



Full paper/Mémoire

Three structural modifications in the series of layered solids $T(H_2O)_2[Ni(CN)_4] \cdot xH_2O$ with $T = Mn, Co, Ni$: Their nature and crystal structures

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ABSTRACT

In the studied series of layered solids, the available coordination sites at T metal centers are occupied by water molecules which serve to stabilize additional water molecules in the interlayer region through hydrogen bonding interactions. The stability of these 2D solids results from these interactions between coordinated and weakly bonded water molecules. In this contribution, the crystal structures and related properties of the titled compounds are reported. Three different structural modifications for a given T metal were found. The refined crystal structures were supported by the recorded infrared, Raman, and UV–vis spectra and thermogravimetric data. Two of these modifications were found to be room and high temperature thermodynamic products and the remaining one a room temperature kinetic product.

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1. Introduction

The layered solids herein studied are obtained by the assembling of the planar anionic block $[Ni(CN)_4]^{2-}$ through a transition metal ion (T^{2+}) which links neighboring blocks at their N ends. In the as-synthesized material, the available coordination sites on the T metal centers found at the layer plane are occupied by coordinated water molecules which, in turn, serve to stabilize additional water molecules in the interlayer region through hydrogen bonding interactions. From this fact, the layer–layer distance and the material crystal structure depend on the amount of water molecules found in that region and on the resulting hydrogen bonding interactions among them. This suggests that in such a system of layered solids, the

water content modifies the host structure resulting in different phases. This possibility is explored in this study where for a given T metal three different phases were found. The crystal structure of these phases was resolved and refined from X-ray powder diffraction (XRD) data. The structural information was complemented with infrared (IR), UV–vis, Raman and thermogravimetric (TG) data.

Within this family of layered solids, structural information is available [1–5] for some T metals. For $T = Fe, Co$ and Cd , a phase containing six water molecules per formula unit, $T[Ni(CN)_4] \cdot 6H_2O$, which crystallizes with an orthorhombic unit cell (*Pnma* space group) has been documented and their crystal structures refined [1–4]. For $T = Ni$, the existence of three different phases, named K, L_0 and L_1 , has been reported [5], all of them crystallizing with an orthorhombic unit cell of different cell edges. To the best of our knowledge, the crystal structure of these three phases remains unknown. No additional information is available about the members of the studied series of layered compounds.

The existence of available coordination sites on the layer plane for this series of solids has stimulated the

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