

Crystal structures of some manganese(II) and cadmium hexacyanoferrates (II,III) and structural transformations related to the sorption of Cesium

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Mn^{2+} and Cd^{2+} form a family of isostructural hexacyanoferrates(II,III). Their crystal structures, including those of mixed compositions containing K^+ and Cs^+ as charge balance cations, were resolved and refined from XRD powder patterns. The crystal structures of $\text{M}_3[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$ and $\text{MCs}_2[\text{Fe}(\text{CN})_6]$ (where $\text{M}=\text{Mn}, \text{Cd}$) were refined in the space group $\text{Fm}\bar{3}\text{m}$. The mixed salts, $\text{MK}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, were found to be orthorhombic (space group $\text{Pmn}2_1$). The orthorhombic structure results from a local distortion due to monohydrated potassium ions located in interstitial sites. On ionic exchange in an aqueous solution containing Cs^+ , the orthorhombic distortion disappears and the cubic cell is obtained. Cs^+ is a large ion, which practically fills the available interstitial voids stabilizing the cubic structure. In solutions of K^+ and Cs^+ the single salts, $\text{M}_2[\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ (monoclinic $\text{P}2_1/\text{n}$) also transform, in this case liberating M^{2+} ions and forming the corresponding mixed salts. An analogous but slow structural transformation was also observed in the anhydrous forms of these single salts. These structural transformations could be relevant to the use of these compounds as ion exchangers and particularly for the sorption of $^{137}\text{Cs}^+$ from radioactive waste solutions. The XRD data were complemented with structural information from infrared (IR), Mössbauer and water vapor adsorption techniques. © 2004 International Centre for Diffraction Data. [DOI: 10.1154/1.1782651]

Key words: manganese hexacyanoferrates(II,III), cadmium hexacyanoferrates(II,III), crystal structure, ferrocyanide, ferricyanide, Rietveld, Mössbauer, ionic exchange

I. INTRODUCTION

Hexacyanoferrates is a well-known family of compounds mainly because they have interesting coordination chemistry (Sharpe, 1976; Dunbar and Heintz, 1997). These complexes have a microporous structure which supports their applications as adsorbent (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 $^{137}\text{Cs}^+$ 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). The strong doubly bridging CN ligand leads to an effective spin coupling of the metal centers in these complexes. This fact has stimulated the study of these compounds as prototype of molecular magnetic materials with high Curie temperature (T_c) (Ferlay *et al.*, 1995; Entley *et al.*, 1995; Holmes *et al.*, 1999), including compositions where the magnetic order can be induced by an external stimuli, e.g., irradiation with light (Sato *et al.*, 1996; Verdaguer, 1996). Other applications include: Battery building (Neff, 1985), heavy metal removal during wine production (Wenker *et al.*, 1990), photographic industry (Mikhailov, 1991), and as materials for electrochromic devices (Byker, 1994). It is surprising that many of these studies have not been preceded by a detailed structural characterization. The crystal structures of these materials remain poorly documented.

The crystal structure of hexacyanoferrates (II,III) is known for only a few compositions. These materials are usually available as fine powders, on which single crystal method in the crystal structure determination is not possible. The powerful codes now available for crystal structure refinement from XRD powder patterns, based in the Rietveld method (Rodriguez-Carvajal, 1998; Pecharsky and Zavalij, 2003), were not available when many of these compounds were studied several decades ago. For $\text{Mn}(2+)$ and $\text{Cd}(2+)$ hexacyanoferrates(II,III) the crystal structures are known only for the single ferrocyanide salts, $\text{M}_2[\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ ($\text{M}=\text{Mn}, \text{Cd}$) (Gomez and Reguera, 2002; Gomez *et al.*, 2002). In this paper the crystal structures of $\text{M}_3[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$, $\text{MCs}_2[\text{Fe}(\text{CN})_6]$ and $\text{MK}_2[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ are resolved from XRD powder patterns. Mössbauer and IR spectra were used as a source of complementary structural information of the studied materials. The structural transformations in $\text{M}_2[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ and $\text{MK}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ related to the ionic exchange in solutions containing K^+ and Cs^+ are also discussed. The Mn^{2+} and Cd^{2+} complexes are considered together because they form isostructural compounds.

II. EXPERIMENTAL

The studied materials can be considered as a tridimensional assembling of the molecular block, $[\text{Fe}(\text{CN})_6]^{3-}$ or $[\text{Fe}(\text{CN})_6]^{4-}$, through an appropriate metal (Mn^{2+} or Cd^{2+}). In some cases, from the required charge balance, an alkali (exchangeable) cation must be introduced in their composition. Since these anionic molecular blocks form insoluble salts with transition metal cations, an easy way to prepare these materials is through the precipitation method. As source of the molecular block, an alkali ferrocyanide or

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