

## Crystal Structure and Magnetic Properties of Cyanide-Bridged Bimetallic Fe<sup>II</sup>–M<sup>II</sup> Coordination Polymers (M<sup>II</sup> = Mn and Ni)

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Prussian Blue (PB) phases constitute an especially amazing and evergreen family of materials that stimulated an astonishing rebirth of interest in the magnetism of complex solids, and a revival of inorganic cyanide chemistry. The present work forms part of a study of the synthesis and properties of low dimensional and hitherto unknown "tube like" cyanide-bridged bimetallic coordination polymers. In this paper we present the single crystal structures and magnetic properties of two cyanide-bridged Fe<sup>II</sup>–M<sup>II</sup> complexes, [ $\{\text{Fe}^{\text{II}}(2,2'\text{-bipy})(\text{CN})_4\}\text{Mn}^{\text{II}}\} \cdot \text{MeOH}$ ] (1) and [ $\{\text{Fe}^{\text{II}}(\text{tn})(\text{CN})_4\}\text{Ni}^{\text{II}}\} \cdot 2\text{MeOH}$ ] (2), they were made by using the N,N-chelated tetracyanoferrate(II) species as "donor" building blocks. Compound 1 is a two-dimensional coordination polymer, consisting of ribbon-like chains crosslinked to give neutral two-dimensional (4,4) sheets of [ $\{\text{Fe}^{\text{II}}(2,2'\text{-bipy})(\text{CN})_4\}\text{Mn}^{\text{II}}\}$ ] and methanol molecules of crystallization. Each [ $\text{Fe}^{\text{II}}(2,2'\text{-bipy})(\text{CN})_4\}^{2-}$ ] unit uses four cyanide groups to connect to four Mn<sup>II</sup> ions. The structure of 2 is a three-dimensional polymeric network extended through Fe<sup>II</sup>–CN–Ni<sup>II</sup> linkages, each [ $\text{Fe}^{\text{II}}(\text{tn})(\text{CN})_4\}^{2-}$ ] ion connecting to four planar Ni<sup>II</sup> ions *via* the CN<sup>-</sup> groups. Magnetic measurements show that 1 displays ferromagnetic coupling between the nearest neighbour Mn<sup>II</sup> d<sup>5</sup> high-spin ions across the diamagnetic Fe<sup>II</sup> d<sup>6</sup> centers. Bulk samples of 2 appear to contain two crystalline phases, one of which (probably not that of the structure shown) displays long-range magnetic order, with T<sub>C</sub> = 16.0 K.