Title: Preparation of helicoidal coordination complexes: Host-guest molecular systems.

Student: Èric Martínez Illamola

Date: 01/2020

Supervisor/s: Dra. Leoni Barrios Moreno
Departament de Química Inorgánica

Helicates are a metallo-supramolecular compounds where one or more ligand wrap one or more metal ion, these helicates (host) contain a cavity that can be occupied by a small specie (guest), providing a resource to implement multiple functions in one molecule. Our helicates are a dinuclear tripled-stranded helicates that contain two metals and three ligands, and form a cavity in the center.

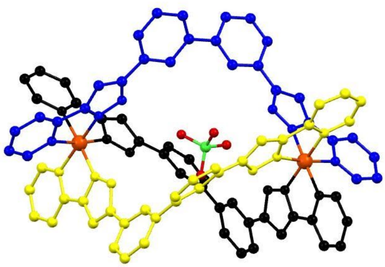


Figure 1. Structure of $ClO_4 \subset [Fe_2(H_2L6)_3](ClO_4)_3 \cdot 16(MeCN)$ omitting the hydrogens, the counterions and the solvent molecules. Made with Mercury.

Which are the properties that we are interested with? There are a lot of possibilities, but mainly we are interested in two properties: spin crossover (SCO) and single ion magnet (SIM). Spin crossover allow us to use these systems as a sensor (the system response into an external stimulus) and the single ion magnet compounds can be magnetized by applying a magnetic field and then keep the magnetization after remove the magnetic field (the slow relaxation of the magnetization is an interesant propriety for the storage of information).

In our experiments, the ligand (25 mg of H_2L6) and the mol relation of the ligand and the metal (3 mol of ligand for 2 mol of metal) are a fixed variables, the metal (Fe(II), Co(II) and Ln(III)) and the guest (PF_6^-, ClO_4^- and $Cr(Ox)_3^{3-}$) are the main variables and the metal salt, the solvents, the crystalize method, etc, are the secondary variables. We did several tries to synthesize helicoidal systems with different reactives in different experimental conditions. Only one of them result in the formation of: $ClO_4 \subset [Fe_2(H_2L6)_3](ClO_4)_3 \cdot 16(MeCN)$.

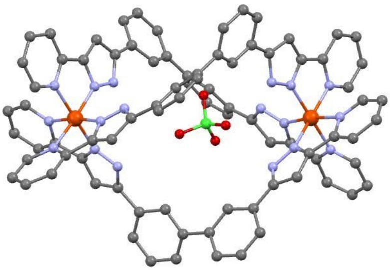
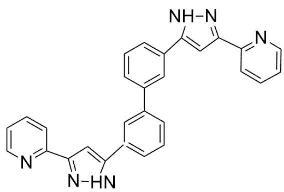


Figure 2. Structure of $ClO_4 \subset [Fe_2(H_2L6)_3](ClO_4)_3 \cdot 16(MeCN)$ omitting the hydrogens, the counterions and the solvent molecules. Made with Mercury.

The ligand H_2L6 is the most important component in terms of stability, because: 1) act as a ligand and is coordinated with the metals (N-Fe links); 2) allow the formation of the hydrogen bonds with the guest (N-H-O links); 3) the aromatic chain with the π-π interaction between different helicoidal molecules provide an extra stability to the system; 4) the biphenyl group makes the ligand large enough to form a cavity big enough to encapsulate our guest; 5) thanks to the free rotation of the biphenyl group the structure have the flexibility enough to accommodate to the stability requirements.



5

Figure 3. H2L6: 3,3'-bis(3-(pyridin-2-yl)-1H-pyrazol-5-yl)-1,1'- biphenyl. Made with Chemdraw

Keywords: Helicoidal system, host-guest system, triple-stranded helicate, spin crossover, single ion magnet