Journal of Solid State Chemistry 181 (2008) 2899–2907

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

# Porous framework of $T_2[Fe(CN)_6]\cdot xH_2O$ with $T=$ Co, Ni, Cu, Zn, and $H_2$ storage

M. Avila [a], L. Reguera [b], J. Rodríguez-Hernández [c], J. Balmaseda [d], E. Reguera [a,c,*]

[a] *Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada-Unidad Legaria, IPN, México, D.F.*
[b] *Facultad de Química, Universidad de La Habana, Cuba*
[c] *Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana, Cuba*
[d] *Departamento de Polímeros, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México, D.F., México*

ARTICLE INFO

*Article history:*
Received 23 May 2008
Accepted 20 July 2008
Available online 30 July 2008

*Keywords:*
Crystal chemistry
Prussian blue
Hydrogen storage
Structural studies

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*-3*m*) 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, $[Fe(CN)_6]$. 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 $H_2$.

## 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 $\pi$ 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 –M–C–N–*T*–N–C–M– sequence [13]. This series of compounds crystallizes with a cubic or pseudo-cubic unit cell, usually in the highly symmetric *Fm*-3*m* 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

---

* Corresponding author at: Instituto de Ciencia y Tecnologia de Materiales, Universidad de La Habana, La Ciudad de La Habana, Cuba. Fax: +53 7 29 6000.
*E-mail address:* ereguera@yahoo.com (E. Reguera).

0022-4596/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2008.07.030

coordination [14]; for Mn and Cd hexacyanometallates (II) a different metals sequence is observed, –M–C–N–*T*…*T*–N–C–M– [15,16], and there are compositions where the N end behaves as a bifurcated ligand coordinating two *T* metals [17]. Within the series $T_2[Fe(CN)_6]\cdot xH_2O$ with $T =$ Mn, Co, Ni, Cu, Zn, Cd; only for Mn and Cd the crystal structure is known [15,16]. For Co, Ni, Cu, and Zn the structure and related properties remain unknown. In this contribution the crystal structures and properties for these four metals are reported, where atypical structures for Co and Zn were also observed. This series of hexacyanoferrates (II) has attracted certain attention as prototype of materials for the hydrogen storage [9], supposing that it has a PB analogues type structure with 50% of vacancy for the building unit, $[Fe(CN)_6]$, and as a consequence, with also 50% of available metal (*T*) coordination sites at the cavities surface to interact with hydrogen molecule once the crystal water is removed. This supposes that the framework is preserved for the anhydrous phase. Our results, based on a detailed structural study, herein discussed, are quite different. For Ni and Cu on the water removal the porous framework collapses. For Co, a structure of stacked layers was observed. Neighboring layers remain linked through a network of hydrogen-bonding interactions between coordinated and weakly bonded waters. For Zn, the porous framework remains stable but with a system of narrow channels and a small free volume.

## 2. Experimental section

The samples to be studied were obtained by mixing aqueous solutions (0.01 M) of the metal chloride (in excess) and ferrocyanic acid ($H_4[Fe(CN)_6]$ prepared *in situ* [18]). The precipitate formed was aged 24 h within the mother liquor, then separated by filtration and washed several times with distilled water and finally air dried until it had a constant weight. The same result was obtained from metal sulfate or nitrate. When these compounds are precipitated from sodium or potassium ferrocyanides, the mixed salts containing Na or K are obtained. The nature of the obtained solids was established from energy-dispersed spectroscopy (EDS) analyses, X-ray diffraction (XRD), and infrared (IR) and Mössbauer data. The degree of hydration and thermal stability of the samples were estimated by using thermogravimetric (TG) curves. The metal atomic ratio found from EDS spectra for the obtained solids, close to 2:1, agrees with the expected formula unit, $T_2[Fe(CN)_6]\cdot xH_2O$.

