

synthons, formed by coordinated water molecule and two carboxylic group on each Cu²⁺ ions could create supramolecular dimer of two mononuclear complex molecules or 2D-supramolecular layers of 1D-coordination polymers.

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Keywords: hydrogen bonds, supramolecular structure, N,N-diethylnicotinamide

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Synthesis, crystal structure and thermal behavior of M(C₆H₁₆N₃)₂(VO₃)₄ compounds

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The use of organic molecules for the design of new inorganic materials has allowed the preparation of compounds with major technological applications [1]. In this context, vanadium derivatives seem to be good candidates to obtain new materials because of its rich crystal chemistry [2]. For this reason, our research has been focused in the synthesis and characterization of hybrid vanadates with aromatic and aliphatic amines [3]. In this work we report the synthesis, structure and thermal properties of a family of three isostructural compounds with M(C₆H₁₆N₃)₂(VO₃)₄ formula, where M=Co²⁺, Ni²⁺ and Cu²⁺, as well as the relationship between the crystal structure and the thermal stability.

Co(C₆H₁₆N₃)₂(VO₃)₄, **1**, Ni(C₆H₁₆N₃)₂(VO₃)₄, **2** and Cu(C₆H₁₆N₃)₂(VO₃)₄, **3**, have been synthesized using mild solvothermal conditions. The crystal structures were solved using single-crystal X-ray diffraction data. They crystallize in the monoclinic system, space group P2₁/c. The cell parameters are very similar for the three phases, but they do not follow the Vegard law [4]. These compounds show a two-dimensional crystal structure, with sheets composed of [VO₃]_nⁿ⁻ chains and metal centres octahedrally coordinated chelated by two 1(2-aminoethyl)piperazonium ligands. The copper(II) containing phase show slight differences in the bond distances of the octahedra due to a Jahn-Teller effect.

The thermogravimetric decomposition curves of the three phases show a sequence of overlapped processes of mass loss from approximately 250 °C to almost 500 °C for compounds **1** and **2**, whereas, for compound **3**, these processes occur between 185 and 470 °C. Time-resolved X-ray diffractometry show that phases **1** and **2** are stable until 270 °C and 280 °C, respectively, while the copper(II) phase is less stable, and its structure collapses at 180 °C. The destruction of the crystal structure is due to the calcination of the organic ligand according to the thermogravimetric data. Above these temperatures the formation of amorphous compounds takes place.

The temperature at which the crystal structure of **3** collapses is significantly lower, comparing with the isostructural phases **1** and **2**. This fact is closely related with the presence of Cu²⁺ and the slight differences observed in the crystal structure when this metal is present.

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Keywords: organic-inorganic materials, thermoanalysis, structure-thermal stability relationship

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Catalytic behaviour of two structurally related vanadyl arsenates

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Among open-framework metal phosphates, transition metal containing ones constitute an important group due to their potential activity as redox catalysts [1]. Other anionic moieties such as borates, arsenates, sulphates and selenates have been used successfully in the preparation of novel open framework structures, some of them with catalytic properties [2]. During the course of our research, we have synthesized and characterized two new fluorovanadyl-hydrogenarsenate with ethylenediammonium and piperazonium as templating agents, with formulae (C₂N₂H₁₂)_{0.5}[(VO)(HASO₄F)], EnVAs, and (C₄N₂H₁₄)_{0.5}[(VO)(HASO₄F)], PipVAs, [3] with catalytic properties [4].

EnVAs and PipVAs have been synthesized by mild hydrothermal conditions under autogenous pressure. The crystal structures have been solved from single-crystal X-ray diffraction data. The phases crystallize in the P2₁/c monoclinic space group with cell parameters a = 7.8634(4)Å, b = 7.7658(4)Å, c = 10.4195(6)Å, β = 101.524(5)° for EnVAs and a = 6.301(1)Å, b = 10.244(1)Å, c = 10.248(1)Å and β = 95.225(1)° for PipVAs. These phases exhibit a very similar layered inorganic framework. In both cases, the structure is built from secondary building units (SBU) which are formed by [V₂O₈F₂]_n dimmers of edge-sharing vanadyl octahedra, connected by the vertices to two hydrogenarsenate tetrahedra. The repetition of this SBU unit originates sheets along the [1 0 0] direction. The ethylenediammonium and piperazinium cations are located inside the interlayer space.

Both phases have been evaluated as catalysts for the oxidation of thioethers and alkenes, using H₂O₂ and t-butyl hydroperoxide (TBHP) as oxidants. Both phases act as heterogeneous catalysts for these reactions. The intrinsic activity of EnVAs was higher than that of PipVAs for the oxidation of sulfides. Similar results were obtained when using either H₂O₂ or TBHP as oxidants. However, the steric effects were enhanced when TBHP was used and higher selectivities towards sulfoxides were achieved with this oxidant. The different catalytic behaviour between EnVAs and PipVAs, could be explained taking into account the structural differences between them. The catalytic activity of the V-based materials in the epoxidation of simple alkenes and allylic alcohols was assessed. Upon reuse, both materials

show no significant decrease in their catalytic properties.

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Keywords: vanadium_arsenate, structural_characterization, catalytic_oxidation.

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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)₂C(OH)₂ and (py)₂CO) 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)(H₂O)]·2H₂O (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)₂(H)(OH) form. In the presented compound a disorder between (py)₂(O)(OH) and (py)₂(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 [Ni₂(bipy)_{1.5}(PDC)₂(H₂O)₂].3.5H₂O

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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 [Ni₂(bipy)_{1.5}(PDC)₂(H₂O)₂].3.5H₂O (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 [Ni₂(bipy)_{1.5}(PDC)₂(H₂O)] 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].