

The existence of ferrous ferricyanide

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Abstract

Evidence in the literature on the synthesis of ferrous ferricyanide is critically discussed. Pyrolysis and pressure effects on Prussian Blue lead to ferrous ferrocyanide together with decomposition by-products, and not to ferrous ferricyanide. The latter compound could be a precursor in the formation of Turnbull's Blue or an excited state of Prussian Blue, but it is not a stable chemical species.

Introduction

The iron hexacyanoferrates have been an exhaustively studied family of complexes. The best known and most stable member is ferric ferrocyanide or Prussian Blue (PB). Ferric ferricyanide, Prussian Brown (PBr), is an unstable product which, in air, passes through a green phase, Prussian Green (PG), and ends up in PB. PG is not a definite compound but a mixture of PBr and PB [1, 2]. Ferrous ferrocyanide, Williamson's White (WW), is a white product that oxidizes rapidly in air to PB [3, 4]. When solutions of Fe^{2+} and $[\text{Fe}(\text{CN})_6]^{3-}$ are mixed, the insoluble Turnbull's Blue (TB) precipitates. TB is not ferrous ferricyanide but a ferric ferrocyanide, similar but not identical to PB [1]. The elusive ferrous ferricyanide cannot be detected in the reduction of PBr [1] or in the oxidation of WW or PB [1, 2]. However, many researchers have endeavored to obtain this (notorious) species [5–10]. In this paper we present a critical review of the published results, together with new experimental evidence on this subject, and arrive at the conclusion that ferrous ferricyanide does not exist as a stable chemical species.

Experimental

Samples of PB, PBr, WW and TB were prepared as described elsewhere [1, 2, 4] and then aged in order to obtain different species of ferric ferrocyanide to be pyrolyzed in vacuum. To minimize the oxidation of WW during its preparation, the mechanochemical reaction [4] was carried out in a glove box containing Ar (99.99%).

The studied compositions correspond to insoluble Prussian Blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$), soluble Prussian Blue ($\text{FeK}[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$), aged Prussian Brown, ($\text{Fe}(\text{H}_3\text{O})[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$) and Turnbull's Blue ($\text{Fe}_3(\text{OH})[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$), labeled, IPB, SPB, APBr and TB, respectively. These complexes correspond to the samples Nr. 1, 2, 11 and 23 in a previous work [1], whose nature and purity were established by chemical analysis, i.r. and Mössbauer spectroscopies, and X-ray powder diffraction (XRD).

The expected Mössbauer spectrum for a stoichiometric ferrous ferricyanide ($^{\circ}\text{Fe}_3[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$) was experimentally simulated from a mixture of nickel ferricyanide ($\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$) and ferrous cobalticyanide ($\text{Fe}_3[\text{Co}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$) in a 2:3 molar ratio. This mixture and in this molar ratio guarantee the expected low spin iron(III) and high spin iron(II) populations corresponding to a hypothetical stoichiometric ferrous ferricyanide, and in the appropriate structural environments. Nickel ferricyanide and ferrous cobalticyanide were prepared and characterized as previously described [11, 12].

The vacuum pyrolysis of IPB, SPB, APBr and TB samples was carried out at 10^{-6} Torr, during 1 h heating at 250, 350 and 400 °C in sealed glass tubes. To prevent their oxidation the pyrolyzed samples were handled in an Ar atmosphere using a glove box and were then preserved in Nujol. The pyrolysis products obtained in this manner were characterized by i.r. and Mössbauer spectroscopies. The i.r. spectra were recorded in Nujol using an FT-IR spectrometer (Atti Matson, Genesis Series).

The Mössbauer spectra were recorded at room temperature with a ^{57}Co in Rh in source, using a constant acceleration spectrometer. All spectra were fitted using an iterative least squares minimization

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