



Unique coordination of pyrazine in $T[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$ with $T = \text{Mn}, \text{Zn}, \text{Cd}$

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ABSTRACT

The materials under study, $T[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$ with $T = \text{Mn}, \text{Zn}, \text{Cd}$, 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 $T = \text{Fe}, \text{Ni}$ 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 (hydroxalite-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 $T = \text{Co}, \text{Ni}$ 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 $T = \text{Co}, \text{Ni}$ and $M = \text{Ni}, \text{Pd}$,

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Pt, has been intensively studied related with the spin-crossover behavior for the iron atom which shows a pronounced hysteresis loop [7,10–12]. For the remaining divalent transition metals ($T = \text{Mn, Cu, Zn, Cd}$), pillared compounds based on $T[\text{Ni}(\text{CN})_4]$ has not been reported. In this contribution the preparation and characterization of $T[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$ frameworks with $T = \text{Mn, Zn}$ and Cd are discussed. The study of layered cyanometalates is an active research area in solid state chemistry from decades ago [13]. The obtained solids were characterized from chemical analyses, X-ray energy-disperse spectroscopy (EDS), X-ray diffraction (XRD), infrared (IR), Raman, UV–Vis, magnetic, thermogravimetric (TG), scanning electron microscopy (SEM) and CO_2 and H_2 adsorption data.

2. Experimental section

The materials under study were prepared in two stages. Firstly, the layered structure $T[\text{Ni}(\text{CN})_4]$ is obtained, and then the pyrazine pillars between neighboring layers are incorporated. The starting layered solids, $T[\text{Ni}(\text{CN})_4]$, are obtained by mixing 0.1 M aqueous solutions of $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$ and TCl_2 ($T = \text{Mn, Cd}$) or ZnSO_4 under continuous stirring. The precipitated solid is then separated from the mother liqueur and washed several times with distilled water in order to remove all the accompanied ions. For the second stage, the formed layers are separated (detached) in a 0.3 M solution of citric acid followed by addition, drop by drop, of a diluted solution of ammonium hydroxide solution (20% v/v) until the precipitate disappearance. A solution of pyrazine (0.07 M) is then added under stirring and the formation of the pillared solid is achieved when the solution pH is adjusted to be in the 4–5 range, by adding the appropriate amount of diluted citric acid. The precipitate formed within the mother liqueur is then maintained for 12 h at 60 °C in a sealed flask before the solid fraction separation by centrifugation at room temperature. The obtained product is washed several times with distilled water and then air dried until it had constant weight. From 5 mmol of both the complex anion and the involved metal, and 0.07 mmol of pyrazine, about 100 mg of dried solid were obtained. That amount of dried solid represents a yielding of 40%, 49%, and 58% for Mn, Zn and Cd, respectively. The samples prepared according to that synthetic route were characterized from chemical analyses, EDS, XRD, IR, Raman, UV–Vis, TG, SEM and adsorption data.

EDS spectra were recorded with a Noran analytical system coupled to a SEM microscope from Jeol (Japan). This microscope was also used to obtain the SEM images. The elemental analyses were carried out with a Fisons Elemental Analyzer Model EA1108, using He as carrier/reference gas at a flow rate of 120 mL/min, and a TCD detector. The TG curves were run using a high resolution TA Instrument (Hi-ResTM) thermo-gravimetric analyzer TGA 2950 and instrument control software thermal advantage version 1.1A. The TGA 2950 was used in dynamic rate mode where the heating rate is varied dynamically according to a ramp in response to the derivative of weight change (as derivative increases, heating rate is decreased and vice versa). The heating rates were constrained to be at the 0.001 to 5 K/min range with an instrumental resolution of 5. The furnace purge was nitrogen using flow rates of 100 mL/min. IR spectra were collected by the KBr pressed disk technique using an FT spectrophotometer (Spectrum One from Perkin–Elmer). Raman spectra were collected in the 3500–100 cm^{-1} frequency range, an Almaga XR dispersive Raman spectrometer equipped with an Olympus microscope (BX51) was used to obtain the Raman spectra. An Olympus $\times 50$ objective (N.A. = 0.80) was used both for focusing the laser on the sample and collecting the scattered light in a 180° backscattering configuration. The scattered light was detected by a charge coupled device (CCD)

detector, thermoelectrically cooling to -50°C . The spectrometer used a grating (675 lines/mm) to resolve the scattered radiation and a notch filter to block the Rayleigh light. Raman spectra were accumulated over 25 s with a resolution of $\sim 4 \text{ cm}^{-1}$. The excitation source was 532 nm radiation from a Nd:YVO₄ laser (frequency-doubled) and the incident power at the sample was of $\sim 2.5 \text{ mW}$. UV–Vis spectra were recorded with a Perkin–Elmer spectrometer using the integration sphere method.

The CO_2 and H_2 adsorption data were recorded using an ASAP 2020 analyzer (from Micromeritics). Sample tubes of known weight were loaded with an appropriate amount of sample, $\sim 40 \text{ mg}$, and sealed using TranSeal. Previous to the CO_2 and H_2 adsorption, the samples were degassed on the ASAP analyzer at room temperature until a stable outgas rate below $1 \mu\text{m Hg}$ was obtained. The degassed sample and sample tube were weighed and then transferred back to the analyzer (with the TranSeal to prevent exposure of the sample to air). After volume measurement with He, the degassing was continued for 24 h at 60 °C in the analysis port. Measurements were performed at 75 K in liquid N_2 for H_2 and at 273 K within an ice-water bath for CO_2 .

The XRD powder patterns were recorded in the Bragg–Brentano geometry using $\text{CuK}\alpha$ radiation and a D8 Advance (from

Table 1
Crystallographic data for the refined structures.

Data collection	D8 Advance (from Bruker)	
Diffractometer	Graphite	
Monochromator	$\text{CuK}\alpha = 1.54183$	
Wavelength (Å)	5–90	
2θ range (deg)	0.025	
Step size (deg)	15	
Time per step (s)		
	Zn[Ni(CN) ₄] · 2pyz	Mn[Ni(CN) ₄] · 2pyz
<i>Unit cell</i>		
Space group	Pnc2	Pnc2
Parameter (Å)	$a = 6.8199(2)$ $b = 13.9699(3)$ $c = 7.2927(2)$	$a = 6.7808(2)$ $b = 13.9571(4)$ $c = 7.2607(2)$
V (Å ³)	694.8(1)	687.1(2)
Z	2	2
<i>Refinement</i>		
Number of contributing reflections	318	312
Number of distance constraints	4	4
Number of refined parameters		
Structural parameters	41	41
Profile parameters	10	10
Rexp	2.50	3.28
Rwp	5.82	7.21
RB	4.59	7.35
S	2.32	2.19
	Cd[Ni(CN) ₄] · 2pyz	
<i>Unit cell</i>		
Space group	Pnc2	
Parameter (Å)	$a = 6.9776(2)$ $b = 14.1719(3)$ $c = 7.4717(2)$	
V (Å ³)	738.8(4)	
Z	2	
<i>Refinement</i>		
Number of contributing reflections	334	
Number of distance constraints	4	
Number of refined parameters		
Structural parameters	41	
Profile parameters	10	
Rexp	3.41	
Rwp	9.7	
RB	8.9	
S	2.8	

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