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Stabilization of cubic and rhombohedral phases of zinc hexacyanocobaltate (III)

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ABSTRACT

Porous solids with the option of hydrophilic or hydrophobic surface within a same composition are not common materials. Zinc hexacyanocobaltate (III) is one of these materials. From room temperature synthesis a porous cubic phase with cavities of *ca.* 8.5 Å diameter communicated by windows of *ca.* 4.2 Å is obtained. At the cavity surface six Zn atoms with open coordination sites are available. These sites are responsible for the material affinity for polar species, among them water molecules. In the as-synthesized material these coordination sites are occupied by water molecules. On heating above 333 K the crystal water evolves and the material undergoes a structural transformation to form a rhombohedral structure (R-3c), where the Zn atoms are tetrahedrally coordinated to framework ligands and without available coordination sites. This is the hydrophobic phase. The porous network of this phase is formed by ellipsoidal cavities of *ca.* 5.1 × 12.7 × 8.3 Å that are communicated by elliptical windows of *ca.* 3.9 × 5.2 Å. The inverse transformation has a low kinetic and takes place in the presence of a high-chemical potential of water molecules. The structural transformation between the cubic and rhombohedral phases was inhibited by doping the material with a metal that stabilizes one of these structures. The minimum metal concentration that stabilizes a given phase was established.

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1. Introduction

Divalent transition metal hexacyanometallates with porous framework have received certain attention in the last few years, particularly from their demonstrated ability for the H₂ storage [1–11]. In that sense, porous hexacyanometallates have been taken as prototype of materials to understand the nature of those interactions involved in the H₂ stabilization within nanocavities. The porous nature of some hexacyanometallates is known from decades ago [12–15] but, probably related to their lower thermal stability compared with zeolites, for instance, the number of recent studies on their porous framework properties has been relatively limited [16,17].

This family of coordination polymers has also played an important role as prototype of molecular magnets [18]. The CN group has the ability to bridge metal centers through formation of relatively strong bonds at its C and N ends. This bridge ligand has extended anti-bonding orbitals at its C end able to subtract charge from the metal t_{2g} orbitals through a mechanism known as π-back donation. The charge removed from the metal linked at the C end is located at the N end that is the coordination site for a second metal.

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The net effect is the interaction between the metals electron clouds through the CN ligand. From such electron clouds interaction, the magnetic order between neighboring metal centers results. The usual magnetic materials, metals, alloys and ceramics, are compact solids where the surface has no effect on the magnetic properties, except in the nanometric domain. Molecular magnets based on hexacyanometallates offer a unique possibility of combining magnetic properties with a high-available surface. In this sense, molecular magnets sensitive to humidity and the modulation of the magnetic properties through adsorbed species have been reported [19,20].

Within porous solids, the adsorption potential is usually ascribed to the surface atoms electronic structure and the related capability to interact with guest species. Zeolites with charge balancing alkali ions within the cavities show high ability for polar species storage. On the other hand, porous carbons which are practically free of that electrical potential show a higher ability for the adsorption of non-polar species. The existence of dimorphic materials with phases exhibiting these two behaviors is not common. Zinc hexacyanocobaltate (III) and its Fe and Ir analogues are examples of materials with such features [21]. Their 3D frameworks are formed by the assembling of the octahedral building block, [M^{III}(CN)₆], where M = Fe, Co, Ir, through Zn atoms linked at its N ends. The formula unit of these materials is Zn₃[M(CN)₆]₂ · xH₂O. This formula unit contains 12 N ends as coordination sites for