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On the Low Stability of Molecular Magnets Based on Transition Metal Hexacyanochromates (III)

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In the research area of molecular magnets for Prussian blue analogues interesting and unusual effects have been observed, particularly for mixed transition metal salts of the hexacyanochromate (III) anion, $T^{A}_{3-x}T^{B}_{x}[Cr(CN)_6]_2{\cdot}yH_2O$. For single metal salts, $T_3[Cr(CN)_6]_2{\cdot}yH_2O$, with T = Mn(2+), Fe(2+), Co(2+), three paramagnetic ions where long range magnetic order is observed, the materials show low stability. The structural change can be envisaged as a flipping of the CN ligand, from T-N≡C-Cr-C≡N-T to Cr-N≡C-T-C≡N-Cr. The material containing these metals (Mn, Fe, Co) could be stabilized by the incorporation of a second metal that does not form stable hexacyano complexes (Ni, Cu, Zn, Cd). In this contribution such possibility is explored. The role of the porous framework in the material low stability is also discussed. For analog compact solids, $TCs[Cr(CN)_6]$, a relatively high stability on aging was observed. The study of the mixed compositions is preceded by a structural characterization of the simple series where the effect of the crystal water removal is also considered.

1. Introduction

Within the research area of molecular magnets the most interesting behavior has been observed for Prussian blue (PB) analogues. These compounds are 3D coordination polymers where the metal centers remain bridged by CN groups. This ligand has the ability to subtract charge from the metal (M) linked at the C end and locate it at the N end to finally be partially donated to the metal (T)

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