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Spin crossover supramolecular coordination compounds: design, synthesis and properties

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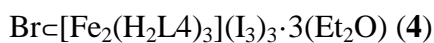
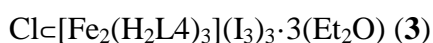
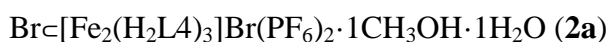
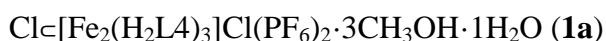
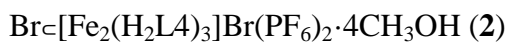
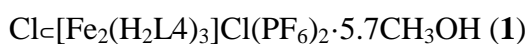
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CHAPTER 7: Conclusions and Future Perspectives

The results obtained in this thesis demonstrate the importance of supramolecular chemistry for the design of potential new SCO clusters. Starting from synthesizing the suitable ligands with appropriate functional groups, novel host-guest systems could be obtained where the guest plays a major role in tuning the physical properties of the host.

Two bis-pyrazolylpyridine ligands, H₂L4 and H₂L6 (Chapter 2) were designed and prepared to achieve the assembly of transition metal ions in a triple-stranded helicate fashion, where the central cavity can encapsulate different counterions depending on the size of this cavity. The N-H groups found in these ligands, which are usually directed toward the internal cavity, help in the encapsulation of hydrogen acceptor anions. With this aim, 16 coordination helicates have been accomplished using these two ligands. Although Co(II) and Ni(II) helicates (chapter 2) with encapsulated Cl⁻ were synthesized, the use of Fe(II) as metal center is most interesting since the ligand field given by the pyrazolyl-pyridine ligand is suitable to induce SCO properties to this metal. As a result, 13 iron-based compounds have been crystallized and studied contributing significantly to the fascinating area of helical SCO compounds. The crystal structure for all the compounds has been resolved, which has allowed for an extensive study of supramolecular interactions and the influence of these interactions on the magnetic properties of the compounds.

Chapter 3 deals with spin-crossover dinuclear triple-stranded helicates compounds with encapsulated halide ions using H₂L4. Six of such helicates with different encapsulated halide ions or counter ions were synthesized:



Compounds **1** and **2** are isostructural and consist of triple stranded helicate that encapsulate a halide ion in their cavity, which participate in six hydrogen bonding interactions with the N-H groups of the ligands, three of them being stronger than the other three. A second halide ion is located near the helical cavity and also participates in hydrogen bonding with one N-H group. Both halide ions are located close to the same iron center (Fe1). The N-H groups close to the other iron center (Fe2) are involved in strong hydrogen bonding interactions with MeOH solvent molecules. This difference induces different magnetic responses for both Fe(II) centers, where Fe1 exhibits the HS state and Fe2 exhibits the LS state at 100 K. Variable temperature crystallographic studies show that Fe1 remains in the HS state over all the measured temperatures and Fe2 exhibits SCO at high temperatures as indicated by Fe-N distances. These mixed spin states are achieved as a result of differing electronic properties around the metal ions caused by different supramolecular hydrogen bonding interactions near both of them.

The nature of the supramolecular interactions of the encapsulated halide (Cl⁻ vs. Br⁻) ion affects the spin transition temperature as seen in the isostructural compounds **1** and **2** where $T_{1/2}$ equal 300 and 270 K, respectively, indicating that Br⁻ stabilizes more the HS state than Cl⁻.

Compounds **1a** and **2a** are the water solvate helicates that form *via* single-crystal to single-crystal solvent exchange, by exposing the crystals to the atmosphere for a few days. This exchange leads to important changes; the $\{X\text{C}[\text{Fe}_2(\text{H}_2\text{L4})_3]\}^{3+}$ helicates are now symmetric and the two Fe centers are crystallographically identical. This increased symmetry is achieved because of the disorder over two positions (50% each) exhibited by the out-of-cavity X⁻ ion, one methanol molecule and one water molecule, the latter two participating in hydrogen bonds with the same X⁻ ion. The disorder locates this ion near one or the other Fe(II) centers resulting in two crystallographically identical Fe(II) ions. For each individual molecule of the solid, both Fe centers need, however, to be necessarily different. This solvent exchange affects dramatically the SCO behavior of the helicates. Two-step SCO according to [LS-LS] → [HS-LS] → [HS-HS] was observed in the bulk magnetic studies.

