



Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Synthesis and characterization of $T[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$ with $T = \text{Fe}, \text{Ni}$; $\text{pyz} = \text{pyrazine}$: Formation of $T\text{-pyz-Ni}$ bridges

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ARTICLE INFO

Article history:

Received 10 December 2010

Received in revised form

7 June 2011

Accepted 12 June 2011

Available online 21 June 2011

Keywords:

Crystal chemistry

Structural study

Layered compound

Pillared solid

Spin transition

ABSTRACT

The formation of $T\text{-pyz-Ni}$ bridges ($\text{pyz} = \text{pyrazine}$) in the $T[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$ series is known for $T = \text{Mn}, \text{Zn}, \text{Cd}$ and Co but not with $T = \text{Fe}, \text{Ni}$. In this contribution the existence of such bridges also for $T = \text{Fe}, \text{Ni}$ is discussed. The obtained pillared solids, $T[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$, were characterized from XRD, TG, UV–Vis, IR, Raman, Mössbauer and magnetic data. Their crystal structures were refined in the orthorhombic $Pmna$ space group from XRD powder patterns. The structural behavior of these solids on cooling down to 77 K was also studied. In the 180–200 K temperature range the occurrence of a structural transition to a monoclinic structure ($P2_1/c$ space group) was observed. No temperature induced spin transition was observed for $\text{Fe}[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$. The iron (II) was found to be in high spin electronic state and this configuration is preserved on cooling down to 2 K. The magnetic data indicate the occurrence of a low temperature weak anti-ferromagnetic interaction between T metal centers within the $T[\text{Ni}(\text{CN})_4]$ layer. In the paramagnetic region for $\text{Ni}[\text{Ni}(\text{CN})_4] \cdot 2\text{pyz}$, a reversible temperature induced spin transition for the inner Ni atom was detected.