The TG curves were run under an $N_2$ atmosphere (100 ml min$^{-1}$) using a thermo-balance (TGA 2950 model from TA instruments) operated in the high-resolution mode. IR spectra were collected by the KBr pressed disk technique using an FT spectrophotometer (Spectrum One from Perkin Elmer). The Mössbauer spectra were recorded at room temperature with a constant acceleration spectrometer operated in the transmission mode and a $^{57}Co/Rh$ source. The spectra were fitted by a least-squares minimization algorithm and pseudo-Lorentzian line shape in order to obtain the values for isomer shift ($\delta$), quadrupole splitting ($\Delta$) and linewidth ($\Gamma$). The value of $\delta$ is reported relative to sodium nitroprusside. The XRD powder patterns were recorded in the Bragg–Brentano geometry using Cu$K\alpha$ radiation and an HZG4 diffractometer. All the patterns were collected from 5° to $90°/2\theta$ with a step size of 0.025°. The XRD powder patterns were indexed using DICVOL program [19]. The crystal structures were solved *ab initio* by direct methods using the program SHELXS [20] from extracted intensities according to the Le Bail method [21]. Physical considerations and information from the remaining techniques were used in order to select the appropriate structural models to be refined, and then to check the obtained structure. The structure refinement was then carried out in parallel for all the probable space groups. The structural refinement was performed with the Rietveld method using the FullProf program [22] and the pseudo-Voigt peak shape function. Peak profiles were calculated within 10 times the full width at half maximum (FWHM). The background was modeled by a third-order polynomial.

The $CO_2$ and $H_2$ adsorption isotherms were recorded using ASAP 2010 and 2020 analyzers (from Micromeritics), respectively. Sample tubes of known weight were loaded with 40–50 mg of sample and sealed using TranSeal. Previous to $CO_2$ and $H_2$ adsorption, the samples were degassed on the ASAP analyzer using a heating rate of 1 °C/min and then maintained at the dehydration temperature indicated by the TG curve to obtain a stable outgas rate below 1-μm Hg. The degassed sample and sample tube were weighed and then transferred back to the analyzer with the TranSeal preventing exposure of the sample to air. After volume measurement with He the degassing was continued for 24 h at the dehydration temperature in the sample port. Measurements were performed at 273 K for $CO_2$ using an ice-water bath and at 75 K for $H_2$ using a liquid $N_2$ bath.

## 3. Results and discussion

### 3.1. Hydration degree and thermal stability

Fig. 1 shows the TG curves for the studied series of hexacyanoferrates (II). The smallest hydration degree and the higher thermal stability were observed for Zn. According to the weight loss this compound crystallizes with about 2.3 water molecules per formula unit. Below 50 °C approximately 0.3 water molecules per formula evolves, probably weakly bonded waters. This small amount of weakly bonded waters suggests that this compound has a compact structure. The cavities of porous hexacyanometallates are usually occupied by hydrogen-bonded water molecules [23]. Then, from 160 °C the remaining two water molecules abandon the solid together to form an anhydrous phase that remains stable up to above 350 °C. The relatively high temperature which these two water molecules evolve suggests that they are coordinated. This corresponds to a coordinated water molecule per Zn atom. According to the formula unit there are six

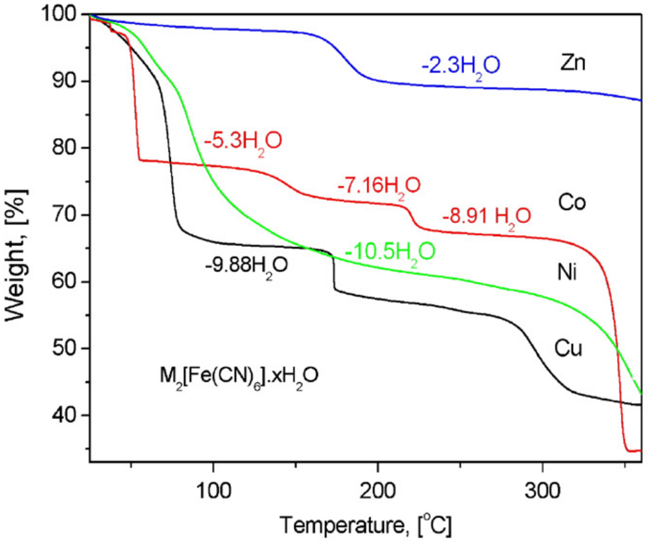

**Fig. 1.** TG curves for the studied series of divalent transition metal hexacyanoferrates (II).