catalysts for the

production of solar fuels. On the later, we target the design of novel multifunctional hybrid materials with co-existence of properties of interest (chemical, structural, magnetic, electrical, optical...) with control of the synergy between physical properties in the search for new phenomena.

Catalytic water oxidation with polyoxometalates: Solution speciation

Water oxidation catalysis is one of the biggest challenges that inorganic chemistry is facing today. The discovery of a fast, robust, and cost-effective catalyst would be key for the realization of artificial photosynthesis, an achievement that could probably solve the energy problem worldwide in the near future.

Oxygen evolution from water is a complex redox process. It occurs at high oxidation potentials, and it involves four electrons. An active water oxidation catalyst (WOC) for such a high-energy, multielectron process will probably need the participation of metal ions, as occurs in natural photosynthesis. It should also meet many important requirements to be technologically relevant: inexpensive, readily available, produced in bulk, and stable to air, light, water, heat and oxidative deactivation.



$$E = 1.229 - 0.059(\text{pH}) \text{ V vs NHE at } 25^\circ\text{C}$$

Polyoxometalates (POMs) are a versatile family of inorganic molecular clusters. In these complexes, a transition-metal core can be stabilized by discrete metal oxide frameworks, usually tungstate or molybdate. These inorganic polyanionic ligands are perfectly stable towards oxidative degradation, and their oxo-bridged structure also allows for reversible proton exchange with the solvent, a feature usually combined with the subsequent oxidation steps in the reaction mechanism of WOCs.

In our group we discovered the excellent catalytic activity of $[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$ (Co_9 , Fig. 1) in homogeneous conditions. However, there is always a problem regarding homogeneous WOCs due to the possible decompositions in reaction conditions into metal oxides, which are also very active for oxygen evolution. Therefore, in situ experiments are very valuable to detect the species present in solution during the reaction.

In collaboration with the research group of Prof. May Nayman (Oregon State University) we have studied the solution behavior of Co_9 by small angle X-ray scattering (SAXS). This powerful technique, rarely used for WOC characterization, allows identifying the shape, size and structure of molecules and particles in solution, with high precision.

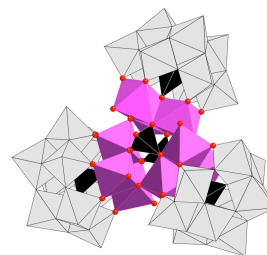


Fig. 1 - Structure of the polyanion $[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$ (Co_9).

The unique geometry and shape of the Co_9 polyanion produces a peculiar X-ray scattering curve. The scattering data demonstrates that Co_9 remains intact in water and NaPi buffered solutions (Figure 2, top) and that these solutions are monodisperse: no other species appear in these conditions. pH dependent measurements indicate that Co_9 shows a remarkable stability from pH 11 to pH 5.5, decomposing above and below this limits. Co_9 also exhibits remarkable stability during oxygen evolution experiments. SAXS data after several hours at pH 8 showed no evidence of nanoparticle formation, maintaining the same features and intensity of the original plot, before the water oxidation reaction.

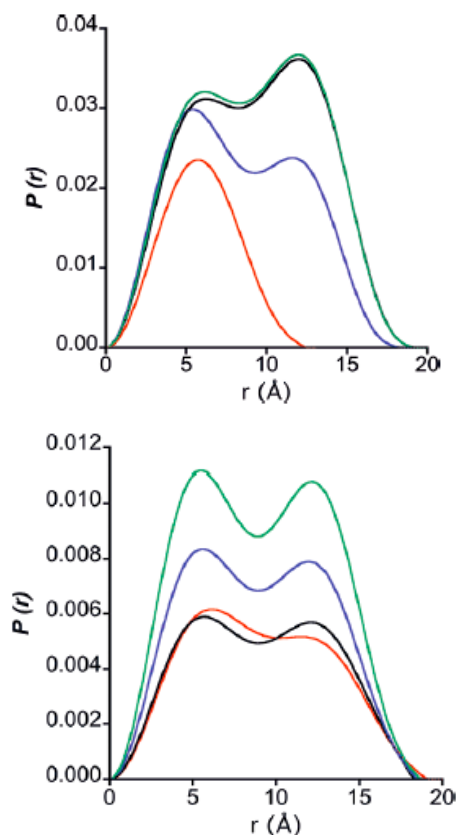


Fig. 2 - (top) SAXS data for a 5 mM aqueous Co_9

solution at pH = 11 (black), pH = 8 (green); pH = 4 (blue) and pH = 1.5 (red). (bottom) SAXS data after successive additions of NaClO as the oxidant every ca. 2.5 h (100:1, oxidant/Co9 ratio) to a 1 mM Co_9 solution in pH = 8 NaPi buffer (0.9 M). Data after first, second, third and fourth additions of NaClO are shown in green, blue, black and red, respectively.

