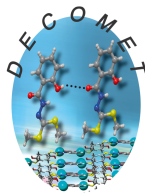


Scientific topics for DECOMET laboratory



1. Magnetochemistry

Scientific background

This research project places itself within the area of molecular and supramolecular magnetochemistry. Since the discovery of new families of molecular magnets (homo metal centered) behaving like single-domain magnetic particles (*Nature*, **1993**, 365, 141), chemists' interest in designing new molecules incorporating only a few paramagnetic centers (simple and well defined paramagnetic system) has been growing over the last few years.

One of the objectives of our research work is to create new magnetic systems in which magnetic molecules can be associated cooperatively (*Nature*, **1995**, 378, 701). For instance, this can be realized through magnetic molecules either attached to surfaces or associated with one another in specific supramolecular networks. The new molecular objects with low nuclearity, at the core of our project, can present very strong magnetic couplings, which seem to be directly correlated to CH- π hydrogen bond interactions (*J. Am. Chem. Soc.*, **2006**, 128, 3140).

Description

As supporting chelating ligands, we focus our attention on polydentate sulfur containing ligands (for the potential deposit on gold surface) because these can be accessible from a synthesis point of view and present numerous possibilities of hydrogen bond or Van der Waals contacts. We have already synthesized a series of ligands derived from salicyl hydrazide acid, which form new mono- and binuclear iron (III) complexes as well as their manganese (II and III) analogues (*Inorg. Chem. Acta*, **2005**, 358, 3881 and Thesis C. Beghidja, ULP, **2005**).

Some of the obtained binuclear complexes exhibit an exceptionally high ferromagnetic coupling (*J. Am. Chem. Soc.*, **2006**, 128, 3140). The results of detailed analyses (via single x-ray crystallography, magnetic measurements and DFT calculations) of these asymmetric molecular objects constitute a breakthrough in magnetochemistry (*Magnétisme moléculaire*, VCH, New York, **1993**) based on CH- π interactions; these interactions imposing an asymmetry at the chelated ligand. A potential control of the magnetic interactions may then be possible via minor modifications of the chelating ligand.

The observed asymmetry arises from a double CH- π interaction at both sides of the metal centers (Figure 1), thus forcing the system to couple ferromagnetically. In the present case, this coupling is very strong with a value close to 20 cm^{-1} . To date, this is the strongest value measured for a binuclear Mn complexes (*J. Am. Chem. Soc.*, **2006**, 128, 3140, *J. Am. Chem. Soc.* **1992**, 114, 1681, *J. Am. Chem. Soc.* **1988**, 110, 7398).

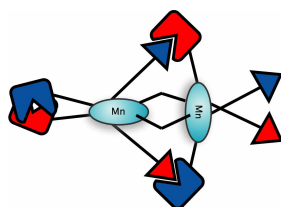
Expected results

This type of molecular construction presents several promising aspects :

- 1) *An extremely strong magnetic coupling that can be improved by an appropriate intramolecular chemistry (for instance by modification of the bridging functions). An increase of the number of paramagnetic centers is also planned in order to synthesize new molecular magnets.*
- 2) *An easily tunable organic part. We may then be able to identify and rationalize which groups are necessary to the 'asymmetric attachment' (in the solid state and in solution). The possibility to break such an attachment (in order to allow the controlled generation of ferromagnetic or antiferromagnetic entities) should also be of interest.*
- 3) *The synthesized magnetic molecules will be considered as building blocks in specific supramolecular networks for, in particular, the establishment of a long distance magnetic order (1D, 2D and 3D).*
- 4) *This approach should yield in the long term the conception of nanometric objets⁷ with magnetic properties directly determined by 'weak' interactions (CH- π interactions) and tunable by an external impulsion that will have to be defined.*

To our knowledge, the proposed approach with this type of molecular systems is completely new and original: in short, it has not yet been explored and presents a great potential.

The molecular objects synthesized in this research program do have, first of all, a great potential application in the area of molecular magnetic storage (*Angew. Chem. Int. Ed.* **2003**, 42, 268), due to the fact that the observed strong ferromagnetic coupling can be associated with a simple and well-defined molecular edifice.



Schematic representation of non-symmetrical situation of both metal centers in magnetic binuclear compounds.

From these preliminary results, we have suggested that such non-symmetrical situation for both Mn(III) ions are directly correlated to the weak CH- π interactions in the molecular species.

This concept has to be refined in a first step, with specific small modifications of the chemical bridge and/or peripheral ligand and synthesis of binuclear compounds with other 3d metals.

