



Hydrothermal recrystallization of transition metal nitroprussides. Formation of the most stable phases



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ABSTRACT

Hydrothermal recrystallization appears to be an appropriate treatment to explore the structural diversity of porous coordination polymers. In this contribution, such a post-synthesis treatment is applied to divalent transition metal nitroprussides, $T[\text{Fe}(\text{CN})_5\text{NO}] \cdot x\text{H}_2\text{O}$ with $T = \text{Mn, Fe, Co, Ni, Cu, Zn, Cd}$. This family of compounds forms an interesting series of nanoporous coordination polymers with a wide structural diversity, related to the synthesis route used and the solid hydration degree (x). The effect of a hydrothermal recrystallization of previously prepared fine powders using the precipitation method, on their crystal structure and related properties is herein discussed. In this series of coordination polymers, for Fe, Co, Ni the precipitated powders are obtained as cubic phase, with a high porosity related to presence of systematic vacancies for building unit $[\text{Fe}(\text{CN})_5\text{NO}]$. For Fe and Co a structural transition, from cubic to orthorhombic, was observed, which is associated to formation of a most compact structure. The crystal structure for the new orthorhombic phases was refined from the collected powder HR-XRD patterns. For Ni, the cubic phase remains stable even for large heating time, which is ascribed to the high polarizing power of this metal. The high porosity for the cubic phase allows an easy accommodation for the local deformations around the Ni atom coordination sphere. The structural information from XRD was complemented with CO_2 and H_2 adsorption and TG data, IR and UV–vis spectra, and magnetic measurements. The magnetic data, through the presence of spin-orbit coupling for Fe and Co in the two phases, provide fine details on the coordination environment for the metal linked at the N ends of the CN group.

1. Introduction

In a recent study on zeolite-like hexacyanometallates, we have observed that the recrystallization under hydrothermal conditions of powder obtained by the precipitation method, results in the formation of materials with improved crystallinity [1]. This treatment also the structural diversity of these materials [1]. In this contribution, such a post-synthesis treatment is applied to fine powders of transition metal nitroprussides, $T[\text{Fe}(\text{CN})_5\text{NO}] \cdot n\text{H}_2\text{O}$, with $T = \text{Mn, Fe, Co, Ni, Cu, Zn, Cd}$. This series of porous coordination polymers is formed by the assembling of the pseudo-octahedral anionic block, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, through monovalent or divalent transition metal ions (T). For the case of metal ions of higher valence, the formed solid is soluble in aqueous media and unstable under UV–vis irradiation. The coordination bond formation, during their synthesis, takes place through the N end of the CN group. The nitrosyl group (NO) remains strongly linked to the Fe

atom through the N end while its O atom is unable to form a coordination bond. The porous framework of this series of coordination polymers is closely related to the bonding feature for the NO ligand [2].

This family of coordination polymers has received certain attention for the separation and storage of small molecules [3], including hydrogen [4–6]. The pore topology and free volume of these materials depend on the orientation on the NO group in the resulting 3D framework [2,5]. For divalent transition metals, at the pore surface, the assembling metal ion is found with an open coordination sphere. In the as-synthesized solid, the available coordination sites are occupied by water molecules, which, at the same time, stabilize additional water molecules through hydrogen bonding interactions. The number of these last water molecules and the orientation of the NO group in the 3D framework determine the material structure (phase). This explains that for this series of coordination polymers, certain structural diversity is observed [2,7].

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For Mn^{2+} , Fe^{2+} , Zn^{2+} , and Cd^{2+} , the crystal growth using slow diffusion method of both anion and cation, results in the formation of trihydrates, which crystallize with a monoclinic unit cell in the $P21/n$ space group [8–10]. When the crystals are air dried, a weakly bonded water molecule evolves and a dihydrate is obtained with a more symmetric unit cell, orthorhombic in the $Pnma$ space group [7]. When the samples are prepared by the precipitation method, the orthorhombic dihydrate is directly obtained for Mn^{2+} , Zn^{2+} and Cd^{2+} [7], but for Zn^{2+} a hexagonal modification (R-3 space group) can also be formed [11]. For Cu^{2+} , the powder crystallizes as a layered dihydrate with an orthorhombic unit cell in the $Amm2$ space group [12]. For Fe^{2+} , Co^{2+} and Ni^{2+} the powders are cubic phases ($Fm-3m$ space group) with relatively large free volume related to presence of systematic vacancies for both, the building block, $[\text{Fe}(\text{CN})_5\text{NO}]$ and the metal (T) [2,4,6,7]. The structure for these last three metals is formed by the accommodation of the building blocks $[\text{Fe}(\text{CN})_5\text{NO}]$ in such a way that six unlinked NO ligands are oriented toward a metal (T) site, which remains vacant. This results in the formation of a hydrophobic cavity of about 4 Å. To preserve the charge neutrality, an equal number of vacancies for the building block, $[\text{Fe}(\text{CN})_5\text{NO}]$, must be present in the resulting 3D framework. These last vacancies generate a system of cavities of about 9 Å diameter, which are communicated by windows of about 4 Å (transversal cross section). These windows are delimited by neighboring $\cdots\text{T}-\text{N}-\text{C}-\text{Fe} \cdots$ chains and the mentioned hydrophobic cavities [5].