Spin crossover phenomena in Fe^{II} complexes from polysulfonate-substituted triazole ligands

Spin crossover (SCO) compounds are a paradigmatic example of bistability at the molecular level, where the electronic state of a metal complex can be switched from a low-spin (LS) to a low-lying metastable high-spin (HS) configuration through external stimuli: thermally, under light irradiation or pressure. In such compounds, cooperativity and memory effect may appear in bulk, when a structural phase transition is associated to the electronic transition.

We have obtained a polyanionic Fe^{2+} trimer (Figure 3) with the anionic ligand 4-(1,2,4-triazol-4-yl)ethanesulfonate (**L1**) that exhibits a thermally induced spin transition above room temperature as the dimethylammonium salt. The terminal Fe^{2+} centers maintain HS configuration at all temperatures, while the central Fe^{2+} is in its LS state at room temperature. It switches to the HS state above 360 K ($T_{1/2}(\uparrow) \approx 400$ K) with appearance of a very large hysteresis (Figure 4) since it does not relax to the LS ground state down to $T_{1/2}(\downarrow) = 310$ K). This is among the widest thermal hysteresis ranges found for SCO materials.

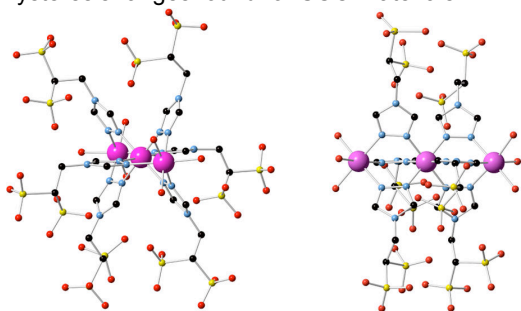


Fig. 3 - Two views of the molecular structure of $[\text{Fe}_3(\mu\text{-L1})_6(\text{H}_2\text{O})_6]^{6-}$ (H-atoms omitted for clarity). Color code: Fe = purple; S = yellow; O = red; N = blue; C = black.

Furthermore, this material shows remarkably slow dynamics, exhibiting temperature-induced excited spin state trapping (TIESST) phenomena. The metastable HS state can be easily quenched via gradual cooling (5 K min^{-1}) from 400 K. Once it is trapped, the HS state remains metastable. Thermal energy is not able

to promote relaxation into the LS ground state below 215 K (Figure 5). Above this temperature, relaxation to the ground state is allowed but it still occurs at a very slow pace, with a characteristic $T_{\text{TIESST}} = 250$ K, the highest temperature ever observed for thermal trapping of an excited spin state in a switchable molecular material. The extremely slow relaxation exhibited at such high temperatures opens unique possibilities for room-temperature applications.

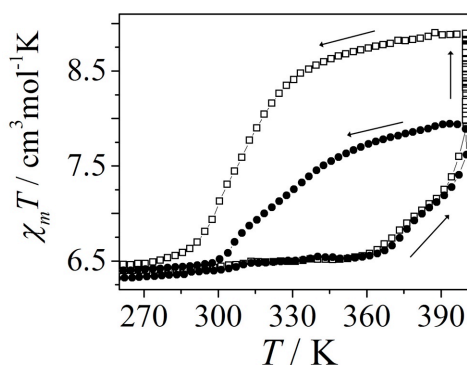


Fig. 4 - $\chi_m T$ vs T plots for $[(\text{NH}_2(\text{CH}_2)_2)_6][\text{Fe}_3(\mu\text{-L1})_6(\text{H}_2\text{O})_6]$ in the 270–400 K range. Scan rate $\approx 0.1 \text{ K min}^{-1}$. Empty squares show the magnetic behavior when the sample is maintained at 400 K until saturation.