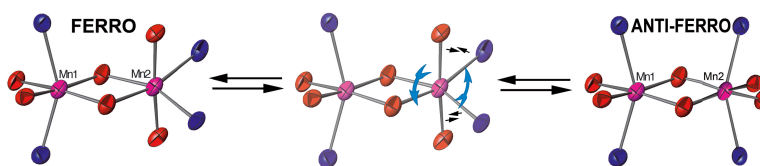
Methodology

Some results concerning new mononuclear complexes have been recently obtained in our laboratory (See DECOMET report). **As a first step**, we plan to prepare a series of **20 new ligands**. The design of these ligands is based on slight structural modifications allowing to comprehend connectivity patterns within both mononuclear and binuclear complexes. Moreover, considering several paramagnetic metal centers (V, Cr, Mn, Fe, Co, Ni) and their incorporation into both homonuclear and heteronuclear molecular species, we aim to synthesize **more than 300 new complexes** in this application.

After the synthetic work, the new molecules obtained will be fully characterized, crystallographically and magnetically. This corresponds to a large part of the project

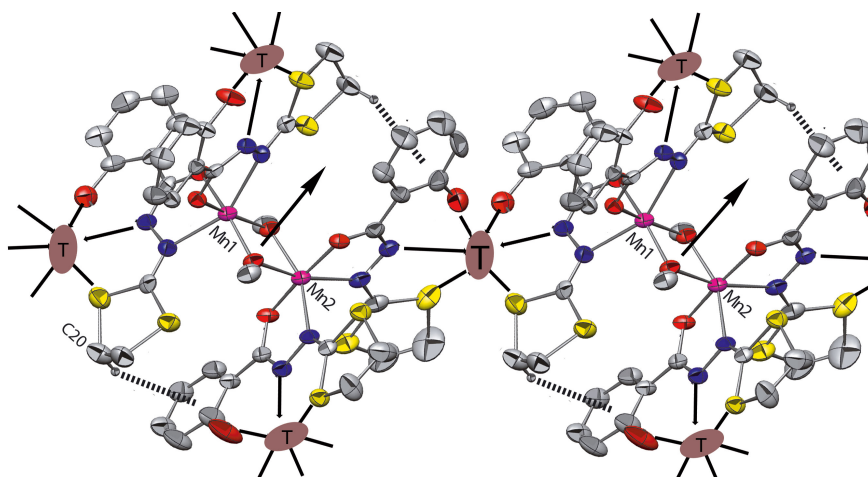
A systematic approach is essential to find the chemical origin of the strong ferromagnetic coupling detected in the $\text{Mn(III)}_2(\mu\text{-OMe})_2(\text{HL}^{(2)})_4$ compound.

Our aim is, **in a second step**, to be able to switch, in selected binuclear compounds, from ferromagnetic to antiferromagnetic coupling, as a function of chemical or physical impulsion to be defined (isomerization or redox/proton transfer, for instance) (*J. Am. Chem. Soc.*, **2001**, 123, 4304). A schematic representation of this concept is presented in figure 2.



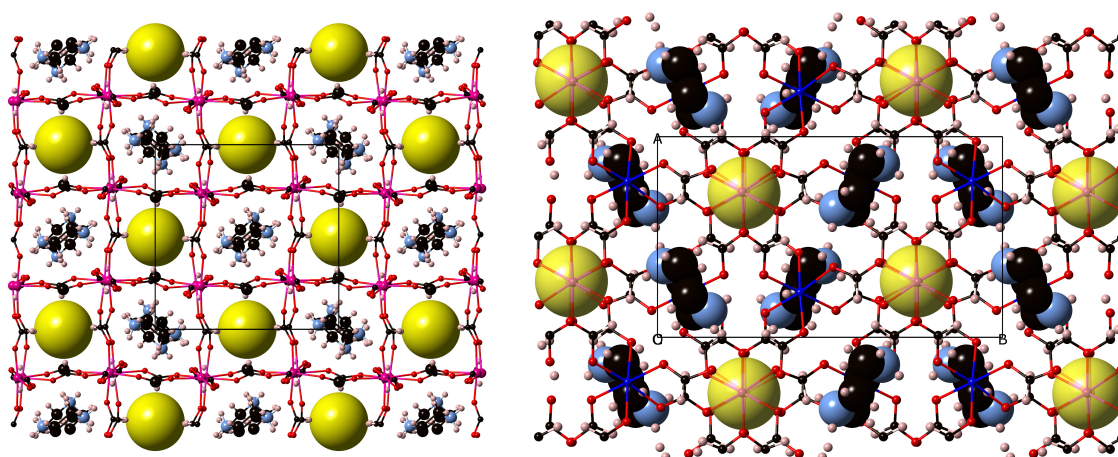
Schematic representation of non-symmetrical situation (at left) and hypothetical symmetrical situation (at right) of both metal centers in magnetic binuclear compounds.

