Crystal structures of cubic nitroprussides: M[Fe(CN)$_5$NO]$\cdot x$H$_2$O(M =Fe,Co,Ni). Obtaining structural information from the background

A. Gómez
Department of Physics, University of Guelph, Guelph, Ontario NIG 2W1, Canada

J. Rodríguez-Hernández
Institute of Materials Science and Technology, 10400 Havana University, Havana, Cuba

E. Reguera[a]
Institute of Materials Science and Technology, 10400 Havana University, Havana, Cuba and Center of Applied Science and Technology of IPN, CICATA-Unidad Legaria, Mexico, D. F.

A new structural model is proposed for cubic nitroprussides and the crystal structure for the complex salts of Fe(2+), Co(2+), and Ni(2+) refined in that model. In cubic nitroprussides the building unit, [Fe(CN)$_5$NO]$^{2-}$, and the assembling metal (M=Fe^{2+},Co^{2+},Ni^{2+}), have $\frac{3}{4}$ occupancy with three formula units per cell (Z=3). This leads to certain structural disorder and to different local environments for the outer metal. The crystallographic results are supported by the Mössbauer and infrared data. The XRD powder patterns, index in a cubic cell (*Fm*3*m* space group), show a sinuous background because of diffuse scattering from positional disorder of the metal centers. Because of this, the crystal structures were refined allowing the metal centers to move from the (0,0,0) and (0,0,1/2) positions (away from positional symmetry restrictions). The refinement under these conditions leads to excellent agreement factors (R_{wp}, R_p, S), good pattern background fitting, and produced a refined structural model consistent with the crystal chemistry of nitroprussides. The studied materials are obtained as hydrates. On heating, the crystal water evolves, and below 100 °C an anhydrous phase is obtained, preserving the framework of the original hydrates. The loss of the crystal water leads to cell contraction that represents around 2% of cell volume reduction. On cooling down from room temperature to 77 and 12 K, a slight expansion for the -M-N≡C-Fe-C ≡N-M- chain length is observed, suggesting that at low temperature and reduction in the metals charge delocalization on the CN bridges takes place. For M=Fe and Co the crystal structure was also refined for the anhydrous phase at 12, 77, and 300 K. © *2007 International Centre for Diffraction Data.* [DOI: 10.1154/1.2700265]

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I. INTRODUCTION

Nitroprussides are salts of the pentacyanonitrosylferrate anion, [Fe(CN)$_5$NO]$^{2-}$. For divalent transition metals, insoluble salts, as fine powders, are obtained. Two properties have attracted the attention on these molecular materials in the past few years. Their nanoporous framework can accommodate small molecules (Balmaseda *et al.*, 2003; Reguera *et al.*, 2004; Culp *et al.*, 2006) and the light induced metal (Fe) to ligand (NO) charge transfer [Gu *et al.*, 1997; Gütlich *et al.*, 2001 (and references therein)]. This last effect has been taken as prototypical for switching on/off molecular devices (Gu *et al.*, 1996). These properties suggest the convenience of a proper description of their crystal structure. Fortunately it has been carried out for practically all the divalent transition metals (Mullica *et al.*, 1989, 1990, 1991a, b, 1992, 1993; Benavante *et al.*, 1997; Gómez *et al.*, 2001, 2004; Reguera *et al.*, 1996; Rodríguez-Hernández *et al.*, 2005), except for the cubic phases of Fe(2+) and Ni(2+). For Co(2+) the reported structure (Mullica *et al.*, 1991b) must be reconsidered.

The building unit, [Fe(CN)$_5$NO]$^{2-}$, of these materials is relatively small and the metals remain linked through a strong ligand, the CN group, forming a practically rigid block. These are ideal features for a successful crystal structure refinement using the Rietveld method. The building unit is a pseudo-octahedral block with five coordination sites (the N ends of the CN groups). This introduces certain particularity to the obtained 3D cubic structure when a metal like Fe^{2+}, Co^{2+}, or Ni^{2+} is used to assemble neighboring building blocks. In such a 3D network systematic vacancies of both the building unit and the metal appear. This leads to certain structural disorder and to the appearance of a sinuous contribution to the XRD powder pattern background. This sinuous contribution can be attributed to the metal centers out of the restricted symmetry positions. Because of this, the pattern background could be used to obtain a refined structural model close to the true material crystal structure. The aim of this contribution is the crystal structure refinement for the cubic hydrated phases of Fe^{2+}, Co^{2+}, and Ni^{2+} nitroprussides, considering the diffuse component of the pattern background in the refinement process. For iron and cobalt the crystal structures of the anhydrous phases at 12, 77, and 300 K were also refined.

[a]Author to whom correspondence should be addressed. Electronic mail: ereguera@yahoo.com