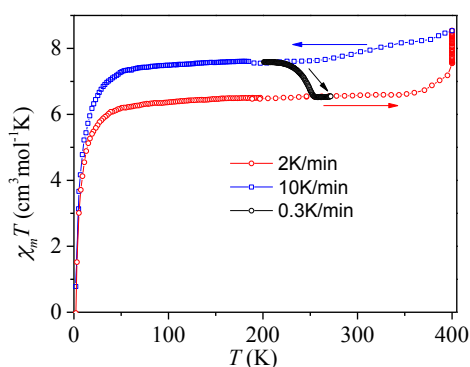


Fig. 5 - $\chi_m T$ vs T plots for $(\text{NH}_2)_2\text{CH}_2][\text{Fe}_3(\mu\text{-L1})_6(\text{H}_2\text{O})_6]^{6-}$ in the 2–400 K range: heating up to 400 K until saturation (red circles), cooling down at 10 K min^{-1} (blue circles), and warming up again at 0.3 K min^{-1} (black circles).

Spontaneous magnetization in homometallic μ_6 -oxalate coordination polymers

Over the past decades, organic/inorganic hybrid coordination polymers have occupied a prominent position in the field of materials science because of their wide range of technological applications. The design tools are well established and involve the use of connectors (inorganic units, metal complexes, etc.) and linkers (organic molecules) as the main

building units. Both parts play a crucial role in the functionality of the final structure. In the field of magnetic materials, molecule-based magnets have successfully reached features usually associated with classic inorganic solids, such as high ordering temperatures or large magnetic hysteresis. These unique materials possess, at the same time, properties typically associated with molecules: light-weight, transparent, easily processable, etc.

We have obtained a novel family of high temperature molecule-based magnets from the mixing of two short-pathway connecting organic ligands: oxalate (ox) and 1,2,4-triazolate (trz); with stoichiometries $[M_2(H_2O)(\mu_2-ox)][M_2(\mu_3-trz)_6]$ [$M = Fe$ (**1**), Co (**2**), Ni (**3**)], $[Zn_2(H_2O)(\mu_3-trz)_2(\mu_2-ox)]$ (**4**), $[Mn_3(\mu_3-trz)_2(\mu_6-ox)(\mu_3-F)_2]$ (**5**), and $[Fe_3(\mu_3-trz)_2(\mu_6-ox)(\mu_2-F)_2]$ (**6**). The crystal structure of **1–3** is dominated by the formation of 1D μ_3 -triazole chains interleaved by oxalate-bridged dimers, where the oxalate anion acts in its classic μ_2 -bis-chelating coordination mode (Figure 6).

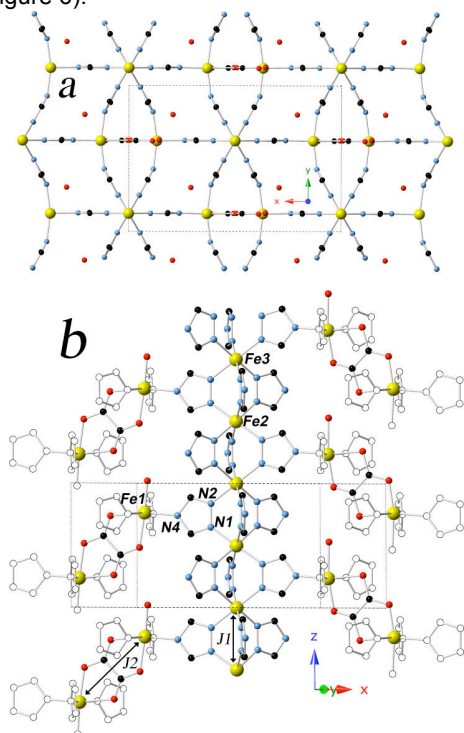


Fig. 6 - (a) Projection of the crystal structure of **1** on the ab plane. (b) Representation along the c axis, highlighting the triply bridged $\{Fe(trz)_3\}$ chains. Color code: Fe, yellow; C, black; N, blue; O, red. H atoms omitted for clarity.

The introduction of fluoride anions yields different coordination polymers for the larger metal dications (**5**, Mn and **6**, Fe), whose structure is dominated by the formation of corrugated 2D layers containing μ_6 -oxalate

connectivity (Figure 7). These are the first compounds where the oxalate ligand connects six paramagnetic centers. It is worth noting the success of this mixed-ligand homometallic strategy to induce complex magnetic structures. In this case, it has allowed for the first time, the identification of a μ_6 -oxalate bridge, a connectivity expected to stabilize magnetic ground states in homometallic compounds because of the appearance of competing interactions. This is confirmed by the experimental data. **5** and **6** exhibit spontaneous magnetization below 9 and 66 K, respectively, arising from the uncompensated alignment of spin centers around the μ_6 -oxalate bridged, composed by multiple spin-frustrated triangles (Figure 8). 66 K represents the highest ordering temperature ever observed for an oxalate-based magnet.

