

Crystal structures of hexacyanometallates with bifurcated cyano groups

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Abstract

The crystal structures for $T_2[M(CN)_6]$ where $T = \text{Mn, Cd}$; $M = \text{Fe, Ru, Os}$, were refined from the corresponding XRD powder patterns using the Rietveld method in the hexagonal P-3 (147) space group with $Z = 1$. In the structure of these families of anhydrous hexacyanometallates (II) the N end of the CN group appears bifurcated, serving as a ligand for two neighbouring T metals. Such a coordination mode has not been reported before for transition metal hexacyanometallates but it is consistent with the magnetic properties and Mössbauer, IR and Raman spectra of the studied compounds. The anhydrous solids are obtained by dehydration of the corresponding octahydrates. In the hydrated form the metals (Mn, Cd) linked at the N ends have a mixed coordination sphere formed by three N atoms and three coordinated waters, with two of these latter forming bridges between two neighbouring metals. The loss of these structural waters leaves the metals (T) in an unstable state with only three ligands in their coordination sphere and a structural transformation involving a change in the CN group electronic configuration is induced. The metal coordination through bifurcated CN groups leads to a remarkable increase in the charge overlapping between the metal centres, which appears attractive for molecular magnet design.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In hexacyanometallates the metal centres are usually found bridged by CN groups where the C and N ends remain linked to only one metal. The metal linked at the C end is always found with octahedral coordination to form the anionic hexacyanometallate octahedral block, $[M^n(CN)_6]^{6-n}$. The 3D framework is formed when neighbouring blocks are linked at their N ends through a second transition metal (T). From a recent study on the magnetic properties of $Mn_2[M(CN)_6]$, with $M = \text{Fe, Ru and Os}$, conclusive evidence concerning the bonding of a single N end to two manganese atoms has been obtained [1]. $Mn_2[M(CN)_6] \cdot 8H_2O$ and $Cd_2[M(CN)_6] \cdot 8H_2O$ form two isomorphous series of hexacyanometallates (II) [2–4], crystallizing in the monoclinic space group $P21/n$ (14),

and from spectroscopic evidence in their anhydrous state such isomorphous behaviour is preserved [1–5]. For $Cd_2[Fe(CN)_6]$ the crystal structure has been solved and refined from XRD powder patterns and a combination of radial distribution function (RDF) and direct methods in the hexagonal P-3 (147) space group [6]. In that structural model the N end of the CN groups appears coordinating two neighbouring outer metals (Cd). In this contribution the refined crystal structures in the P-3 model for these two series as anhydrous phases are reported and their physical properties are discussed from the refined structures. For comparison, the crystal structure refinement of the cadmium iron anhydrous phase was revised and the resulting parameters are also reported.

In $Mn_2[M(CN)_6] \cdot 8H_2O$ and $Cd_2[M(CN)_6] \cdot 8H_2O$ series two neighbouring assembling metals (Mn, Cd) are linked by two water bridges to form a small cluster of two metals

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