Atypical Coordination in Transition Metal Hexacyanometallates

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INTRODUCTION

When in the titled materials the 3D framework is formed by practically linear T-N-C-M-C-N-T chains, they are known as Prussian blue (PB) analogues where the two metal centers have octahedral coordination. PB analogues crystallize with a cubic unit cell. However, for different combinations of T and M metals deviations from that regularity are observed, particularly for the T metal coordination modes. The metal M is always found with an octahedral coordination to form the octahedral anionic building block, $[M^n(CN)_6]^{n-6}$. In this contribution such deviations or atypical coordination modes are summarized. The coordination for the T metal determines many of the solid physical properties, among them the porous framework, the magnetic interaction between metal centers, and the thermal stability. Atypical coordination modes for the metal T were observed for T = Zn with M = Fe^{II}, Ru^{II}, Os^{II}; Fe^{III}, Co^{III}, Rh^{III} and Ir^{III}, and for Mn(2+) and Cd(2+) with M = Fe^{II}, Ru^{II}, Os^{II}.

EXPERIMENT

The following compositions (and series labeled as bold number) involving these metals were prepared using previously reported procedures [1–6]: **1**) $Zn_3A_2[M(CN)_6]_2.xH_2O$ with A=Na, K, Rb, Cs, NH_4; and M = Fe^{II}, Ru^{II}, Os^{II}; $Zn_3[M(CN)_6]_2$ with M = Fe^{III}, Co^{III}, Rh^{III} and Ir^{III}; **2**) $T_2[M(CN)_6].8H_2O$ with T = Mn, Cd; and M = Fe^{II}, Ru^{II}, Os^{II}; **3**) $T_2[M(CN)_6]$ with T = Mn, Cd; and M = Fe^{II}, Ru^{II}, Os^{II}. These three series were characterized from chemical analyses, magnetic measurements, TG curves, and XRD, IR, Raman and Mössbauer data. HR-XRD data in the temperature range 12-300 K were recorded at XPD-10B beam line of the LNLS synchrotron radiation facility. For series **1** and **2** the crystal structure was refined using available structural model, but for series **3** the structural model to be used was derived with the use of Mössbauer spectra and calculation of the radial distribution function [5, 6].

RESULTS AND DISCUSSION

All the compositions included in series **1** crystallize with a rhombohedral unit cell (R-3c space group). That structural regularity is related with a tetrahedral coordination for the Zn atom (Figure 1). In the sub-series $Zn_3A_2[M(CN)_6]_2.xH_2O$ the metal A is a non-framework species (exchangeable) located within the porous framework of these solids, formed by elliptical cavities of about 12.5 x 9 x 8 Å. When this subseries is dehydrated the A metal migrates within the cavity and a new unit cell (monoclinic) results. For series **2** neighboring Mn (Cd) atoms remain linked by a double aquo bridges (Figure 2) with also a non-bridged water molecules in their coordination environment. Between these Mn atoms and through the aquo bridges an anti-ferromagnetic interactionis established. When all the crystal water molecules are removed the occurrence of a structural transformation is detected. The formed anhydrous solid shows a relatively high stability even in a humid environment, their Mössbauer spectrum is a quadrupole splitting doublet of very low isomer shift value, the lowest one observed within transition metal hexacyanoferrates (∼0.08 mm/s relative to sodium nitroprusside), the frequency for the ν(CN) vibration is also extremely low (< 2040 cm^{-1}) and the superexchange integral (J) between the manganese atoms shows a dramatic increase (4.11 cm^{-1}), of about 15 times the origi-

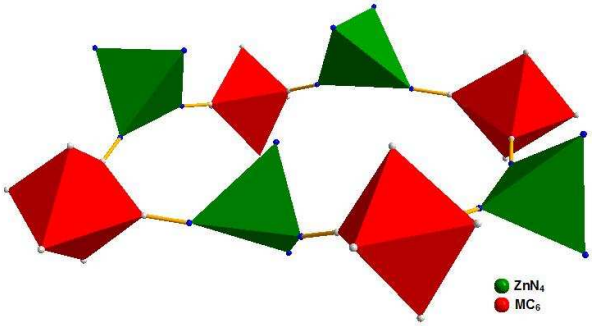

FIG. 1: Octahedral, MC_6, and tetrahedral, ZnN_4, building blocks forming an elliptical window.

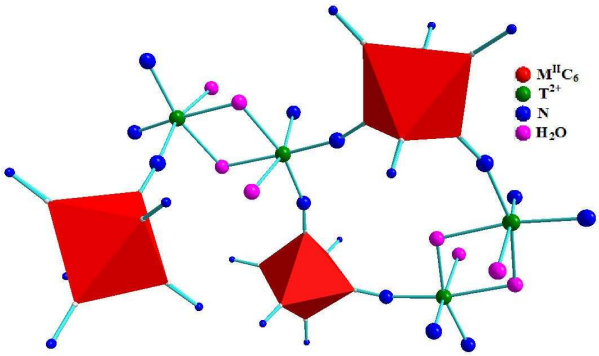

FIG. 2: View of the unit cell of the series $T_2[M(CN)_6].8H_2O$; T=Mn and Cd; M= Fe, Ru, Os.