

## MS25.P05

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**Dynamic behavior in a dryness sensitive 3d-4f metal–organic framework**

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Coordination networks with well-defined nanochannels hold great promise for a number of applications owing to guest adsorption, removal, and exchange behaviors in the channels [1]. An intriguing property is the ability to ‘breathe’ when the material is exposed to an external stimulus (e.g., pressure, temperature, light, gas or solvent adsorption), sometimes with large variations (> 5 Å) in their unit-cell parameters [2]. The creation of dynamic pores can be achieved through different ways, e.g., that flexible building units are linked via strong bonds, or rigid building blocks are connected via weak bonds. Another possible option is the combination of flexible building blocks and weak linkages. For weak linkages, guest molecules readily give rise to changes in the bond direction and distance or to cleavage of bonds.

A new three-dimensional heteronuclear metal-organic framework has been synthesized using the 1,2,4,5-benzenetetracarboxylate ligand (hereafter *bta*) as a linker and Pr(III)-Cu(II) dinuclear units as nodes. The resulting structure shows an expanding-shrinking porous transition only in the presence of a dryness environment from [Pr<sub>4</sub>(H<sub>2</sub>O)<sub>18</sub>Cu<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>bta<sub>5</sub>]<sub>n</sub>•14nH<sub>2</sub>O (**1a**) compound towards the [Pr<sub>4</sub>(H<sub>2</sub>O)<sub>18</sub>Cu<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>bta<sub>5</sub>]<sub>n</sub>•16nH<sub>2</sub>O shrunk compound (**1b**). The present compound belongs simultaneously with the type IV of Férey and V of Kitagawa classification, which corresponds with a 3D complex which shows a sponge-like dynamic (expanding and shrinking channels).

These structure exhibits channels along the *a* direction, which guest several crystallographic water molecules are accommodated. The unexpected dynamic behavior produces a phase transition from extended structure **1a** toward a shrunk one **1b**. The difference between the open and closed forms is striking: the bonding structure of the framework is slightly changed, involving the torsion of the interlayer organic linkers and the creation of two extra bonds among these linkers and two different copper ions, resulting in the compression of the *b* axis by more than 2 Å, and the consequent unit cell volume decrease by over 11.5%.

The sensibility of the crystal structure at dryness environment has been proved with thermogravimetric studies, combined with synchrotron X-ray measurements as a function of the temperature.

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**Humidity- and pressure-induced hydration of K,Na-rich****laumontite**

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K,Na-rich laumontite [Ca<sub>4-x</sub>K<sub>x</sub>Na<sub>x</sub>(H<sub>2</sub>O)<sub>m</sub>][Al<sub>8</sub>Si<sub>16</sub>O<sub>48</sub>] strongly differs in the hydration ability from common Ca-laumontite [Ca<sub>4</sub>(H<sub>2</sub>O)<sub>m</sub>][Al<sub>8</sub>Si<sub>16</sub>O<sub>48</sub>]. At the humidity increase Ca-laumontite hydrates with an abrupt volume expansion; K,Na-rich laumontite has been assumed incapable of the hydration [1]. A sample of K,Na-rich laumontite [Ca<sub>2.73</sub>K<sub>1.03</sub>Na<sub>1.44</sub>(H<sub>2</sub>O)<sub>m</sub>][Al<sub>7.93</sub>Si<sub>16.07</sub>O<sub>48</sub>] (Akhaltzikhe, Georgia) has been studied by the single-crystal X-ray diffraction method at various humidity and at the compression in water up to 1.14 GPa in a diamond anvil cell.

At the increase of relative humidity from 30% to 70% at ambient pressure the H<sub>2</sub>O content of K,Na-rich laumontite increased from 11.9 to 13.2 molecules per formula unit (pfu) due to the gradual occupancy growth of most water sites. The further sample wetting had no significant effect on the hydration degree.

In fully hydrated Ca-laumontite the occupancies of all water sites approach to maximum [2]. In contrast, in the most hydrated (at ambient pressure) K,Na-rich laumontite the hydration degree is substantially lower. In order to explain this we suppose the channel cages to contain water-cation assemblages of two types: Ca<sub>2</sub>□<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub> (□ is a vacancy) and (Ca,Na)<sub>2</sub>(K,H<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>. The Ca-laumontite structure contains only the first-type assemblages and hydrates with an abrupt volume expansion due to the appearance of additional water molecules in the mentioned vacancies [2]. As K,Na-rich laumontite does not demonstrate such expansion and keeps a part of corresponding water sites vacant we suppose its first-type assemblages to remain low-hydrated state at any ambient pressure humidity.

The high-pressure experiments have shown the additional hydration of K,Na-rich laumontite. Its most intensive step under 0.1 GPa with a significant volume expansion despite pressurizing was a result of the first-type assemblages hydration. The further pressure increase caused the regular additional hydration due to the gradual occupancy growth of most water sites with a volume compression. At pressure about 0.8 GPa the limit of water content near 15 H<sub>2</sub>O molecules pfu was reached. In contrast, Ca-laumontite is incapable of the pressure-induced additional hydration [3].

The differences between hydration behavior of Ca-laumontite and K,Na-rich laumontite are caused by the presence of additional cations in latter. Being situated in the second type assemblages these ones prevent the structure expansion and allow water molecules to occupy water site vacant in the first type assemblages. We suppose the mechanism of these effects to be attributed with an influence of additional cations on the H-bond net.

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**Zero-dimensional coordination compounds incorporating imidazole based ligands**

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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<sub>2</sub>, ZnCl<sub>2</sub> and CuCl<sub>2</sub>, respectively. The three zero-dimensional compounds include two dinuclear metalloacycles [Zn<sub>2</sub>(L2)<sub>2</sub>Cl<sub>4</sub>]•2CH<sub>3</sub>CN and [Cu<sub>2</sub>(L3)Cl<sub>4</sub>]•3CH<sub>3</sub>CN and one tetranuclear metalloacycle [Cd<sub>4</sub>(L1)<sub>4</sub>I<sub>8</sub>]•2CH<sub>3</sub>CN•2H<sub>2</sub>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.

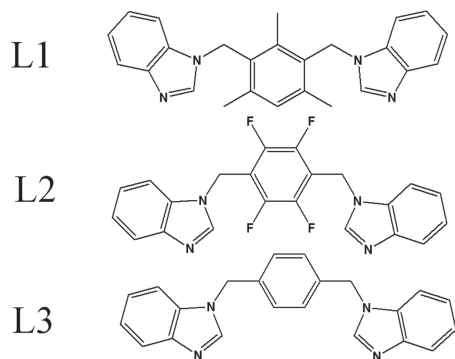


Figure 1: Imidazole functionalized ligands

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**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 oC. 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 600oC 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.

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**Keywords:** ferromagnetic, X-ray, XAS

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

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