

Crystal structures of three anhydrous nitroprussides: $M[\text{Fe}(\text{CN})_5\text{NO}]$ ($M=\text{Mn}, \text{Zn}, \text{Cd}$)

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(Received 14 June 2006; accepted 27 December 2006)

The crystal structures of Mn, Zn, and Cd nitroprussides in their anhydrous state, $M[\text{Fe}(\text{CN})_5\text{NO}]$ ($M=\text{Mn}, \text{Zn}, \text{Cd}$), were refined from XRD powder patterns using the Rietveld method. These compounds have a porous framework useful for adsorption and storage of small molecules. Water crystallization can be removed by heating below 100 °C without disrupting the 3D network by introducing certain structural modification mainly around the M site (Mn, Zn, Cd). For $M=\text{Mn}$ and Cd, the compounds were found to be orthorhombic with space group $Pnma$ [Mn: $a=13.7844(1)$, $b=7.3750(2)$, $c=10.9470(2)$ Å, $V=1112.8(1)$ Å³, $Z=4$; Cd: $a=13.9566(3)$, $b=7.5040(4)$, $c=11.0230(2)$ Å, $V=1154.4(1)$ Å³, $Z=4$]. Anhydrous zinc nitroprusside crystallizes in rhombohedral with space group $R\bar{3}$ [$a=b=19.2525(1)$, $c=17.7107(2)$ Å, $\gamma=120.0^\circ$, $V=5685.1(1)$ Å³, $Z=18$]. When exposed to humid air, these anhydrous compounds become hydrated. The XRD powder patterns were recorded under vacuum on samples dehydrated *in situ*. The structural information from XRD was complemented with thermo-gravimetric, infrared, and Mössbauer data. © 2007 International Centre for Diffraction Data. [DOI: 10.1154/1.2434787]

Key words: nitroprusside, porous material, Rietveld, crystal structure, Prussian blue analogues

I. INTRODUCTION

Divalent transition metal nitroprussides form an interesting family of molecular materials. The NO group has π -anti-bonding orbitals at the N end of relatively low energy and in an appropriate disposition to accept electrons from iron t_{2g} orbitals. This allows the metal-to-ligand charge transfer in nitroprussides by the sample illumination with radiation of an appropriate wavelength. Such photo-induced metal-to-ligand charge transfer generates excited states, which have been studied in order to explore the potential applications of these materials for holographic information storage (Gütlich *et al.*, 2001) and also for optically switchable molecular communication devices (Gu *et al.*, 1997). These features are closely related to the nature of the NO group. The NO ligand remains unbounded at the O end, leaving a small space that “absorbs” the variation in the N-O distance during the metal-ligand electron transfer. However, our main motivation for the crystal structure resolution of the anhydrous phases of nitroprussides is related to their open channel porous framework. Water crystallization (coordinated and zeolitic) can be removed under moderate heating without disrupting the framework, and the free space in the structure becomes accessible for adsorption and storage of small molecules (Balmaseda *et al.*, 2003). In this way, nitroprussides are among the most efficient H₂ sorbents among porous coordination polymers reported to date (Culp *et al.*, 2006).

The studied materials result from the 3D assembling of a molecular block, the pentacyanonitrosylferrate(II) anion $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, through divalent transition metals (M) linked at the N end of the CN groups. The resulting materials have the formula unit $M[\text{Fe}(\text{CN})_5\text{NO}] \cdot x\text{H}_2\text{O}$. This family of coordination compounds shows a pronounced polymorphism related to the different ways to accommodate the pseudo-octahedral block to form a 3D framework, and also to the hydration degree of the obtained solid (Reguera *et al.*, 1996). In the studied nitroprussides, the water crystallization always appears associated to the M metal, as coordinated water molecules or as zeolitic waters stabilized through hydrogen bonding interactions with the coordinated ones. For Mn, Cd, and Zn, the crystals preserved within the mother liquor are trihydrates, monoclinic $P2_1/n$ for Mn and Cd (Mullica *et al.*, 1990) and rhombohedral $R\bar{3}$ on a hexagonal lattice for Zn (Mullica *et al.*, 1989). When these trihydrates are aged in a dry atmosphere, a water molecule per formula unit is lost and the resulting dihydrates are found to be orthorhombic $Pnma$ (Reguera *et al.*, 1996; Gómez *et al.*, 2001).

In this paper the crystal structures for the anhydrous phases of Mn, Zn, and Cd nitroprussides are reported. The structural study, carried out from XRD powder patterns recorded in vacuum on samples dehydrated *in situ*, was complemented with thermo-gravimetric (TG), infrared (IR), and Mössbauer data.

II. EXPERIMENTAL

The studied samples were obtained by mixing 0.01 M aqueous solutions of sodium nitroprusside and Mn(2+),

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