

show no significant decrease in their catalytic properties.

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### Reversible phase transformation of a pyridyl ketone based coordination polymer

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The reactions of di-2-pyridyl ketone (dpk) with metal ions have been particularly well studied over the years. The structural diversity of the complexes stems from the ability of the deprotonated diol- or hemiketal-type ligands ((py)<sub>2</sub>C(OH)<sub>2</sub> and (py)<sub>2</sub>CO) to adopt a variety of bridging coordination modes. Employment of a second ligand in this chemistry gives an extraordinary structural flexibility in the resulting mixed-ligand systems [1].

In this work, we present the synthesis and structural characterization of the compound [M(dpk)(PDC)(H<sub>2</sub>O)]·2H<sub>2</sub>O (where PDC= pyridine-2,5-dicarboxylate and M= Ni or Co). This compound can be obtained by solvothermal synthesis as well as by slow evaporation. The crystal structure can be described as monomers that are joined hydrogen bonds forming 1D arrays. These chains are placed in alternative fashion.

The interest of this structure is vested in the coordination of the dpk ligand. Only a few complexes exhibit the dpk ligand in the (py)<sub>2</sub>(H)(OH) form. In the presented compound a disorder between (py)<sub>2</sub>(O)(OH) and (py)<sub>2</sub>(O)(H) forms can be observed. The present type of ketone reduction during the formation of compound appears to be very rare [2], [3].

The thermal behaviour of the compound was analyzed by both thermogravimetric (TG) and thermodiffraction (TDX) techniques. Apparently, the departure of the water molecules induces a phase transition accompanied with the formation of an amorphous phase. X-ray powder diffraction analysis revealed that the transformation is reversible when water is added over the polycrystalline sample.

These types of reversible structural transformations in non-coordination supramolecular systems are not common since the structural destruction accompanying with the guest removal is too severe to recover the crystallinity after re-adsorption. This is not the case for flexible coordination polymers which contain the bridging spacers maintaining the skeleton of the whole structures. In fact, the guest-induced crystalline-to-amorphous transformation is characteristic of the third generation compounds which are typically found in the

flexible coordination frameworks supported by weak molecular interactions, such as hydrogen bonds, π-π stacking, van der Waals forces and others [4], [5].

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### Structural transformation of the porous MOF [Ni<sub>2</sub>(bipy)<sub>1.5</sub>(PDC)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-3.5H<sub>2</sub>O

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Solid-state structural transformations involving coordination polymers induced by light, heat, guest removal, etc. are very fascinating and one of the hot topics in solid-state chemistry. These structural transformations normally involve significant rearrangement of molecular components in the crystals [1], [2]. In recent years, many researchers have been attracted on the assembly and crystal engineering of metal-organic frameworks (MOFs) and coordination polymers due to their structural motifs and potential applications in porous, magnetic, luminescent and catalytic materials [3].

Our group is working on the combination of different ligands and transition metals. In this work, we present a 3D compound with formula [Ni<sub>2</sub>(bipy)<sub>1.5</sub>(PDC)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-3.5H<sub>2</sub>O (acronym, h-NiPB) (where bipy=4,4'-bipyridine and PDC=pyridine-2,5-dicarboxylate). Compound h-NiPB was synthesized by using mild solvothermal conditions. The crystal structure can be described as a three-dimensional lattice formed by layers of Ni-PDC, which are connected by bipyridine molecules. As a consequence, channels are formed in which the crystallization molecules of water are located. The thermodiffraction analysis shows that the compound h-NiPB undergoes a phase transition between 110-130°C. This transformation is associated to the loss of the water molecules in the channels and to the departure of one of the two terminal water species.

The resulting compound (dh-NiPB) exhibits the [Ni<sub>2</sub>(bipy)<sub>1.5</sub>(PDC)<sub>2</sub>(H<sub>2</sub>O)] formula, and its structure was solved by X-ray Powder Diffraction. Both phases have similar structural features; the most difference is the disposition of the Ni-PDC layers. As a result of the departure of the coordination molecule of water, the formation of a new bond is induced. This is, a carboxyl oxygen to the metal center. The thermal process involving the topochemical transformation of hydrogen-bond interaction into covalent bonding was previously described [4].