

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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Keywords: transformation, MOF

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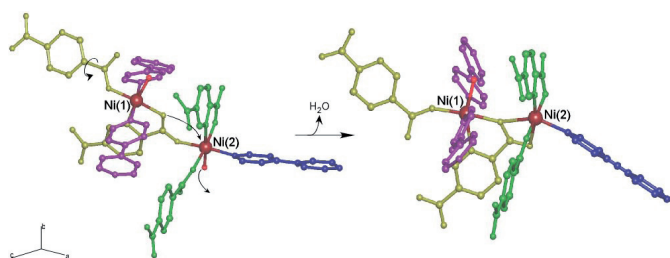
Structural transformation of the porous MOF [Ni₂(bipy)_{1.5}(PDC)₂(H₂O)₂].3.5H₂O

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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].



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This work has been financially supported by the Ministerio de Ciencia e innovación, MICIN (MAT2010-15375) and the Gobierno Vasco (Basque University System Research Groups (IT-177-07)), which we gratefully acknowledge. SGIker technical support (MEC, GV/EJ, European Social Fund) is gratefully acknowledged. A. Calderón-Casado thanks to the UPV/EHU fellowships.

Keywords: MOFs, transformation, 3D compound

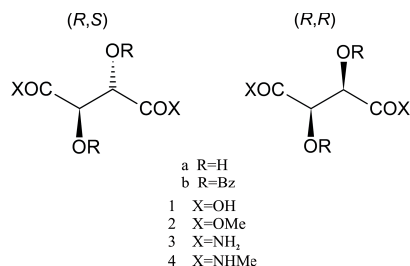
MS24.P65

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The many facets of tartaric acid its diesters and diamides

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Versatile possible chemical modifications, a variety of stereochemical forms and a great hydrogen bond capacity make tartaric acid and its derivatives interesting objects for structural studies. We have investigated the crystal structures of several derivatives of (*R,S*)-tartaric acid (the so called *meso* tartaric acid) and performed comparative analysis with their *R,R* counterparts. The obtained results have been analyzed in terms of chirality, conformation, molecular and crystal symmetry and supramolecular synthon robustness. Among the factors that affect molecular conformation local dipolar CH/CO interactions, intramolecular hydrogen bonds and a tendency to situate hydroxyl groups in mutually *gauche* orientation have been considered. The role of hydroxyl substituents as symmetry breaking elements will be illustrated. A link between hydrogen-bond synthons, as identified by X-ray analysis, and grow synthons present in solution as a consequence of thermodynamically driven self-association equilibria will be addressed. In this respect, a particular attention will be paid on formation of polyamide supramolecular ladder motifs, which in condensed media are by far more important than the maintenance of the preferred molecular conformation.



Keywords: tartaric acid derivatives, H-bond synthons, symmetry breaking

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Crystal engineering in mercury (II) coordination compounds based on pyrazine carboxamide ligand

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Crystal engineering is a flourishing field of research in modern chemistry. Contemporary crystal engineering involves the design and synthesis of crystals. The aim of this endeavour is the development of new crystalline materials with a variety of properties, functions and applications.

Among the non-covalent motifs, Hydrogen bonding, metal-ligand coordination and pi-pi stacking have been employed as synthetic paradigm to rationally design superstructures.

Herein, we report crystal engineering of mercury (II) halides of *N*-Phenyl-2-pyrazine carboxamide, which are obtained of *N*-Phenyl-2-pyrazine carboxamide with mercury (II) chloride & Bromide.

In this regards, To explore the supramolecular trends exhibited by molecules that can engage simultaneously in metal-ligand coordination, hydrogen bonding, and pi-pi stacking interactions, *N*-Phenyl-2-pyrazine carboxamide was prepared and its coordination chemistry and crystalline packing behavior was investigated. This ligand consists of three structural parts: (1) a pyrazine group that can coordinate to a metal, (2) a carboxamide group, which can have hydrogen bonding interactions through the amide nitrogen atom as well as via the carbonyl oxygen atom, and (3) a phenyl group, which can be involved in pi-pi stacking interactions.

In our design, the metal center assemble the ligand into the required geometrical orientation. From the packing Diagram of carboxamide ligand, it is clear that hydrogen bonding between amide moiety and (Ph)C-H and pi-pi stacking between pyrazine and Phenyl ring are the dominant factors. In [HgCl₂(L)], the molecule contains One Hg(II) with distorted tetrahedral geometry, two chlorine and a carbonyl oxygen and pyrazine nitrogen atom. For [HgBr₂(L)], the structure consists of two ligands and two Hg ions bonded to form dimeric complexes. Each metal is four coordinated and bonded to two halogen atoms, one pyrazine nitrogen atom, and one carbonyl oxygen atom from the second ligand. All two complexes have been expanded by Hydrogen Bonding and pi-pi stacking to supramolecular entities.

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Synthesis and crystal structure of Ho(phen)₂(NO₃)₃

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Rare earth metal cations are of growing importance for their