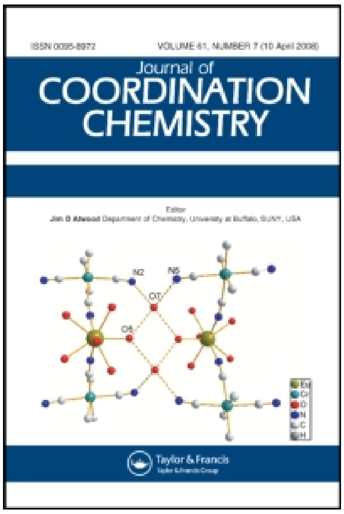

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Ferrous Ferricyanide: Aqueous Preparation

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SHORT COMMUNICATION
Ferrous Ferricyanide: Aqueous Preparation

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Ferrous Ferricyanide is not normally produced by adding a ferrous salt to a ferricyanide compound in aqueous solution, although it has been formed by vacuum pyrolysis of ferric ferrocyanide. An aqueous preparation is described here which yields ferrous ferricyanide. The most important condition is the maintenance of a reducing condition, such as excess potassium ferrocyanide, KI, or sucrose. Neither pH nor ionic strength play a significant role.

INTRODUCTION

Until a few years ago, Prussian Blue and Turnbull's Blue were thought to be the distinct compounds ferric ferrocyanide and ferrous ferricyanide. Mössbauer evidence showed both to be the same,[1,2] namely Prussian Blue. Ferrous ferricyanide has recently been prepared by gentle vacuum pyrolysis[3,4] of Prussian Blue. We report now another preparation of ferrous ferricyanide, which was accidentally discovered in the course of preparing soluble and insoluble Prussian Blue, and which proceeds in aqueous solution at room temperature.

SAMPLE PREPARATION AND ANALYSIS

Insoluble Prussian Blue ($Fe_4[Fe(CN)_6]_3$) is formed by the dropwise addition of $K_4Fe(CN)_6$ into acidic $FeCl_3$ (HCl added). A mixture[5] of soluble ($KFeFe(CN)_6$) and insoluble Prussian Blue is obtained by dropwise addition of $FeCl_3$ to $K_4Fe(CN)_6$. These aqueous solutions are all nominally 0.2 normal. It was noticed that precipitate from $FeCl_3$ dropwise added to a considerable excess of $K_4Fe(CN)_6$ was black, rather than the normal Prussian Blue color. Mössbauer spectra indicated that considerable high-spin ferrous iron was present.

The Mössbauer spectra were obtained with a constant acceleration spectrometer. Calculation of the velocity was obtained by laser interferometry.[6] Velocities are reported with respect to iron foil. Although both RT (room temperature) and liquid nitrogen data were taken, the RT data alone are reported since the spectra are better resolved at this temperature.

To maintain an excess of ferrocyanide, $FeCl_3$ was dropwise added into saturated $K_4Fe(CN)_6$, and the resulting black compound gives the Mössbauer spectrum of Figure 1a. Of the three resolved peaks, the right one is clearly indicative of high-spin ferrous iron. The unambiguous identification of the center line is effected by isotopic enrichment. In Figure 1b, the high-spin iron has been labelled by using $^{57}FeCl_3$ as reactant. Also, by using $^{56}FeCl_3$, the low-spin iron can be viewed clearly (Figure 1c). No resolved quadrupole splitting is apparent in this ferricyanide iron, but the line width is larger than in the comparable Prussian Blue, 0.460 mm/s vs. 0.395 mm/s. (Figure 1d). Prussian Blue is recovered from ferrous ferricyanide by exposure to warm dilute HCl for one hour. The resulting ferrous ferricyanide is quite similar to that previously reported by vacuum pyrolysis of Prussian Blue[4]. A major difference, however, is that no cyanide rotation is permitted under the gentle reaction condition. In Figure 1c, the ferricyanide ion is quite clean and is not overlapped with some ferrous iron as occurs when $^{56}Fe_4[Fe(CN)_6]_3$ is pyrolyzed[7].

In searching for the experimental conditions which lead to the formation of ferrous ferricyanide, pH and ionic strength were varied without effect. Ultimately. a reducing solution turned out to be the dominant requirement. In Figure 2, stoichiometric amounts of $FeCl_3$ and $K_4Fe(CN)_6$ have been reacted in the presence of (a) concentrated KI and (b) sucrose. In Figure 1(c), $FeCl_2$ and $K_3Fe(CN)_6$ were reacted in concentrated KI to produce ferrous ferricyanide.

Infrared bands at 600 (weak) and 500 cm^{-1} (medium) are characteristic of Prussian Blue. The ferrous ferricyanide, whether from the chemical preparation or the pyrolysis of Prussian Blue, shows a new strong band at 590 cm^{-1}, similar to that of $K_4Fe(CN)_6$.

