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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  $\text{CdI}_2$ ,  $\text{ZnCl}_2$  and  $\text{CuCl}_2$ , 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.

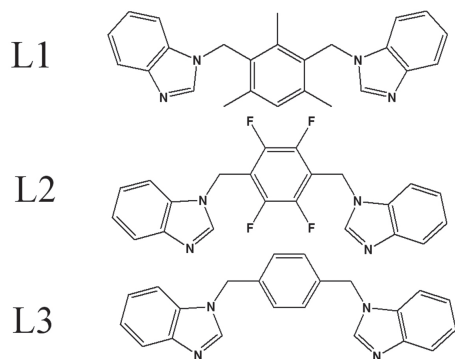


Figure 1: Imidazole functionalized ligands

[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<sub>1-x</sub>Co<sub>x</sub>O bulk samples synthesized via a standard solid state reaction route with different Co molar concentrations of 4, 8, 12, 15 and 21%.

Paramagnetic Zn<sub>1-x</sub>Co<sub>x</sub>O 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 was 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

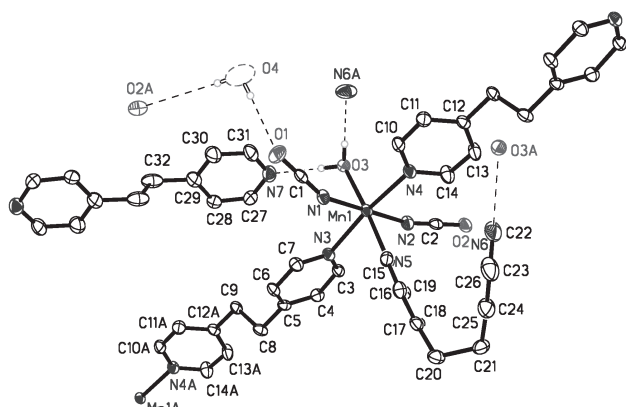
**Organic-inorganic Mn(II)-cyanate compound with five dispositions of bpa ligand**

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An hybrid organic-inorganic chain compound of the family Mn(II)-bpa-(NCO) is presented:  $[\text{Mn}_4(\text{NCO})_8(\mu\text{-bpa})_4(\text{bpa})_4(\text{H}_2\text{O})_4]_n \cdot 2n(\text{bpa}) \cdot n\text{H}_2\text{O}$  (**1**). It contains, unusually, five different dispositions for the bpa [1,2-bis(4-pyridyl)ethane] ligand. Water molecules and free bpa ligands occupy the voids of the structure. Single-crystal X-ray diffraction reveals **1** to crystallize in the P21/n monoclinic space group. It consists of infinite chains of Mn(II) cations extending along the [100] direction and bridged by single N,N'-bpa bridges [Mn-N(3): 2.336(2) Å; Mn-N(4): 2.344(2) Å], that are in anti conformation with a torsion angle of 177.03° (Mn...Mn intrachain distance: 13.9 Å, Fig. 1). The distorted octahedral coordination of the cation is completed by a terminal bpa ligand [Mn-N(5): 2.296(2) Å], two N-terminal cyanate ligands [Mn-N(1): 2.189(2) Å; Mn-N(2): 2.163(2) Å], and a water molecule [Mn-O(3): 2.000(2) Å]. These chains are connected through intermolecular hydrogen bonding involving the atoms O(3) (water molecule) and N6 (non coordinating N-atom of the terminal bpa) [O(3)...N(6): 2.789(3) Å] or C(8) (ethane group of the bridging bpa) [O(3)...C(8): 3.414(4) Å]. Besides, the C(11) (bridging bpa) establish intermolecular connection with the O(2) (cyanate oxygen) [C(11)...O(2): 3.324(3) Å]. Interchain Mn...Mn distances are 8.6 Å and 9.0 Å and the packing is on the plane (110). The disposition of these sheets gives raise to hollows that are occupied by free molecules (water and bpa). Thus, a free bpa ligand acts as a solvate molecule occupying the voids in the lattice, in the same way as a water molecule acts.

