

The structure of two manganese hexacyanometallates(II): $\text{Mn}_2[\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ and $\text{Mn}_2[\text{Os}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$

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The crystal structures of two manganese hexacyanometallates(II), $\text{Mn}_2[\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ and $\text{Mn}_2[\text{Os}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$, were refined from X-ray powder diffraction data using the Rietveld method, with the reported structure for $\text{Mn}_2[\text{Ru}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ used as a structural model. These compounds are isomorphous and crystallize in the monoclinic space group $P2_1/n$. Their crystallization water is not firmly bound and can be removed without disrupting the $\text{M}-\text{C}\equiv\text{N}-\text{Mn}$ network. In the dehydrated complexes, the outer cation (Mn) remains linked to only three N atoms from CN ligands while the inner cation (Fe,Os) preserves its coordination sphere. The IR, Raman, and Mössbauer spectra for the hydrated and anhydrous forms are explained based on the refined structures. © 2002 International Centre for Diffraction Data. [DOI: 10.1154/1.1469023]

Key words: ferrocyanide, osmocyanide, X-ray diffraction, Rietveld method, Mössbauer, infrared, Raman

I. INTRODUCTION

Transition metal hexacyanometallates(II), $\text{T}_2[\text{M}^{\text{II}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$, where T is a transition metal, are known to crystallize in cubic space group $F43m$ (Rigamonti, 1937; Rigamonti, 1938; Ratuszna *et al.*, 1995). These crystal structures are highly symmetric, with all cyanide groups linking metal centers in a three-dimensional framework. The outer metal (T) is located in two independent crystallographic sites: one of them coordinated to six cyanide groups through N, while the other one is in the middle of the cubic cavity formed by the framework. Such an arrangement, in which $-\text{T}-\text{N}\equiv\text{C}-\text{M}-\text{C}\equiv\text{N}-\text{T}-$ connections are typical, has been reported for Co, Ni, and Cu hexacyanoferrates(II) (Rigamonti, 1937; Rigamonti, 1938; Ratuszna *et al.*, 1995). Manganese hexacyanoruthenate(II), however, crystallizes in a different space group ($P2_1/n$), in which $-\text{Ru}-\text{C}\equiv\text{N}-\text{Mn}-(\text{H}_2\text{O})_2-\text{Mn}-\text{N}\equiv\text{C}-$ bridges are observed; two neighbor manganese atoms are linked by two water molecules (Ruegg *et al.*, 1971). Such a structure is expected to have interesting absorption properties when dehydrated. Manganous ferrocyanide and osmocyanide have been reported as being isomorphous to the ruthenium complex; their structures, however, have not been reported (Reguera *et al.*, 2001). The present study deals with the structural refinement of these two complexes. Since no single crystals were available, their structures were refined using the Rietveld method complemented with IR, Raman, and Mössbauer spectroscopies.

II. EXPERIMENTAL

Manganese ferrocyanide was prepared by mixing aqueous solutions of manganese chloride and ferrocyanic acid. The precipitated solid was washed several times with distilled water and dried in a desiccator over silica gel. Manganese osmocyanide was prepared in the same manner but using potassium hexacyanoosmate(II). In this paper these compounds are abbreviated $\text{Mn}_2\text{Fe}^{\text{II}}$ and $\text{Mn}_2\text{Os}^{\text{II}}$. The stoichiometry suggested by these abbreviations was checked by X-ray fluorescence analysis. Their hydration degree was determined using thermogravimetry.

IR spectra were recorded in the range $4000-400\text{ cm}^{-1}$ using the KBr disk technique and a Fourier transform infrared spectrometer (ATI Mattson, Genesis Series). Raman spectra were obtained using a 1403 Spex double monochromator in the frequency range of $1900-2400\text{ cm}^{-1}$. Mössbauer spectra were collected at room temperature with a ^{57}Co in Rh source, using a constant acceleration spectrometer (from Mostech) operated in the transmission mode. All Mössbauer spectra were fitted with an iterative least-squares minimization algorithm using pseudo-Lorentzian line shapes to obtain the values of isomer shift (δ), quadrupole splitting (Δ), linewidth (Γ), and relative area (A). Isomer shift values are reported relative to sodium nitroprusside.

X-ray diffraction (XRD) powder patterns were obtained with a Siemens D5000 diffractometer with a graphite monochromator and $\text{Cu } K\alpha$ radiation ($\lambda = 0.1541838\text{ nm}$). Patterns were taken in the interval from 10° to 100° (2θ) with a step size of 0.03° and a counting time of 20 s. Since preferred orientation was observed when the samples were pressed into the diffractometer sample holder, the powder was ground in an agate mortar and then suspended in acetone, which was rapidly dried over a glass sample holder. This procedure eliminated the preferred orientation, so that

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