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Porous framework of $T_2[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ with $T = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$, and H_2 storage

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ABSTRACT

The materials under study were prepared from aqueous solutions of ferrocyanic acid and salts of the involved transition metals and their crystal structure solved and refined from X-ray powder diffraction data. Complementary information from thermogravimetric, infrared and Mössbauer data was also used for the structural study. Three different crystal structures were found: hexagonal ($P-3$) for Zn with the zinc atom coordinated to three N ends of CN groups plus a water molecule, cubic ($Pm-3m$) for Ni and Cu, and monoclinic ($P2_1/m$) for Co. For Ni and Cu the obtained solids have an open channel framework related to 50% of vacancies for the building unit, $[\text{Fe}(\text{CN})_6]$. In the as-synthesized material the framework free volume is occupied by coordinated and hydrogen-bonded water molecules. These of hexacyanoferrates (II) have received certain attention as prototype of materials for the hydrogen storage. In the anhydrous phase of Ni and Cu, 50% of the metal (T) coordination sites, located at the cavities surface, will be available to interact with the hydrogen molecule. However, when the crystal waters are removed the porous frameworks collapse as it is suggested by H_2 and CO_2 adsorption data. For Co, a structure of stacked layers was found where the cobalt atoms have both tetrahedral and octahedral coordination. The layers remain together through a network of hydrogen-bonding interactions between coordinated and weakly bonded water molecules. No H_2 adsorption was observed in the anhydrous phase of Co. For Zn, the porous framework remains stable on the water removal but with a system of narrow channels and a small available volume, also inaccessible to H_2 .

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1. Introduction

Transition metal hexacyanometallates have received relatively large attention in the last few years. This family of coordination polymers has been studied as prototype of molecular magnets [1–5] and more recently as materials for the hydrogen storage [6–12]. The CN ligand has the ability to serve as bridge group between neighboring metal centers, removing electron density from the metal linked at its C end, through a π back-bonding interaction, to increase the charge density on the N end that is the coordination site for the other metal. This leads to the overlapping between the electron clouds of neighboring metal centers and to their spin coupling and, thereby, a magnetic ordering is established. This supports the role of hexacyanometallates as prototype of molecular magnets. The same mechanism explains the

relatively large ability that some porous hexacyanometallates show for the hydrogen storage [12]. The electron density concentration at the N end contributes to increase the electric field gradient at the cavity surface, enhancing the framework interaction with the quadrupole moment of the hydrogen molecule. This interaction allows the H_2 stabilization within the cavity. In addition, the anhydrous phase of porous hexacyanometallates with cubic structure has metal centers with open coordination sphere at the cavity surface. The possibility of H_2 coordination to these metal sites has also motivated the interest of hexacyanometallates as prototype of porous solids for the hydrogen storage.

The best-known hexacyanometallates are the so-called Prussian blue (PB) analogues, where the involved transition metals have octahedral coordination and in the $-\text{M}-\text{C}-\text{N}-\text{T}-\text{N}-\text{C}-\text{M}-$ sequence [13]. This series of compounds crystallizes with a cubic or pseudo-cubic unit cell, usually in the highly symmetric $Fm-3m$ space group [13]. Deviations or atypical structures regarding PB analogues are known. In hexacyanometallates (II) and some hexacyanometallates (III) the Zn atom is found with tetrahedral

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