As a third step, we consider that such binuclear complexes with potential very strong ferromagnetic interaction and axial magnetic anisotropy are excellent candidates to be incorporated into polymeric and/or supramolecular networks that could present interesting magnetic properties, if one achieves correctly the designed interactions (*J. Am. Chem. Soc.* **2006**, 127, 3090). In fact, the ligands used in our molecular complexes present several potential coordination sites, as shown in figure 3. In these conditions, formation of polymeric materials with the binuclear complex as magnetic building blocks will be an important challenge for this research project.



Representation of hypothetical 3D polymer obtained from binuclear magnetic building blocks (T is a 4f metal, for instance)

2. Multifunctionality of metal-organic framework and organic-inorganic hybrids



Two structural variants of magnetic porous framework with channel (left) and cavity (right).

From an independent approach in producing multifunctional metal-organic framework and organic-inorganic hybrids, we have used hydrothermal techniques in generating a whole gamut of materials which have proved very valuable in the development of clever materials that can find applications in microelectronics, information storage, fuel and toxic gas storage and even in as support for medications. Our work on the syntheses and study of their crystal chemistry and physical properties of transition metal – organic – framework using polytopic ligands containing carboxylate or N-donor groups is very well developed and highly recognized internationally. We have developed different techniques for the syntheses, including electrocrystallization, hydrothermal in traditional ovens and more recently, hydrothermal using microwave heating. These provide a whole gamut of parameters, temperature, pressure and time, to generate kinetically and thermodynamically stable multi-dimensionality materials. In addition, we have established ourselves as the leading magnetochemist in the field of MOF (*Chem. Soc. Rev.*, **2009**, 38). On the way we have performed many different type of studies to enhance the potentials of these materials, for example the single-crystal to single-crystal transformations, luminescence, proton conductivity, electron conductivity, gas-storage, iodine-uptake and release for medical applications.

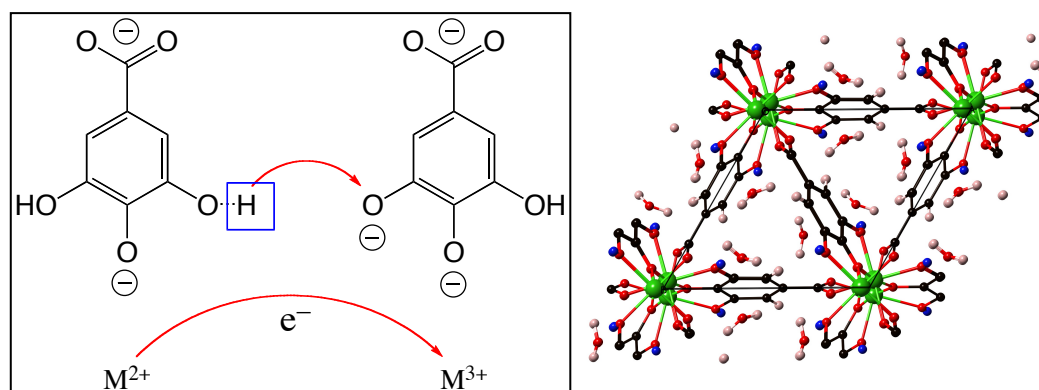
While the present work will be continuing, we would like to advance in our synthetic tools by introducing coupled electrochemical-hydrothermal crystal growing. This should allow us to tune the

valency of the metals in-situ especially important for our final part of our proposal - **Proton-Coupled Electron-Transfer in Metal-Organic Frameworks**. This will need additional set-up and man-power, though it should not cost enormously.

3. Proton-Coupled Electron-Transfer in Metal-Organic Frameworks

In addition we propose a new project dealing primarily with the energy conversion in metal-organic frameworks, in particular in developing materials for the understanding electron-transfer coupled with proton displacement. The second stage will be to use solar light on the materials developed to split water into solar fuels such as hydrogen and oxygen (Nocera, D. et al. *Chem. Rev.* **2010**, *110*, 6474–6502). This proposal is an unexplored aspect of the activities for this type of materials.

Given that solar energy is abundant the only problem is the need to store it in other forms that can be used at leisure. The materials envisaged and the processes of their synthesis are both inexpensive and if successful the project should lead to large-scale solar energy supply at affordable costs. The co-development of porous metal-organic frameworks for the storage of hydrogen and other fuel gases is highly desirable and may provide suitable storage materials.



Scheme showing the concerted Proton-Coupled Electron-Transfer for charge balance, and Structure of Ni-gallate, Ni^{II}(C₇H₄O₅)·2H₂O, showing the movable hydrogen atoms in blue.

The principle of our logic in the synthesis of Proton-Coupled Electron-Transfer is presence of the two sources (see Scheme), one for the proton and the other of the electron, in the same compound. Thus, we want a material with excess proton and another that is deficient of proton as depicted in the scheme above. The transfer of an electron, by excitation with either an electric current or by optical pumping, will transfer the electron from the divalent metal to the trivalent one. The consequence of this electron transfer is the motion of the hydrogen atom from one of the phenol hydroxide to the charged oxygen atom.