# Structure of Porous Copper Prussian Blue Analogues: Nature of Their High H$_2$ Storage Capacity

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Within porous Prussian blue to copper the highest H$_2$ storage capacity is observed. Such behavior finds explanation in the crystal structure for Cu$_3$[M(CN)$_6$]$_2$ with M = Fe, Co, Ir. The crystal structure of Prussian blue analogues is usually solved and refined with a cubic unit cell in the *Fm$\bar{3}$m* space group, which corresponds to a random vacancy distribution. However, a careful evaluation of X-ray diffraction powder patterns of copper-containing compositions reveals a deviation from that structural model. The crystal structure for the considered series of copper hexacyanometallates(III) was found to be also cubic but in the *Pm$\bar{3}$m* space group related to a nonrandom vacancy distribution. To this model 50% of vacancies for the building block, [M(CN)$_6$], corresponds, which is quite different from the value of 33.3% in the *Fm$\bar{3}$m* structural model. Mössbauer spectra and high pressure H$_2$ adsorption isotherms support the assignment of the *Pm$\bar{3}$m* space group for the studied series of copper Prussian blue analogues. The implications of a nonrandom vacancy distribution on the physical properties of these materials are discussed.

## 1. Introduction

Transition metal hexacyanometallates have received renewed interest in the past two decades, mainly due to their role as prototypes of molecular magnets[1] and more recently in studies related to H$_2$ storage.[2–11] The CN ligand behaves as a bridging group linking neighboring metal centers. Its ability to subtract electrons from the metal linked at the C end, through a $\pi$-back-donation mechanism, and to locate the removed charge on the N end, explains the magnetic properties of hexacyanometallates. The CN group allows the interaction between the electron clouds of neighboring metal centers distant about 5 Å and cooperative magnetic interaction results.

When the CN group coordinates only two metal centers (M, T) and the −T−N≡C−M−C≡N−T− chains are practically linear, a three-dimensional framework of cubic symmetry is formed. In such a structure the two metal centers have octahedral coordination and the compounds are known as Prussian blue (PB) analogues. Many PB analogues have a porous framework related to the existence of systematic vacancies of the building unit, the octahedral block [M(CN)$_6$]. At the surface of a cavity created by a vacancy, six metal centers with an incomplete coordination sphere are found. In the as-synthesized material, these coordination sites are occupied by water molecules. The cavity filling is completed by additional water molecules hydrogen bonded to the coordinated ones. Both weakly bonded and coordinated water molecules can be removed by moderate heating, usually below 100 °C, preserving the solid framework.[2,9] The resulting free space is appropriate for small molecule storage, among them H$_2$.[2–6,9,11] The availability on the surface of the cavity of metal centers with an open coordination sphere has stimulated the evaluation of this family of porous solids for H$_2$ storage.[2–6,9,11] Porous solids with exposed transition metal sites at the surface of cavities are being intensively studied for hydrogen storage.[12–18]

Prussian blue analogues are commonly obtained as fine powders, and their crystal structure must be solved and refined from X-ray diffraction (XRD) powder patterns. The crystal structures of PB analogues are usually described using a structural model based on a cubic unit cell in the *Fm$\bar{3}$m* space group.[2–6,19,20] This model supposes a random distribution for the vacancies within the framework.[19] For copper a deviation from that structural model has been observed. Its XRD powder pattern belongs to the *Pm$\bar{3}$m* space group,[9,21] but the corresponding crystal structure has not been solved and reported. From a structural study using neutron diffraction of PB samples, Fe$_4$[FeCN)$_6$]$_3$·*y*H$_2$O, recrystallized in concentrated HCl solution, the pattern indexing in the *Pm$\bar{3}$m* space group has been reported.[22] Within divalent transition metal hexacyanocobaltates(III), the highest H$_2$ storage capacity has been observed for copper,[2,4] a behavior also observed for the iridium series,[9] which could be related to the crystal structure adopted by the copper analogues.

In this contribution the refined crystal structures for three copper hexacyanometallates(III) (Fe, Co, Ir) are discussed. The derived structural model for copper PB analogues is supported by Mössbauer spectra recorded for mixed Cu$_{3-x}$Fe$_x$[Co(CN)$_6$]$_2$·*y*H$_2$O samples and also by high pressure H$_2$ adsorption isotherms. The implications of a nonrandom vacancy distribution on the physical properties of these materials are discussed.

## 2. Experimental Section

The samples to be studied, Cu$_3$[M(CN)$_6$]$_2$·*y*H$_2$O, were obtained mixing 0.01 M aqueous solutions of copper(2+) sulfate and of the involved potassium hexacyanometallates (M = Fe,

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