For Copper: A Unique Behaviour within Prussian Blue Analogues

Reguera, E.[1] and Rodriguez-Hernandez, J.[1]

[1]Universidad de la Havana - C. Havana Havan Cuba

INTRODUCTION

In Prussian blue (PB) analogues the 3D framework is formed by practically linear T-N-C-M-C-N-T- chains, and the solids crystallize with a cubic unit cell where the metal centers (M, T) are found with octahedral coordination. In that framework the T-N-C-M-C-N-T chain length coincides with the unit cell edge (a). Within PB analogues for copper deviation from the usual regularities in the materials properties are observed, among them: the smallest cell edge, an extremely low dehydration temperature, the largest metal-metal electron cloud overlapping, the highest affinity for the H_2 adsorption, and a well ordered system of vacancies [1–4]. Within divalent transition metals octahedral compounds for the copper ion a non cubic structure due to the Jahn-Teller effect for the copper (2+) ion is usually observed. However, with the exception of M = Pt, which crystallizes with a tetragonal unit cell, the remaining copper PB analogues show cubic structure. All these features stimulated a detailed structural study in that series of copper compounds from magnetic measurements, and HR-XRD, Mössbauer, IR, TG and H_2 adsorption data. The obtained results are herein summarized.

EXPERIMENT

The following compositions involving copper were prepared using previously reported procedures [1–4]: $Cu_3[M(CN)_6]_2.yH_2O$ with M = Fe^{III}, Co^{III}, Ir^{III}; $Cu_{3-x}Mn_x[Co(CN)_6]_2.yH_2O$ with x = 0, 0.7, 1.4, 3; and $Cu[Pt(CN)_6].yH_2O$. HR-XRD data in the 12-300 K temperature range were recorded at XPD-10B beam line of the LNLS synchrotron radiation facility. Details on the remaining characterization techniques used are provided elsewhere [1–4]. The crystal structures refinement was carried out using the Rietveld method.

RESULTS AND DISCUSSION

The series $Cu_3[M(CN)_6]_2.yH_2O$ and $Cu_{3-x}Mn_x[Co(CN)_6]_2.yH_2O$ form porous solids with a cavity size of about 8.5 Å diameter, due to the presence of systematic vacancies for the building block, $[M(CN)_6]$. At the cavity surface six T metal centers with an unsaturated coordination sphere, in the anhydrous phase, are available. For the mixed series the variation of the unit cell edge (a) shows a positive linear correlation with the amount of Mn atoms (x) in the formula unit [4]. This behavior corresponds to a solid solution formation and this indicates that the two
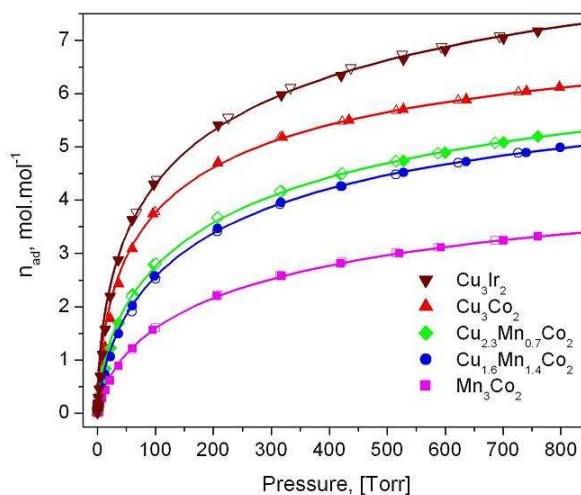

FIG. 1: Hydrogen adsorption isotherms at 75 K for the series $Cu_{3-x}Mn_x[Co(CN)_6]_2$ and $Cu_3[Ir(CN)_6]_2$
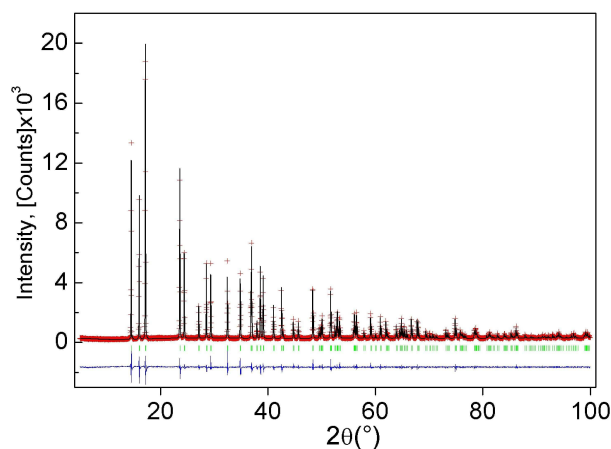

FIG. 2: Experimental XRD powder patterns and the calculated and difference profiles obtained from the Rietveld refinement of the crystal structure for $Cu[Pt(CN)_6].yH_2O$

metals (Cu, Mn) are randomly distributed on the cavity surface. The unique behavior for copper within porous PB analogues is attributed to the ability of the copper atom located at the cavity surface to receive charge from the CN ligand in order to reach an electronic configuration close to $3d^{10}$. Such ability is complemented by the trend of the CN ligand to donate charge to the metal through the 5σ orbital which has certain anti-bonding character [1]. These combined effects leads to a pronounced overlapping between M and Cu atoms electron clouds and this explains the high