

MÖSSBAUER SPECTROSCOPIC STUDY OF PRUSSIAN BLUE FROM DIFFERENT PROVENANCES

E. REGUERA, J. FERNÁNDEZ-BERTRÁN, A. DAGO and C. DÍAZ
Centro Nacional de Investigaciones Científicas, P.O. Box 6990, Havana, Cuba

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Ferric ferrocyanides synthesized from different sources of ferric cations and ferrocyanide anions and those derived from ferrous ferricyanide, ferrous ferrocyanide and ferric ferricyanide have been studied using Mössbauer and XRD techniques. Structural information of the effect of the provenance on the properties of the final compound is obtained. Significant correlations between isomer shift and quadrupole splitting of inner and outer iron cations have been observed.

1. Introduction

Prussian Blue (PB), both in insoluble (IPB) and soluble (SPB) forms, is usually prepared by mixing solutions of ferric and ferrocyanide salts. The compound made by mixing solutions of ferrous salt and ferricyanide ion is known as Turnbull's Blue (TB). Both compounds have a characteristic deep blue colour. In addition, on aging, compounds prepared from solutions of ferrous and ferrocyanide salts (Williamson White, WW) and from solutions of ferric and ferricyanide salts (Prussian Brown, PBr) also acquire the same deep blue colour.

For a long time, the main questions about these compounds were whether PB and TB were the same compound or not and whether there were well-defined (localized or unlocalized) valences for the structurally different iron atoms. The answers to these questions were given by Mössbauer spectroscopy, revealing that PB and TB have identical spectra with one high-spin Fe^{3+} and a low-spin Fe^{II} site corresponding to ferric ferrocyanide [1]. Therefore, in TB a charge transfer from Fe^{2+} (high spin) to Fe^{III} (low spin) or flipping of the CN ligand by 180° should occur at the moment of combination, similar to that observed in heat-treated IPB [2].

The compounds discussed above crystallize in the cubic system. They are members of a family of compounds named Prussian Blue analogs [3,4]. IPB has the formula $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$, while SPB is a mixed K salt, $\text{KFe}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$. The structure of the latter can be described as a cubic network of $\text{Fe}^{\text{II}}-\text{C}-\text{N}-\text{Fe}^{3+}$