

The structure of three cadmium hexacyanometallates(II): $\text{Cd}_2[\text{Fe}(\text{CN})_6]\cdot 8\text{H}_2\text{O}$, $\text{Cd}_2[\text{Ru}(\text{CN})_6]\cdot 8\text{H}_2\text{O}$ and $\text{Cd}_2[\text{Os}(\text{CN})_6]\cdot 8\text{H}_2\text{O}$

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Abstract

$\text{Cd}_2[\text{M}^{\text{II}}(\text{CN})_6]\cdot 8\text{H}_2\text{O}$, where $\text{M}=\text{Fe}$, Ru and Os , form a family of isomorphous compounds which crystallize in the monoclinic $\text{P2}_1/\text{n}$ space group. M^{II} cations present their usual octahedral coordination, while the cadmium atom coordinates to three nitrogen atoms from the cyanide groups and three water molecules forming a distorted octahedron. The rest of the water molecules are located in small channels in the structure and are hydrogen bonded to the coordinated ones. Adjacent cadmium octahedra share one edge to form the moiety: $\text{Cd}_2\text{N}_6(\text{H}_2\text{O})_4$, in such a way that two metal sequences are observed: $\text{M}^{\text{II}}-\text{Cd}-\text{M}^{\text{II}}$ and $\text{M}^{\text{II}}-\text{Cd}-\text{Cd}-\text{M}^{\text{II}}$, forming a tridimensional network. Coordinated and zeolitic water molecules can be removed preserving the $\text{M}-\text{C}\equiv\text{N}-\text{Cd}$ framework. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

Transition metal hexacyanometallates form a family of microporous materials which have been studied in connection with their potential applications as adsorbents [1,2], molecular sieves [3], ion exchangers [4,5], and in certain catalytic processes [6,7]. This family of complexes also shows promising perspectives as molecular magnets [2,8], electronic switching and electrochromic devices [9] and in battery building [10]. In all these applications the understanding of the structure of the compounds is a primary task.

Transition metal hexacyanides usually crystallize in the cubic face-centered cell of Prussian Blue (space group $\text{Fm}\bar{3}\text{m}$) [11], where all the metal centers are connected by CN ligands. A unique structure in this family of complexes was found for manganous hexacyanoruthenate (II) octahydrate, $\text{Mn}_2[\text{Ru}(\text{CN})_6]\cdot 8\text{H}_2\text{O}$ [12]. In the structure of this compound the outer cations (Mn) are found in an $\text{Ru}-\text{Mn}-\text{Mn}-\text{Ru}$ sequence connected by a bridge of two water molecules [12]. A third water molecule acts as ligand but without a bridging configuration. A similar co-ordination has been reported for the analogues manganous ferrocyanide and osmocyanide [11]. In a recent study

on reduction of cadmium ferricyanide by heating and milling [13], it was observed that the obtained cadmium ferrocyanide behaves as dehydrated manganous ferrocyanide [14]. This suggests that cadmium ferrocyanide and its ruthenium and osmium analogues, whose structures have not been reported, could be isomorphous to manganous ruthenocyanide.

In the present work we are reporting the structural characterization of cadmium ferrocyanide, ruthenocyanide and osmocyanide. These three compounds were found isostructural to the corresponding manganous hexacyanides (monoclinic octahydrates, space group $\text{P2}_1/\text{n}$) and their structure refined using the Rietveld method. The XRD study was complemented with Mössbauer, IR and Raman data. Coordinated and zeolitic water molecules in these compounds can be removed preserving the nature of the complex.

2. Experimental

Cadmium ferrocyanide was prepared by mixing aqueous solutions of cadmium chloride and ferrocyanic acid. The precipitated solid was washed several times with distilled water and dried in a desiccator over silica gel. Cadmium ruthenocyanide and osmocyanide were prepared in the same manner but using the corresponding potassium

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