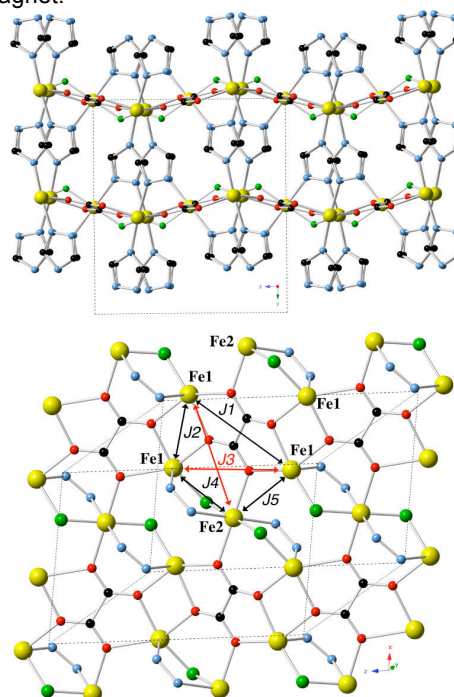


Fig. 7 - (a) Projection of the crystal structure of **6** on the bc plane. (b) Representation of the multiply bridged planes along the a axis, defined by the μ_6 -ox, μ_2 -F⁻, and μ -trz bridges. Color code: Fe, yellow; C, black; N, blue; O, red; F, green. H atoms omitted for clarity.

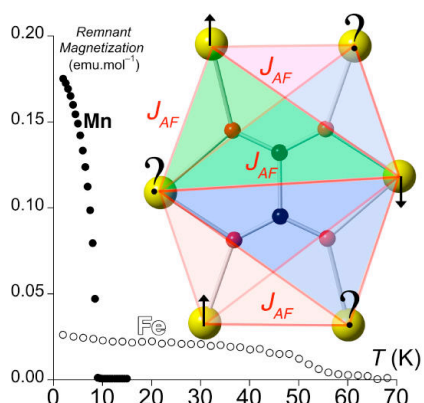


Fig. 8 - Remnant magnetization for compounds 5 and 6, showing the appearance of spontaneous magnetization. (inset) Scheme of the spin frustrated spin network around the μ_6 -oxalate connectivity.

Articles

“Magneto-chiral dichroism: Bring to light”

(News&Views)

Nat. Phys. (2015) 11, 7-8

J. R. Galan-Mascaros

K.-Y. Wang, B. S. Bassil, Z. Lin, I. Römer, S. Vanhaecht, T. N. Parac-Vogt, C. Sáenz de Pipaón, J. R. Galan-Mascaros, L. Fan, J. Cao, U. Kortz

“Water Oxidation at Electrodes Modified with Earth-Abundant Transition-Metal Catalysts”

ChemElectroChem (2015) 2, 37-50

J. R. Galan-Mascaros

“Spontaneous Magnetization in Homometallic μ_6 -Oxalate Coordination Polymers”

Inorg. Chem. (2015) 54, 4678–4687

M. N. Corella-Ochoa, J. Benet-Buchholz, M. Martínez-Belmonte, J. R. Galan-Mascaros

“Solution Speciation and Stability of Cobalt-Polyoxometalate Water Oxidation Catalysts by X-ray Scattering”

Eur. J. Inorg. Chem. (2015) 2833–2840

S. Goberna-Ferrón, J. Soriano-López, J. R. Galan-Mascaros, M. Nyman

“Activity and Stability of the Tetramanganese Polyanion $[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ during Electrocatalytic Water Oxidation”

Inorganics (2015) 3, 332–340

S. Goberna-Ferrón, J. Soriano-López, J. R. Galan-Mascaros

“Easy Excited-State Trapping and Record High T_{TIESST} in a Spin-Crossover Polyanionic Fe^{II} Trimer”

J. Am. Chem. Soc. (2015) 137, 11924–11927

V. Gómez, C. Sáenz de Pipaón, P. Maldonado-Illescas, J. C. Waerenborgh, E. Martín, J. Benet-Buchholz, J. R. Galan-Mascaros

“ Ln_{12} -Containing 60-Tungstogermanates: Synthesis, Structure, Luminescence, and Magnetic Studies”

Chem. Eur. J. (2015) 21, 18168–18176