



# Low temperature structural transformation in $T[\text{Ni}(\text{CN})_4] \cdot x\text{pyz}$ with $x=1,2$ ; $T=\text{Mn,Co,Ni,Zn,Cd}$ ; pyz=pyrazine

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## ABSTRACT

The materials under study are pillared solids  $T[\text{Ni}(\text{CN})_4] \cdot x\text{pyz}$  with one and two ( $x=1,2$ ) pyrazine (pyz) molecules and where  $T=\text{Mn, Co, Ni, Zn, Cd}$ . Stimulated by their structural features and potential role as prototype of porous solids for hydrogen storage, the structural stability under cryogenic conditions for this series of pillared solids was studied. At low temperature, in the 100–200 K range, the occurrence of a reversible structural transformation was found. For  $T=\text{Mn, Co, Zn, Cd}$ , with  $x=2$ , the structural transformation was observed to occur around 185 K, and the low temperature phase crystallizes with a monoclinic unit cell (space group  $Pc$ ). This structure change results from certain charge redistribution on cooling within the involved ligands. For  $T=\text{Ni}$  with  $x=1$ , both the low and high temperature phases crystallize with unit cells of tetragonal symmetry, within the same space group but with a different unit cell volume. In this case the structure change is observed around 120 K. Above that temperature the rotational states for the pyrazine molecule are thermally excited and all the pyrazine molecules in the structure become equivalent. Under this condition the material structure is described using a smaller structural unit. The structural study using X-ray powder diffraction data was complemented with calorimetric and Raman spectroscopy measurements. For the low temperature phases the crystal structures were solved from Patterson methods and then refined using the Rietveld method.

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## 1. Introduction

Tridimensional (3D) solids prepared by incorporation of pillars (L) in layered compounds (2D) form an interesting class of porous materials. Within pillared 2D solids divalent transition metal (T) salts of the tetracyanometallate complex anion,  $T[\text{M}(\text{CN})_4]$ , with  $M=\text{Ni, Pd, Pt}$ , are particularly attractive because allow the incorporation of neutral pillar molecules between metal center on neighboring layers. This family of pillared coordination polymers is receiving certain attention as prototype of porous materials for hydrogen storage [1,2] and also for studies related with their spin crossover behavior [3–10]. Since both the hydrogen storage and spin transition studies usually occur at low temperatures, the interpretation of the obtained experimental results must be accompanied of the availability of information

on the material structural stability under cryogenic conditions. To the best of our knowledge, for the series of materials herein studied, such information is not available.

For  $T=\text{Co, Ni}$ , the incorporation of pyrazine (pyz), 4,4'-bipyridine and 4,4'-dipyridylacetylene as pillar groups between T metal centers on neighboring layers has been reported [1,2]. The obtained materials crystallize with a tetragonal unit cell ( $P4/m$  space group) creating a 3D porous framework formed by interconnected rectangular channels of the same width but of different height; this last feature due to the length of the used pillar molecule. These 3D frameworks of tailored channel size and shape have been used in studies oriented to shed light on the role of the pore dimension and geometry on the hydrogen storage in porous solids [2]. Related to the ability of the iron (2+) atom to form both high and low spin complexes, the series  $\text{Fe}_{1-x}\text{T}_x[\text{M}(\text{CN})_4] \cdot \text{pyz}$  where  $T=\text{Co, Ni}$  and  $M=\text{Ni, Pd, Pt}$ , has been intensively studied in order to understand the nature of their low temperature spin-crossover behavior, particularly the pronounced hysteresis loop that is observed [4–8]. In a recent paper, we have reported the preparation and characterization of  $T[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$  frameworks with  $T=\text{Mn, Zn}$  and  $\text{Cd}$  where the

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