

## Mixed Valence State Systems in Cobalt Iron Hexacyanides

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### INTRODUCTION

The cyanide ligand allows the formation of bridges between neighboring transition metals, T-N-C-M, to form 1D, 2D and 3D solids. The CN group at C end has low energy and extended  $\pi$ -anti-bonding orbitals which overlap with the inner metal (M)  $t_{2g}$  orbitals. During the NC-M bond formation the ligand donates large amount of electron density to the metal. The charge concentration on this last one induces certain  $\pi$ -back donation toward the ligand. These back-donated metal electrons are localized at the N end of the group, which is the coordination site for the second metal (T). The net result is an overlapping for electron densities of neighboring metals centers. This unique ability of the CN group supports the interesting physical applications that transition metal cyanides show, among them magnetic properties. The super-exchange integral between neighboring metals is enough high to allow the magnetic order close to room temperature for some compositions [1]. The coupling of the metals electronic structures through the CN bridges also reduces the height of the energy barrier for charge exchange processes between neighboring metal centers [2]. This explains that in Prussian blue (PB) analogues (3D hexacyanides) the charge transfer can be observed by the sample illumination with radiation corresponding to the UV-Vis spectral range [2]. This possibility supports the photo-induced magnetic order at low temperature for some PB analogues, and particularly in Co(III) hexacyanoferrate (II) [3]. Under normal conditions this is a non-magnetic material because the involved metals have no unpaired electrons. When the sample is illuminated a charge transfer from iron to cobalt with formation of Co(2+) hexacyanoferrate (III) takes place. Below 20 K the formed species remains stable and a long range magnetic order is established. In this contribution the formation of Co(III) hexacyanoferrate (II) under mild conditions is explored and their structure established. The solids containing that species would be suitable for photo-induced magnetic order studies.

### EXPERIMENT

The materials to be studied were prepared using a previously reported procedure [2, 4–6]. Two routes were used to form the Co(III)-Fe(II) species: a) heat induced charge transfer in  $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$  to obtain the mixed valence states (MVS) system  $(\text{Co}^{2+})_{3-x}(\text{Co}^{\text{III}})_x[(\text{Fe}^{\text{II}})_{2-x}(\text{Fe}^{\text{I}})_x(\text{CN})_{12}]$ ; b) the precipitation mixing aqueous solutions of  $\text{Co}^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ , these last ones prepared dissolving the corresponding potassium salts. All the samples

were characterized from chemical analysis, magnetic measurements, Mössbauer, X-ray diffraction (XRD), infrared (IR) and thermogravimetric (TG) data. XRD powder patterns were recorded under vacuum at different temperatures in the 12-300 K range using the XPD-10B beamline of the LNLS radiation facility. From the recorded XRD patterns the materials crystal structure was solved and refined. The refinement process was carried out using the Rietveld method. The structural model to be refined was established combining XRD, Mossbauer and IR data.

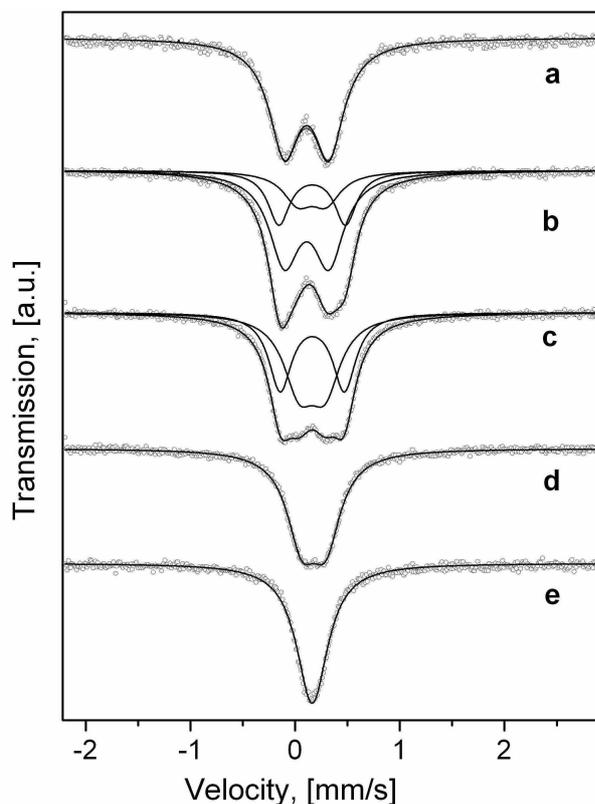


FIG. 1: Mössbauer spectra at room temperature for : (a)  $\text{Co}^{2+}_3[\text{Fe}(\text{CN})_6]_2 \cdot y\text{H}_2\text{O}$  ; (b)  $(\text{Co}^{2+})_x(\text{Co}^{\text{III}})_{1-x}\text{K}[(\text{Fe}^{\text{II}})_{1-x}(\text{Fe}^{\text{I}})_x(\text{CN})_6]$ ; (c,d)  $(\text{Co}^{2+})_{1.5x}(\text{Co}^{\text{III}})_{1-x}\text{K}[\text{Fe}^{\text{II}}(\text{CN})_6]$ ; e)  $\text{CoK}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$

### RESULTS AND DISCUSSION

According to the chemical analyses, IR and Mössbauer data the obtained solids are solids solutions of the involved metals, particularly the se-