

## MS25.P05

Acta Cryst. (2011) A67, C393

**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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**Keywords:** metal-organic frameworks, dynamic, bimetallic

## MS25.P06

Acta Cryst. (2011) A67, C393

**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.

This work was supported by Russian Foundation for Basic Research (grant 10-05-00483).

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**Keywords:** zeolite, hydration, pressure

## MS25.P07

Acta Cryst. (2011) A67, C393-C394

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

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