Compounds **3** and **4** consist of $\{X\text{C}[\text{Fe}_2(\text{H}_2\text{L4})_3]\}^{3+}$ triple-stranded helicates similar to the one seen previously where the counter ions are now three triiodide (I₃⁻) linear ions

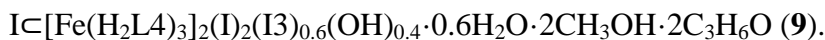
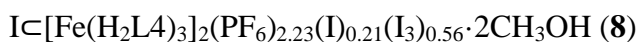
occupying the outer space formed between the helical strands together with solvent ether molecules. The location of the I_3^- ions between the ligand strands allows for “lone pair- π ” interactions of I_3^- with several aromatic rings. In fact, a total of six contacts fulfill the criteria to consider such interaction, as a rare example where the three atoms of the anion interact with one or more aromatic rings.¹ This change in the counterions affects dramatically the magnetic properties of the iron(II) centers. Both Fe(II) centers remain now in the HS state over all the temperatures. This difference is caused by the nature of the counter-anions and solvent molecules, which exhibit different interactions with the helicate. In **3** and **4**, the I_3^- ions exhibit lone pair- π interactions with the ligand strands, while ether molecules do not interact significantly with the helicates. The only hydrogen bonds now are formed within the helical cavity, between the N-H groups and the encapsulated Cl^- or Br^- ions. The absence of further out-of-cavity interactions stabilizes the HS state. On the other hand, the existence of more hydrogen bonding interaction with out-of-cavity Cl^- or Br^- and methanol molecules in **1** and **2**, stabilize LS states.

Thus three possible magnetic states, [HS-HS], [HS-LS] and [LS-LS] may be observed and stabilized in these helicates over large temperatures ranges, by playing with chemical variables. Some of the above magnetic states can be accessed also as metal-stable, using light irradiation, through the LIEST effect. Solution studies of the $X-Fe_2$ helicates showed the stability of the triple stranded helicates in solution in equilibrium with another helical assembly. The second assembly consists of a dimerized mononuclear helicate $\{X-[Fe(H_2L4)_3][Fe(H_2L4)_3]\}^{3+}$ which also was isolated in the solid state using a different synthetic procedure.

In Chapter 4, the change of the solvents used in the reaction yielded different supramolecular compounds using the same ligands H_2L4 . Dimerized mononuclear helicates $\{X-[Fe(H_2L4)_3]_2\}^{3+}$ were prepared, where a halide ion is encapsulated inside the cavity formed by both parts of the dimers. In every mononuclear helicate, one pyrazolyl-pyridine side of each ligand is not coordinated to any metal ion. The SCO behavior of these dimers is also affected by the nature of the halide ions, which establish hydrogen bonding interactions with the N-H groups of the pyrazole rings.

Five dimerized triple-stranded helicates are presented in this chapter:





The structure always consists of two independent mononuclear triple-stranded helicates $[\text{Fe}(\text{H}_2\text{L}_4)_3]^{2+}$ which form a dimerized assembly by encapsulation of a X^- ion in the central cavity of the dimer to form a $\{\text{X} \subset [\text{Fe}(\text{H}_2\text{L}_4)_3]_2\}^{3+}$ cationic assembly.

In each $[\text{Fe}(\text{H}_2\text{L}_4)_3]^{2+}$ mononuclear helicate, three H_2L_4 ligands offer a distorted octahedral environment around the $\text{Fe}(\text{II})$ center, each chelating with one pyrazolyl-pyridine moiety. These ligands adopt a pseudo-S shape through twisting around the C-C bond between the central phenylene and the pyrazole groups. The two $[\text{Fe}(\text{H}_2\text{L}_4)_3]^{2+}$ mononuclear helicates are intertwined providing a central cavity, which contains the encapsulated X^- ion. In addition, strong $\text{N-H} \cdots \text{N}$ hydrogen bonds are present, involving the pyrazole groups of the intertwined ligands. The adjacent ligands of the intertwined helicates are involved in five strong $\pi-\pi$ interactions between the phenylene or pyrazole analogous aromatic rings. Three sets of such interactions are found in each dimerized helicate. All of these strong supramolecular interactions (i.e. $\text{N-H} \cdots \text{X}$ and $\text{N-H} \cdots \text{N}$ hydrogen bonds and $\pi-\pi$ interactions) stabilize the intertwined helicates.

