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Unique coordination in metal nitroprussides: The structure of $Cu[Fe(CN)_5NO]\cdot 2H_2O$ and $Cu[Fe(CN)_5NO]$

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The structures of copper pentacyanonitrosylferrate dihydrate, $Cu[Fe(CN)_5NO]\cdot 2H_2O$, and anhydrous, $Cu[Fe(CN)_5NO]$, have been determined from their XRD powder patterns and refined using the Rietveld method. The dihydrate structure was solved by direct methods and the anhydrous one was elucidated by chemical intuition. $Cu[Fe(CN)_5NO]\cdot 2H_2O$ is orthorhombic, space group Amm2 (38) and Z = 2. In this structure the iron is coordinated to five CN and a NO ligand, while the copper atom is coordinated, in a unique fashion, to four equatorial CN groups at N ends and two water molecules. $Cu[Fe(CN)_5NO]$ is tetragonal, space group I4 mm (107) and $Z = 2$. This structure is obtained from the dehydration of the orthorhombic one; reordering allows the Cu atom to coordinate not only to the four equatorial cyanides but also to the axial cyanide. The coordination of the iron atom remains as in the orthorhombic structure. Agreement factor obtained from the final refinement were as follows: $R_{wp} = 5.10$ and $R_B = 4.57$ for the orthorhombic structure and $R_{wp} = 6.52$ and $R_B = 7.82$ for the tetragonal one. These crystal structures are also supported by IR and Mössbauer spectroscopic data and thermogravimetry.

KEY WORDS: Copper nitroprussides; copper pentacyanonitrosylferrates; powder diffraction; crystal structure determination; Mössbauer.

Introduction

In a previous paper[1] we carried out a comprehensive study on insoluble metal nitroprussides; stable phases for Mn, Fe, Co, Ni, Cu, Zn and Cd nitroprussides were obtained and characterized. Copper nitroprusside (CuNp), when obtained by precipitation method, presents a unique structure, which has not been observed in other metal nitroprussides. Though studied for 30 years, no consensus has been reached about the CuNp structure, not even about its crystal system.

The first study on anhydrous CuNp was conducted by Ayers and Wagoner,[2] who assigned a cubic cell (a = 7.88 Å) to the observed X-ray diffraction pattern. In 1972, Inoue *et al.*[3] described the CuNp dihydrate structure as tetragonal with cell parameters: a = 10.35 Å and c = 9.80 Å while Brown, in 1975,[4] found two tetragonal phases for CuNp (a = 10.03 Å, c = 10.88 Å; and a = 10.05 Å, c = 10.38 Å), but without specifying the hydration degree. Gentil *et al.*[5] obtained CuNp dihydrate and assigned a tetragonal cell (a = 10.05 Å, c = 10.48 Å) to this compound; however, they failed to index its dehydrated form. In recent years,

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