

# Crystal structure of orthorhombic ferrous nitroprusside: $\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$

J. Rodríguez-Hernández and E. Reguera<sup>a)</sup>

*Institute of Materials and Reagents, University of Havana, San Lazaro and L, 10400 Havana, Cuba*

A. Gómez

*Department of Physics, University of Guelph, MacNaughton Building, Gordon Street, Guelph, Ontario, Canada*

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Ferrous nitroprusside can be obtained in three structural modifications: two different unstable phases, monoclinic trihydrate and cubic pentahydrate, and the stable one, an orthorhombic dihydrate. This contribution reports the crystal structure of the last one. Cell parameters are:  $a = 13.9734$  (2),  $b = 7.4274$  (1), and  $c = 10.4697$  (1) Å; with four formula units per cell ( $Z=4$ ). The crystal structure was refined from the corresponding XRD powder pattern using the Rietveld method. Final agreement factors of the refinement process were  $R_{wp}=8.46$ ,  $R_p=6.54$ , and  $S=1.38$ . The crystal structure is formed by a tridimensional assembling of the  $[\text{Fe}(\text{CN})_5\text{NO}]$  molecular block through iron atoms bounded at the N end of the CN ligands. The NO group remains unlinked at its O atom. The octahedral coordination of the assembling metal is completed with a coordinated water molecule which stabilizes a second water through a strong hydrogen bond interaction. The tridimensional structure appears as piled up rippled sheets leading to a system of interconnected small cavities which increase their available volume on the material dehydration. This complex loses its crystal water below 100 °C and then remains stable up to above 160 °C when the decomposition process begins with the loss of the NO ligand. © 2005 International Centre for Diffraction Data. [DOI: 10.1154/1.1872874]

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## I. INTRODUCTION

In nitroprussides there is an empty low-energy antibonding orbital on the NO group which is accessible through light-induced charge transfer from the iron atom. This leads to the existence of long-living metastable electronic states which support potential applications of these complexes as holographic information storage materials (Haussühl *et al.*, 1995; Imlau *et al.*, 1999; Gutlich *et al.*, 2001) and as optically switchable molecular communication devices (Gu *et al.*, 1996; Gu *et al.*, 1997). In addition, metal nitroprussides show properties as molecular sieves with a tunable system of channels, which allows the separation of molecules of small size (Boxhoorn *et al.*, 1985; Balmaseda *et al.*, 2003). These and others potential applications of these complexes support the interest of their structural study.

Divalent transition metal nitroprussides show a pronounced polymorphic character (Balmaseda *et al.*, 2003; Reguera *et al.*, 1996). In the case of iron, three different phases have been identified (Reguera *et al.*, 1996; Mullica *et al.*, 1991): slowly grown crystals result in a monoclinic trihydrate, which forms an orthorhombic dihydrate on air drying. Mixing aqueous solutions of  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  and  $\text{Fe}^{2+}$  causes a cubic pentahydrate to form. On prolonged aging (at least three years) this cubic phase transforms into the orthorhombic dihydrate, which is the stable phase of this complex (Reguera *et al.*, 1996).

The crystal structure has been resolved for the monoclinic phase (Mullica *et al.*, 1991) but not for the orthorhombic one, which is reported in this contribution. Since the monoclinic single crystals usually break during the drying process (Gomez *et al.*, 2001), the structural refinement was carried out using the Rietveld method. The reported structure for the manganese analog (Benavente *et al.*, 1997) was used as the structural model to be refined. The X-ray powder diffraction (XRD) data were complemented with information from thermogravimetric analysis (TGA) and Mössbauer and IR spectroscopies. The structural study of the cubic polymorph is now in progress.

## II. EXPERIMENTAL

The samples to be studied were obtained from the parent monoclinic and cubic modifications. Single crystals of ferrous nitroprusside were grown for three months using the slow diffusion tube method (Mullica *et al.*, 1990). Upon dehydration, these crystals became brittle and the obtained fine powder was found to be orthorhombic (space group  $Pnma$ ). The same orthorhombic phase was also obtained aging the cubic precipitate formed mixing aqueous solutions containing  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  and  $\text{Fe}^{2+}$  ions (Reguera *et al.*, 1996). The nature of these samples was established through X-ray energy-dispersed (EDS), IR and Mössbauer spectroscopies. Hydration degree was determined by thermogravimetric analysis (TGA).

IR spectra were taken in an ATTI Mattson (Genesis Series) FTIR spectrophotometer using the KBr pressed disk

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: edilso@fisica.uh.cu