The dimerized helicates in these compounds are isostructural, the only significant difference being the nature of the halide- encapsulated guest. The other counter ions and solvent molecules do not interact significantly with the helicates. The encapsulated halide ion in each complex forms strong hydrogen bonds with N-H groups of the pyrazole rings in both mononuclear helicates. The different $\text{X} \cdots \text{H-N}$ hydrogen bond strength in these helicates affect differently the crystal field around the iron centers and thus the SCO behavior. The trend observed for stabilization of the LS state and therefore the increase of the SCO transition temperature was $\text{Cl}^- > \text{Br}^- > \text{I}^-$. This trend matches well the hydrogen bonding ability of the halide ions; the stronger the hydrogen bonding the more stable the LS state and higher the shift of the SCO transition temperature to higher values.

These helicates are stable in solution as shown by ^1H NMR and ESI-MS studies. However, an equilibrium in solution is evident between these assemblies and the

dinuclear triple stranded helicates $[X\text{-Fe}_2(\text{H}_2\text{L4})_3]^{3+}$. Thus, both species are present in solution to different extents in addition to the ones free of encapsulated halide.

As a future perspective, the modification of the ligand by adding different substituents in the pyridine group could be a way to enhance the cooperativity of these systems. In the case of the dimerized helicates this can cause a shifting of the spin transition temperature to lower temperatures and make it accessible around room temperature.

In chapter 2, the encapsulation of ClO_4^- inside the helical cavity of $[\text{Fe}_2(\text{H}_2\text{L6})_3]^{4+}$ is described. The $\text{H}_2\text{L6}$ ligand has a flexible biphenyl spacer which allows for the preparation of triple stranded helicates featuring a bigger cavity. In chapter 5, the encapsulation of $[\text{M(III)(ox)}_3]^{3-}$ ($\text{M} = \text{Fe}$ and Cr ; $\text{ox} = \text{oxalate}$) metal complexes inside the helical cavity of $[\text{Fe}_2(\text{H}_2\text{L6})_3]^{4+}$ is described. Two triple-stranded helicates are presented in this chapter:



The Fe(II) ions of the helicate exhibit SCO behavior and LIESST effect in the case of the encapsulated chromium oxalate complex. Interestingly, the guest $[\text{Cr(III)(ox)}_3]^{3-}$ exhibits SIM-like behavior at low temperatures. This is the first example where a host-guest system exhibits both LIESST effect and SIM behavior. In the only related examples, the same Fe(II) ionic species undergoes a LS to HS transition via LIEEST effect and displays also slow relaxation of magnetization with continuous light irradiation.^{2,3}

As a future perspective, such helicate with a big cavity could encapsulate other oxalato-based guests which could lead to bi-functionality. The bis-pyrazolylpyridine ligands shown in this thesis could be the beginning of a family of ligands that form host-guest helicates with interesting physical properties such as SCO, SMM and luminescence. Since these dinuclear helical assemblies are stable in solution, they are amenable to the possibility of organizing them by deposition on surfaces, which could open a promising approach for the construction of molecular devices.

In chapter 6, the correlation between the local distortion around the Fe(II) cation and the occurrence of SCO was studied. The examples of trapped Fe(II) centers in the HS state exhibit high distortion compared with the Fe(II) centers that exhibit SCO. Hirshfeld

surfaces analyses were used to study and visualize the supramolecular interactions in these helicates to understand the effect of such changes on the SCO behavior.

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- 3 C. Mathonière, H. J. Lin, D. Siretanu, R. Clérac and J. M. Smith, *J. Am. Chem. Soc.*, 2013, **135**, 19083–19086.