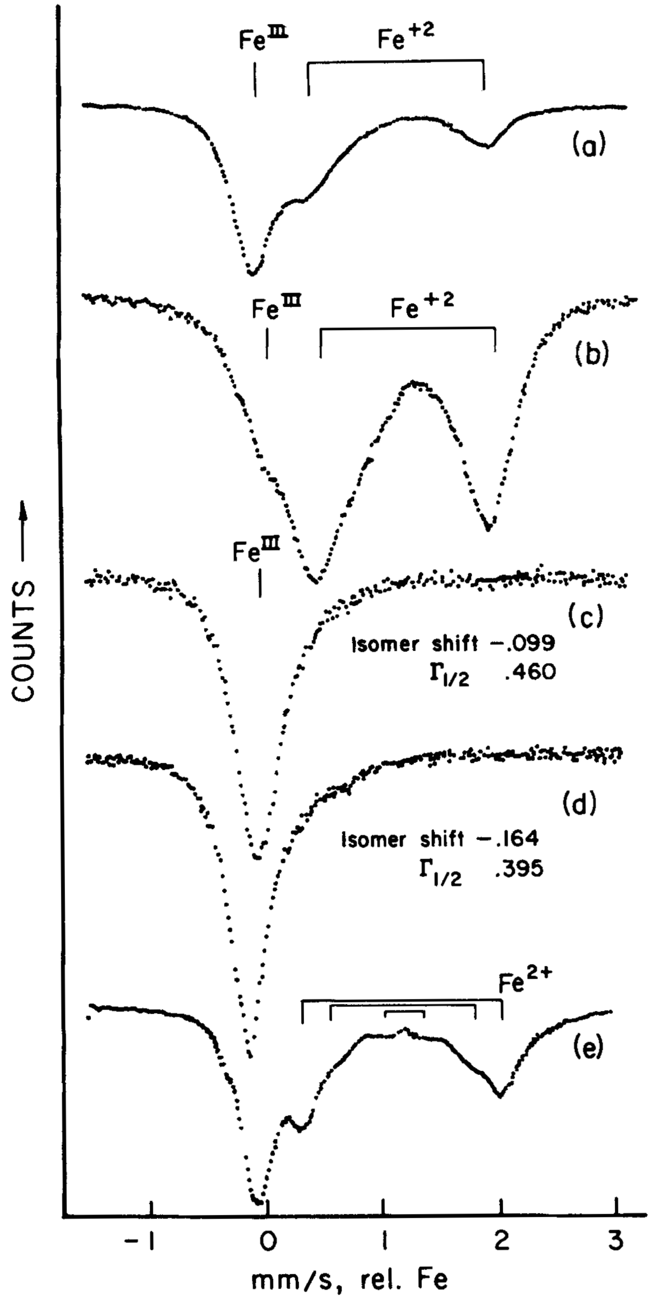

FIGURE 1. (a) $FeCl_3 + K_4Fe(CN)_6$ [saturated solution] (b) $^{57}FeCl_3 + K_4Fe(CN)_6$ [saturated solution] (c) $^{56}FeCl_3 + K_4Fe(CN)_6$ [saturated solution] (d) Previous compound converted to Prussian Blue. (e) Ferrous ferricyanide from 300°C pyrolysis of Prussian Blue.

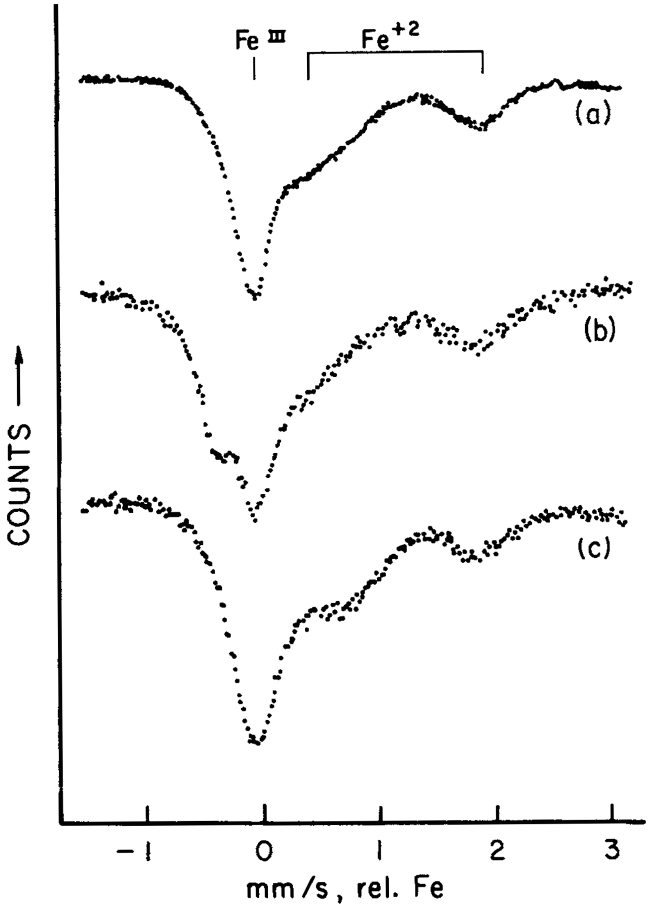

FIGURE 2. (a) $FeCl_3 + K_4Fe(CN)_6$ in concentrated KI solutions. (b) $FeCl_3 + K_4Fe(CN)_6$ in concentrated sucrose solution. (d) $FeCl_2 + K_3Fe(CN)_6$ in concentrated KI solution.

DISCUSSION

The complexity of the Prussian Blue – ferrous ferricyanide system is probably tied to the very close redox potentials, $Fe^{2+} | Fe^{3+}$ and $Fe(CN)_6{}^{4-} | Fe(CN)_6{}^{3-}$, −.77 and −.71 volt in 1 M acid solution[8]. Of the two, the high-spin iron is more accessible to the influence of reagents such as the reducing agents employed here. The mild reducing agents are incapable of converting Fe^{3+} to Fe^{2+}. but only the difference in redox potential (i.e., ~.06 volts) is required to convert ferric ferrocyanide to ferrous ferricyanide.

A problem of this preparation is purity. The initial product is contaminated with the excess $K_4Fe(CN)_6$, and washing to remove this converts some ferrous ferricyanide to Prussian Blue. A better mild reducing agent for incorporation into the wash water would be useful.

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