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# The structure of two orthorhombic nitroprussides: $\text{Cd}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ and $\text{Zn}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$

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## Abstract

When zinc and cadmium nitroprussides, obtained as powders or single-crystals samples, are aged in air they lose crystallization water and change their crystalline structure. In the stable form these two complexes are orthorhombic dihydrates with four molecules in the unit cell. In the aging process the crystals become brittle producing a polycrystalline material. The crystalline structure of these two complexes (orthorhombic dihydrates) was refined from their XRD powder patterns using the Rietveld method. As the starting model in the refining process the reported orthorhombic structure of copper nitroprusside (dihydrate) was used. The main changes in the dehydration process associated with the structural transformation take place in the coordination sphere of the outer cation (Cd or Zn). © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Nitroprusside; Rietveld method; Crystal structure; Powder diffraction; Mössbauer spectra; Pentacyanide

## 1. Introduction

Nitrosylpentacyanoferrates, commonly known as nitroprussides, are members of the polycyanide metal complexes. This family of complexes, mainly hexacyanides, has been widely studied in connection with their properties as molecular sieves, cation exchangers, radionuclide sorbents [1,2] and to carry out some catalytic reactions [3,4]. Within hexacyanides, channels are formed by systematic  $[\text{M}^N(\text{CN})_6]^{(6-N)-}$  vacancies in the structural array. However, in the case of many nitroprussides the complex possess no vacancies and the channels are mainly due to an unbridged nitrosyl group [5]. Their channels are significantly smaller than those observed in hexacyanides, offering a high selectivity during the separation of small molecules [6]. From this point of view, a detailed structural study of nitroprussides is a primary task for their potential applications.

Insoluble metal nitroprussides,  $\text{M}[\text{Fe}(\text{CN})_5\text{NO}] \cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ ) can be obtained as polycrystalline powders mixing aqueous solutions of the ions  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  and  $\text{M}^{2+}$ , or as single crystals through a slowly grown crystal process from the same solutions. It must be noted that their crystalline structures and hydration degrees depend on the preparation method. However, when both polycrystalline and single-crystal samples are aged in air at room temperature, they adopt, with the exception of the copper complex, the same crystal structure, which is different to that of the parent phase. In a previous paper we have discussed these phase transformations of insoluble metal nitroprussides, reporting the end (stable) phases but without a detailed description of their crystalline structure [7]. In principle, the structural refinement in these stable phases could be carried out by the XRD single-crystal method using dehydrated single-crystal samples. However, this possibility is hindered since on dehydration the single crystals become brittle, producing a polycrystalline material. An alternative is to carry out the structural refinement from the XRD powder pattern using the Rietveld method [8]. As starting values of the

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