



An atypical coordination in hexacyanometallates: Structure and properties of hexagonal zinc phases

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Abstract

In hexacyanometallates, the involved transition metals are usually found with octahedral coordination. The exception corresponds to the hexagonal zinc phases where this metal appears tetrahedrally coordinated to N ends from the CN ligands. Those zinc hexacyanometallates where such atypical coordination appears were identified and for four of them the crystal structure was refined from X-ray diffraction powder patterns using the Rietveld method. Zinc hexacyanoferrates (III), hexacyanocobaltate (III), hexacyanoiridate (III) and the mixed zinc–cesium hexacyanoferrate (II) were found to be dimorphic, cubic (Fm-3m) and hexagonal (R-3c), related to the zinc atom in octahedral or tetrahedral coordination, respectively. In the absence of an exchangeable cation, the hexagonal phases result anhydrous. This last feature was attributed to a low polar character for the pores surface. The Mössbauer spectrum of hexagonal zinc hexacyanoferrate (III) is an unresolved quadrupole splitting doublet ($\Delta = 0.18$ mm/s). The iron nucleus is sensing a weak electric field gradient related to a relatively high symmetry for its ligands and charge environment. The IR spectrum appears to be an excellent sensor to identify the coordination for the zinc atom in a given sample. For the tetrahedral coordination, the CN stretching absorption was found at least 8 cm^{-1} above the frequency observed for this vibration in the octahedral one. For hydrated phases, the crystal water evolves on heating preserving the material porous framework. The temperature at which the material becomes anhydrous parallels the polarizing power of the charge balancing cation sited within the channels. Hexagonal Zn–Cs ferrocyanide becomes anhydrous at $100\text{ }^\circ\text{C}$, while for the Zn–Na analogue a heating close to $200\text{ }^\circ\text{C}$ is required. The stability temperature range for the anhydrous phases depends on the nature of the engaged hexacyanometallate anion; the higher stability was observed for hexacyanoferrates (II). Zinc ferricyanide shows the weaker magnetic interaction for the hexagonal modification due to an unfavourable geometry for the overlapping path between the unpaired electrons on the iron(III) atoms. The open 3D porous network is formed by relatively large ellipsoidal cavities, three per cell, communicated through elliptical openings (windows), six per cavity. For dimorphic zinc hexacyanometallates (III), the most compact structure (higher density) corresponds to the hexagonal modification, however, it has the largest cavity windows and cavity (pore) size, and also the higher thermal stability.

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1. Introduction

Transition metal hexacyanometallates, commonly known as Prussian blue analogues, usually have an open-channel framework appropriate for small molecules separation and storage [1–5]. Recent studies have reported their potentiality for hydrogen storage [6–9].

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