

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

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**Synthesis, crystal structure and thermal behavior of  $\text{M}(\text{C}_6\text{H}_{16}\text{N}_3)_2(\text{VO}_3)_4$  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  $\text{M}(\text{C}_6\text{H}_{16}\text{N}_3)_2(\text{VO}_3)_4$  formula, where  $\text{M} = \text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ , as well as the relationship between the crystal structure and the thermal stability.

$\text{Co}(\text{C}_6\text{H}_{16}\text{N}_3)_2(\text{VO}_3)_4$ , **1**,  $\text{Ni}(\text{C}_6\text{H}_{16}\text{N}_3)_2(\text{VO}_3)_4$ , **2** and  $\text{Cu}(\text{C}_6\text{H}_{16}\text{N}_3)_2(\text{VO}_3)_4$ , **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  $\text{P}2_1/c$ . 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  $[\text{VO}_3]_n$  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  $\text{Cu}^{2+}$  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  $(\text{C}_2\text{N}_2\text{H}_{12})_{0.5}[\text{VO}(\text{HASO}_4\text{F})]$ , EnVAs, and  $(\text{C}_4\text{N}_2\text{H}_{14})_{0.5}[\text{VO}(\text{HASO}_4\text{F})]$ , 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  $\text{P}2_1/c$  monoclinic space group with cell parameters  $a = 7.8634(4)\text{Å}$ ,  $b = 7.7658(4)\text{Å}$ ,  $c = 10.4195(6)\text{Å}$ ,  $\beta = 101.524(5)^\circ$  for EnVAs and  $a = 6.301(1)\text{Å}$ ,  $b = 10.244(1)\text{Å}$ ,  $c = 10.248(1)\text{Å}$  and  $\beta = 95.225(1)^\circ$  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  $[\text{V}_2\text{O}_8\text{F}_2]$ , 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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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