

## Thermal-Induced Changes in Molecular Magnets Based on Prussian Blue Analogues

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The thermal-induced changes in molecular magnets based on Prussian blue analogues,  $M_3[Fe(CN)_6]_2 \cdot xH_2O$  ( $M = Mn, Co, Ni, Cu, Zn, \text{ and } Cd$ ), were studied from infrared, X-ray diffraction, thermo-gravimetric, Mössbauer, and magnetic data. Upon being heated, these materials loose the crystalline water that enhances the interaction between the metal centers, as has been detected from Mössbauer spectroscopy data. At higher temperatures, a progressive decomposition process takes place, liberating  $CN^-$  groups, which reduces the iron atom from Fe(III) to Fe(II) to form hexacyanoferrates(II). The exception corresponds to the cobalt compound that undergoes an inner charge transfer to form Co(III) hexacyanoferrate(II). In the case of zinc ferricyanide, the thermal decomposition is preceded by a structural transformation, from cubic to hexagonal. For  $M = Co, Ni, Cu, \text{ and } Zn$  the intermediate reaction product corresponds to a solid solution of M(II) ferricyanide and ferrocyanide. For  $M = Mn$  and  $Cd$  the formation of a solid solution on heating was not detected. The crystal frameworks of the initial M(II) ferricyanide and of the formed M(II) ferrocyanide are quite different. In annealed Mn(II) ferricyanide samples, an increasing anti-ferromagnetic contribution on heating, which dominates on the initial ferrimagnetic order, was observed. Such a contribution was attributed to neighboring Mn(II) ions linked by aquo bridges. In the anhydrous annealed sample such interaction disappears. This effect was also studied in pure Mn(II) ferrocyanide. The occurrence of linkage isomerism and also the formation of Ni(III), Cu(III), and Zn(III) hexacyanoferrates(II) were discarded from the obtained experimental evidence.

### I. Introduction

Prussian blue (PB) analogues, probably the oldest studied family of coordination compounds, have received renewed attention as prototypes of molecular magnets in the past decade.<sup>1</sup> Several PB analogues are included in those molecular materials with the highest temperature of magnetic ordering ( $T_c$ ).<sup>2</sup> In some compositions, unusual effects have been observed. For instance, Co(III) ferrocyanide, which is a nonmagnetic material, becomes magnetic when it is illuminated at low temperatures.<sup>3</sup> This effect in cobalt iron cyanide has been intensively studied as a prototype of a photoinduced molecular magnet<sup>3,4</sup> in recent years, and it has encouraged the study of other transition metal ferricyanides, particularly the heat-treatment effect probably oriented to find a similar charge-transfer process in other Prussian blue analogues.<sup>5–9</sup> For cobalt(II), nickel(II), copper(II), and zinc(II) ferricyanides, the formation of cobalt(III), nickel(III), copper(III), and zinc(III) ferrocyanides has been reported.<sup>5–9</sup> However, nickel(III), copper(III), and zinc(III) are unusual species not detected even in ozonized ferrocyanides.<sup>10</sup> For cobalt(II) and copper(II) ferricyanides, the formation on heating of  $Co^{II}-CN-Fe^{III}$  and  $Cu^{II}-CN-Fe^{III}$  species has also been reported.<sup>5,7</sup> This is an unexpected result since all of the known stable hexacyanide complexes are formed with transition metals where the inner metal has unoccupied the  $e_g$  orbitals to favor a strong cation–ligand interaction with the formation of low-spin complexes. In  $Co^{II}-CN-Fe^{III}$  and  $Cu^{II}-CN-Fe^{III}$  hexacyanides, the elec-

tronic configurations for cobalt and copper atoms are  $t_{2g}^6e_g^1$  and  $t_{2g}^6e_g^3$ , respectively. The formation of these species also supposes the occurrence of a linkage isomerization process up to now only observed in ferrous chromicyanide and manganese cyanide.<sup>11</sup>

The behavior of Prussian blue analogues on heating has been studied;<sup>12</sup> ferricyanides reduce to ferrocyanides releasing  $CN^-$  anions. In this process the liberated  $CN^-$  groups play the role of the reducing agent. In the exhaust reaction gases,  $C_2N_2$  has been detected through the use of mass spectrometry and IR spectroscopy. A similar mechanism is present during the reduction of ferricyanides to ferrocyanides by milling or sonication.<sup>13</sup> In the milling, the colliding points of the microcrystals behave as “hot points” where  $CN^-$  groups are liberated. From all this evidence, we believe that the reported thermal-induced changes in some molecular magnets based on PB analogues<sup>5–9</sup> are related to a simple reduction of ferricyanides to ferrocyanides without the presence of other heat-induced effects, with the exception of the cobalt analogue. In this paper, we present experimental results that support this hypothesis. In addition, some interesting new effects were observed and are discussed.

This work concerns mainly those heat-induced changes in divalent transition metal ferricyanides for heating below 200 °C. Above this temperature ferrocyanides are always formed, and they remain stable approximately up to 350 °C. Their final decomposition leads to the reduction of the transition metals involved, in some cases forming alloys of small particle size. Such metallic end products have been appropriately characterized.<sup>5–8</sup>

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