Considering the above-mentioned structural features for transition metal nitroprussides, powders obtained by the precipitation method were submitted to hydrothermal recrystallization and then characterized according to their crystal structure and related physical and functional properties. Without exception, an improvement for the crystalline order was observed for all the compositions. For Fe^{2+} and Co^{2+} , two new phases were formed, with an orthorhombic structure. For Ni^{2+} the cubic phase appears as the most stable one, independently of its treatment under different conditions. The crystal structure for the orthorhombic phase of Fe^{2+} and Co^{2+} was refined from high-resolution X-ray diffraction (HR-XRD) powder patterns using the Rietveld method. IR, UV–vis spectra and the magnetic data provided complementary structural information. The porous framework accessibility was evaluated from CO_2 and H_2 adsorption isotherms. Related to the small windows size, the porous frameworks for the materials under study appear to be inaccessible for N_2 .

2. Experimental

The powders to be recrystallized were obtained from diluted (0.01 M) aqueous solutions of sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, and of the corresponding sulfate for the involved metals. The formed precipitate was aged within the mother liqueur in the darkness for two weeks and then separated by centrifugation and washed several times with bi-distilled water to remove all the accompanied species. The formed pasty solid was dried in air until it had constant weight. The obtained powders were then recrystallized in water using sealed Teflon lined reactors. The reactors were heated to 140 °C for one hour, then maintained for a week at 110 °C and finally cooled down to room temperature, maintaining the reactor within the used furnace. The nature and purity of the initial powder and its recrystallization product as metal nitroprusside were established from chemical analysis, IR spectra and XRD powder patterns. Details on XRD data acquisition and processing are available from [Supplementary Information](#). The hydration degree was determined from the recorded thermogravimetric (TG) curves.

The XRD powder patterns used for the structural study were recorded with a conventional diffractometer (D8 Advance from Bruker) operated in the high-resolution (HR) mode with Bragg-Brentano geometry and $\text{CuK}\alpha 1$ radiation. Some XRD patterns were recorded with synchrotron radiation using the LNLS facility at different temperatures on cooling in order to discard possible structural transi-

tion at low temperature. The structural refinement was performed with the Rietveld method using the FullProf program [13] and pseudo-Voigt peak shape function. Peak profiles were calculated within ten times the full width at half maximum (FWHM). The [Supplementary Information](#) file provides details on the XRD data recording and on the crystal structure refinement. The interatomic C–N, N–O and Fe–C distances were constrained to take values within certain limits considering previous structural studies for the series of coordination polymers under study [8–10,14].

IR spectra were recorded with both, KBr pressed disk and attenuated reflectance techniques using a Perkin Elmer spectrophotometer. The TG curves were obtained in a HR equipment under an N_2 atmosphere. The H_2 and CO_2 adsorption isotherms were collected at 75 and 273 K with an ASAP 2050 apparatus (from Micromeritics). Previous to CO_2 and H_2 adsorption, the samples were degassed on the analyzer at a heating rate of 5 °C/min up to the dehydration temperature indicated by the TG curve. The degassing process is maintained until a stable outgas rate of 1 $\mu\text{m Hg}$. This process usually requires 24 h of degassing. 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 80 °C in the sample port.

The magnetic data in the 2–300 K temperature range were collected using a MPMS–5 SQUID magnetometer operated at 50 Oe of applied field. The effective magnetic moment, μ_{eff} , was calculated according to $\mu_{\text{eff}} = 2.828 \sqrt{\chi T}$ and considering the diamagnetic correction [15].

3. Results and discussion

3.1. On the nature of the recrystallized solids

According to the recorded XRD powder patterns, for T = Mn^{2+} , Fe^{2+} , Co^{2+} , Zn^{2+} and Cd^{2+} , the recrystallized powders result orthorhombic dihydrates, in the $Pnma$ space group. Except for Fe and Co (see [Supplementary Information](#)), these results are in accordance with previous reports [7]. For Ni^{2+} and Cu^{2+} , the cubic ($Fm-3m$) and layered structure (orthorhombic, $Amm2$) phases, respectively, remain inalterable, except certain improvement in their crystallinity. The occurrence of a structural transition, from cubic to orthorhombic phases for Fe^{2+} and Co^{2+} is probably the most interesting finding of this study. This phase transition, from cubic to orthorhombic, is favored by the formation of a most compact structure. This suggests that under hydrothermal recrystallization, the structure of highest stability, with the smaller free volume, is formed. For Co^{2+} , crystals grown through the slow diffusion method during months, correspond to the cubic phase [16]. With Fe^{2+} , the formed precipitate remains as the cubic phase even after a year of aging within the mother liqueur [2,7]. For this metal (Fe^{2+}), the formation of the orthorhombic phase under hydrothermal treatment of powders of cubic structure was an unexpected result. An analogue behavior was expected for Ni^{2+} , but not observed; always its cubic phase is obtained. In order to understand the nature of such behavior and to explore a possible structural transition also for Ni, mixed compositions containing Ni and Co were prepared and studied. Transition metal nitroprussides form solid solutions [6]. The presence of Co ion in structural positions for Ni^{2+} could induce a structural transition from cubic to orthorhombic phase also for this last metal. This hypothesis supported the study of mixed compositions of these two metals in atomic ratios of 1:1, 1:2 and 1:4. For the three mixtures, the cubic phase was formed during the powders preparation by the precipitation method and then preserved during the hydrothermal heating at different temperatures and for times of heating up to three weeks. According to the variation of the cell edge with the amount of Co atoms in both, the precipitated and recrystallized powders, a true solid solution was formed. A plot of the cell edge versus the sample composition shows a linear dependence ([Fig. 1](#)),

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