The compound shows moderate antiferromagnetic type interactions through single bpa bridges, together with other exchange pathways. Electron spin resonance spectrum for **1** has been recorded at room temperature. The signal can be described as isotropic and is centred at 3300 Gauss.



**Keywords:** manganese, magnetochemistry, EPR

## MS25.P10

*Acta Cryst.* (2011) A67, C395

### Thermal behaviour (HT and LT) in minerals of the cryptomelane group

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Single-crystal X-ray diffraction measurements were carried out on two minerals belonging to the cryptomelane group (hollandite, ideally  $\text{BaMn}^{4+}_6\text{Mn}^{3+}_2\text{O}_{16}$ ; ankangite, ideally  $\text{BaTi}^{4+}_6\text{V}^{3+}_2\text{O}_{16}$ ) at

several temperatures (from 100 to 900 K), to gather information on the structural behavior of these compounds with temperature, as a part of an ongoing study on the crystal-chemistry of the minerals of the cryptomelane group. The structure of the members of this group is characterized by octahedra arranged in edge-sharing columns, which in turn link together, again by edge-sharing, giving rise to walls, two octahedra wide. Cross-linking of these walls by corner-sharing result in a tunnel structure, with a squared 2x2 outline [1]. The ideal topological symmetry of 2x2 tunnel oxides is tetragonal, *I4/m*; the symmetry may lower to monoclinic due to cation ordering within both the octahedral framework and the tunnels [2]. It has been observed that these structural variations, and also phase transitions, may be induced by variations of temperature [3].

Accurate refinements of the unit cell parameters on selected specimens of hollandite from Vagli (Apuan Alps, Tuscany, Italy) and from the Kajlidongri mine (Jhabua district, Madhya Pradesh, India) were carried out in the T range from *ca.* 100 to *ca.* 900 K. At RT the studied samples are monoclinic, *I2/m*. As expected, the unit cell volume increases quite regularly with T, moreover a progressive transition of the symmetry from monoclinic to tetragonal is observed, with *a* approaching *c* and  $\beta$  approaching 90°. The T of transition is estimated at *ca.* 530 K. After a number of successive heating and cooling experiments carried out with various crystals of hollandite, we note that the monoclinic-tetragonal transition is reversible up to a T of *ca.* 900 K. Above that temperature, the transition becomes irreversible.

Complete crystal structure refinements were carried out on samples of ankangite from the Monte Arsiccio mine (Apuan Alps, Tuscany, Italy) in the T range from 100 to 800 K. Ankangite is tetragonal, *I4/m*, within the whole above T range. At varying T we observe, on one side, a regular increase of the unit cell parameters, and of all the interatomic distances, on the other side a significant variation in the occupancy of the extra-framework site. In ankangite the extra-framework cation is Ba, which is hosted in two distinct and partially occupied sites, Ba1 (at 0, 0, ½) and Ba2 (at 0, 0, 0.65). The occupancy at both sites was allowed to refine freely, the only constraint was to fix the displacement parameters at the same average value for each T run. From 100 K up to RT both sites are partially occupied, with a slight preference for Ba1, whereas at higher temperatures (500 and 700 K) all Ba tends to concentrate in the Ba1 site and Ba2 becomes empty. This may have some effect on the incommensurate structures so far observed in members of the cryptomelane group [4].

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**Keywords:** X-ray\_diffraction, low\_temperature, high\_temperature.

## MS25.P11

*Acta Cryst.* (2011) A67, C395-C396

### Metal-organic frameworks as ion-exchangers

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Porosity and sorption processes represent one of the most stimulating current areas of research activity in the field of materials chemistry, in particular when using metal-organic frameworks (MOFs) [1]. Following our on-going research focused on the development of functional MOFs, we report the synthesis, full structural characterization, porosity measurements and ion exchange properties of a new porous MOF with Ce<sup>3+</sup> [2, 3].