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journal homepage: www.elsevier.com/locate/jsscUnique coordination of pyrazine in $T[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$ with $T = \text{Mn, Zn, Cd}$ A.A. Lemus-Santana^a, J. Rodríguez-Hernández^b, L.F. del Castillo^{a,*}, M. Basterrechea^b, E. Reguera^{b,c,**}^a Departamento de Polímeros, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México^b Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana, La Ciudad de La Habana, Cuba^c Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del IPN, Unidad Legaria, México

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ABSTRACT

The materials under study, $T[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$ with $T = \text{Mn, Zn, Cd}$, were prepared by separation of $T[\text{Ni}(\text{CN})_4]$ layers in citrate aqueous solution to allow the intercalation of the pyrazine molecules. The obtained solids were characterized from chemical analyses, X-ray diffraction, infrared, Raman, thermogravimetry, UV–Vis, magnetic and adsorption data. Their crystal structure was solved from *ab initio* using direct methods and then refined by the Rietveld method. A unique coordination for pyrazine to metal centers at neighboring layers was observed. The pyrazine molecule is found forming a bridge between Ni and T atoms, quite different from the proposed structures for $T = \text{Fe, Ni}$ where it remains coordinated to two T atoms to form a vertical pillar between neighboring layers. The coordination of pyrazine to both Ni and T atoms minimizes the material free volume and leads to form a hydrophobic framework. On heating the solids remain stable up to 140 °C. No CO_2 and H_2 adsorption was observed in the small free spaces of their frameworks.

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1. Introduction

The solids herein studied are obtained from a precursor with a layered structure, $T[\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$, where neighboring layers remain together through van der Waals forces or hydrogen bonding interactions whether the interlayers region is occupied by water molecules. Related to these weak interactions between layers, analog solids with layered structure are usually considered as two-dimensional (2D) materials where their physical and chemical properties are dominated by that structural feature [1]. In nature many solids with layered structure are found, among them graphite, clay minerals, double hydroxides (hydrotalcite-like compounds), tetravalent metal phosphates, metal chalcogenides and polysilicates, etc. [2]. Many others synthetic analogs are also known [3]. The solids with layered structure have relatively high specific surface, from 100 to 1000 m²/g [4]. However, the region between layers is usually accessible only for small molecules with appropriate properties to compel the layers separation, for instance, the water adsorption by clays minerals with the corresponding material swelling. To be possible the layers surface accessibility, their partial separation is required. This is achieved incorporating vertical supports or columns (pillars) between

layers. The incorporation of pillars in layered solids is a usual route to obtain porous solids with tailored cavity geometry and volume. The pillars species could also be used to incorporate certain functionality to the obtained porous solid. The pillars species selection for a given layered solid depends on the surface layers properties. For instance, in clays minerals the layers have certain charge unbalancing and in the interlayers region exchangeable cations are found. The cationic exchange with a voluminous species, like the *Keggin ion*, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24} \cdot 12\text{H}_2\text{O}]^{7+}$, leads to the increase for the interlayers distance [5].

The tetracyanonickelate ion, $[\text{Ni}(\text{CN})_4]^{2-}$, related to its planar structure, forms layered solids when precipitates with divalent transition metals (T) which bridge neighboring planar blocks through their N ends. The separation and pillars incorporation between the formed layers, $T[\text{Ni}(\text{CN})_4]$, has been reported for $T = \text{Fe}$ with pyridine [6] and pyrazine (pyz) [7,8], and for $T = \text{Co, Ni}$ with pyrazine [8,9], 4,4'-bipyridine (bpy) and 4,4'-dipyridylacetylene (dpac) [9] as pillars. The use of pillars molecule capable of bridge formation between metal centers at neighboring layers, e.g. pyz, bpy and dpac, allows the preparation of 3D porous framework of tailored geometry. Such porous solids have been evaluated for hydrogen storage in order to shed light on the role of the pore dimension and geometry on the H_2 adsorption [8,9]. According to the structural characterization reported for the porous solids obtained, the pillar molecules are found bridging T metal centers on neighboring layers as vertical columns to form structures based on a tetragonal unit cell ($P4/m$ space group) [8,9]. The series $\text{Fe}_{1-x}\text{T}_x[\text{M}(\text{CN})_4] \cdot \text{pyz}$ where $T = \text{Co, Ni}$ and $M = \text{Ni, Pd}$,

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