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Metalloacycles are zero-dimensional (0-D), cyclic coordination compounds or coordination macrocycles. Since they are essentially comparable to doughnuts they do not pack efficiently. Instead of close packing to occupy all available space, these cyclic units stack to form voids or one-dimensional channels that are occupied by guest molecules. If the guest molecules can be removed while the host framework retains its shape instead of collapsing, a porous material is obtained. The properties of such a material can include gas/vapour/solvent storage, separation and sensing. Indeed, some examples of materials with these properties have been published [1].

The imidazole based ligands described here are flexible and can undergo free rotation around the methylene groups. This allows the framework to contract and expand in order to accommodate guest molecules of different sizes. Common features of the ditopic ligands used in this study are the benzimidazole coordinating groups, which have a high affinity for metals. These imidazole derived ligands are easily functionalized while different aromatic spacer groups can be incorporated between the benzimidazole arms. Our investigation centres on the design of targeted architectures. However, despite continuous efforts to predict and define parameters governing the assembly of these 0-D (i.e. discrete) architectures their rational design is not always possible [2].

Three metalloacycles were obtained from the reaction of the ditopic imidazole functionalized ligands L1, L2 and L3 as shown in Figure 1 with the metal salts CdI_2 , ZnCl_2 and CuCl_2 , respectively. The three zero-dimensional compounds include two dinuclear metalloacycles $[\text{Zn}_2(\text{L2})_2\text{Cl}_4] \cdot 2\text{CH}_3\text{CN}$ and $[\text{Cu}_2(\text{L3})\text{Cl}_4] \cdot 3\text{CH}_3\text{CN}$ and one tetranuclear metalloacycle $[\text{Cd}_4(\text{L1})_4\text{I}_8] \cdot 2\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$. It has been shown that acetonitrile solvent molecules incorporated in the tetracycle can be displaced by iodine molecules, which proves that this framework is robust and might be capable of including various different guest molecules in its solvent-filled channels. The framework also undergoes a structural change in the presence of methanol and the versatility of this combination of molecular building blocks is illustrated by different topologies formed under different crystallization conditions.

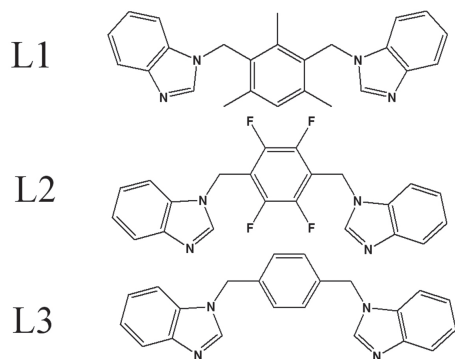


Figure 1: Imidazole functionalized ligands

[1] L. Dobrzańska, G.O. Lloyd, H.G. Raubenheimer, L.J. Barbour *J. Am. Chem. Soc.* **2005**, *127*, 13134-13135. [2] T. Jacobs, PhD. thesis, *Self-Assembly of New Porous Materials*, University of Stellenbosch, South Africa, **2009**.

Keywords: discrete, porosity, exchange

MS25.P08

Acta Cryst. (2011) **A67**, C394

Short and long-range structure of ZnO:Co diluted magnetic semiconductor

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The incorporation of magnetic ions in an oxide matrix has been widely studied as an alternative to achieve room temperature ferromagnetism (RTFM) in diluted magnetic semiconductor (DMS). In a previous work, we reported the absence of intrinsic ferromagnetism in high-quality bulk samples synthesized in oxygen atmosphere at 1400 °C. We concluded that the presence of Co is not a sufficient condition to induce a ferromagnetic behavior. In this work, we report RTFM in hydrogenated Zn_{1-x}Co_xO bulk samples synthesized via a standard solid state reaction route with different Co molar concentrations of 4, 8, 12, 15 and 21%.

Paramagnetic Zn_{1-x}Co_xO samples were annealed in a gaseous mixture of argon 95% and hydrogen 5% at 600°C for 3 hours. The effects of hydrogenation on the crystal structure of the samples were determined by using x-ray diffraction (XRD). Structural analysis was performed using the Rietveld method as implemented by the software package Fullprof. Co K-edge x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) was used to determine the valence state and to evaluate the local environment of Co in the ZnO lattice. The microstructure and composition distributions were characterized by scanning electron microscopy (SEM) and energy dispersive x-ray (EDS) measurements. X-ray absorption measurements were taken in the transmittance mode at the XAS beamline from the Brazilian Synchrotron Light Laboratory (LNLS), Campinas, Brazil. Magnetic characterizations were performed using a superconducting quantum interference device (SQUID) magnetometer in the temperature range between 10K and 300K.

The conjugated different techniques confirmed the Zn replacement by Co ions in the wurtzite ZnO structure, which retains a high crystalline quality. No segregated secondary phases neither Co-rich nanocrystals were detected. SQUID magnetometry demonstrates a two-phase behavior, with the coexistence of paramagnetic and ferromagnetic phases up to room temperature for whole set of samples. The magnetization saturation show an increase as Co concentration increases but the magnetic moment has a constant value 0.003 mB per Co ion inserted in the matrix independently of x. We discuss the observed room temperature ferromagnetism of our hydrogenated samples considering the current models for the magnetic properties of diluted magnetic semiconductors.

The authors are grateful to FAPEMIG, FAPESP and CNPq for financial support.

Keywords: ferromagnetic, X-ray, XAS

MS25.P09

Acta Cryst. (2011) **A67**, C394-C395

Organic-inorganic Mn(II)-cyanate compound with five dispositions of bpa ligand

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