

# On the crystal structures of some nickel hexacyanoferrates (II,III)

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The crystal structures of some nickel hexacyanoferrates (II, III), including mixed compositions containing  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ , were resolved and refined from XRD powder patterns. Data from infrared, Mössbauer and adsorption techniques provided complementary structural information. The crystal structures of  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot 16\text{H}_2\text{O}$  and  $\text{NiCs}_2[\text{Fe}(\text{CN})_6]$  were refined in space group Fm3m.  $\text{NiNa}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$  and  $\text{NiK}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$  were found to be orthorhombic (space group Pmn2<sub>1</sub>). This structure (Pmn2<sub>1</sub>) results from a distortion around the alkali ion, which appears as a monohydrated interstitial species. On ionic exchange in an aqueous solution containing  $\text{Cs}^+$ , the orthorhombic distortion disappears and the cubic cell is obtained.  $\text{Cs}^+$  is a large cation and space is not available for interstitial water molecules. This orthorhombic model is also supported by the Mössbauer spectra of the ferrous analogs,  $\text{FeK}_2[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$  and  $\text{Fe}[\text{Pt}(\text{CN})_6]$ . © 2004 International Centre for Diffraction Data. [DOI: 10.1154/1.1757448]

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## I. INTRODUCTION

Hexacyanoferrates, a well-documented family of coordination compounds, have received renewed attention in the last decade, mainly because they are prototypes of molecular magnetic materials with high Curie temperatures ( $T_c$ ) (Ferlay *et al.*, 1995; Entley *et al.*, 1995; Holmes *et al.* 1999). Some hexacyanoferrates have a microporous structure, which could make them useful as adsorbents (Cartraud *et al.*, 1981; Balmaseda *et al.*, 2002), molecular sieves (Boxhoorn *et al.*, 1985), and in some catalytic processes (Kuyper and Boxhoorn, 1987; Reguera *et al.*, 1992). Due to high insolubility and ion exchange properties, they have found applications in <sup>137</sup>Cs removal from radioactive waste solutions (Ayrault *et al.*, 1998), in valuable metal recovery from industrial wastes (Adekola *et al.*, 1997), and in the therapy of humans and animals affected by nuclear accidents (Roberts, 1987). Many other potential and practical uses are mentioned by Balmaseda *et al.* (2003). All these applications depend on the crystal structures of the compounds.

Only a few of the hexacyanoferrate (II,III) structures are known. These materials are usually available only as fine powders, on which single crystal methods for crystal structure determination are not possible. The powerful codes now available for crystal structure refinement from XRD powder patterns, based on the Rietveld method (Pecharsky and Zavalij, 2003), were not available when many of these compounds were studied several decades ago. The Rietveld method has been used to refine the structures of some copper and nickel ferrocyanides and some copper and cobalt ferricyanides (Ratuszna *et al.*, 1995). However, by using high

quality XRD data and constraints from physical considerations, the refinement results can be significantly improved. In this paper the crystal structures of the nickel series, including mixed salts with  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ , are reported. These structures were refined from XRD powder patterns, complemented by spectroscopic and adsorption data. The obtained results reveal that the exchangeable alkali cation ( $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Cs}^+$ ) plays a significant role in the crystal structure of the studied materials.

## II. EXPERIMENT

The studied materials were prepared by precipitation, resulting in the following compositions:  $\text{NiNa}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ ,  $\text{NiK}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ ,  $\text{NiCs}_2[\text{Fe}(\text{CN})_6]$ , and  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot 16\text{H}_2\text{O}$ . Aqueous solutions of nickel chloride and the appropriate alkali ferrocyanide were mixed with stirring, and allowed to sit for 24 h. The obtained precipitates were then isolated by filtration and washed several times with distilled water. To obtain  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot 16\text{H}_2\text{O}$ , ferricyanic acid was used as the source of the complex anion. All the samples were air-dried for at least a week. Their nature and purity were established by IR, X-ray diffraction (XRD), Mössbauer and X-ray fluorescence analyses, and the hydration degree determined using thermogravimetry (TG) and water vapor adsorption isotherms.

IR spectra were collected in the 4000–400  $\text{cm}^{-1}$  region by means of a Equinox 55 spectrophotometer (from Bruker) using KBr pressed disks and Nujol mull methods. Some cyanometallates react with alkali halides during the milling and disk preparation for IR spectroscopy (Fernandez and Reguera, 1997). Mössbauer spectra were run at room temperature in a constant acceleration spectrometer operated in

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