Preparation of Ferrous Ferricyanide (Not Turnbull's Blue)

J. G. Cosgrove,[1a] R. L. Collins,*[1a] and D. S. Murty[1b]

Contribution from the Physics Departments, The University of Texas at Austin, Austin, Texas, and Saint Mary's University, Halifax, Nova Scotia, Canada.

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Abstract: Despite the good intentions of the preparative chemist, both Turnbull's Blue and Prussian Blue are the same material, ferric ferrocyanide. That is, the high-spin iron is ferric and the low-spin iron is ferrous. Ferrous ferricyanide *can* be prepared from ferric ferrocyanide by vacuum pyrolysis at 400°C, with loss of entrapped water. It is concluded that the contained water creates an internal pressure, and so favors the formation of ferric ferrocyanide. The absence of this pressure favors ferrous ferricyanide. This ferrous ferricyanide is stable if kept dry but converts to ferric ferrocyanide rapidly on contacting with warm dilute HCl or slowly on standing in humid air. Identification of valences was made with Mössbauer spectroscopy.

The synthesis of ferrous ferricyanide was discovered, accidentally, in the course of determining the consequences of vacuum pyrolysis of Prussian Blue. It had been suggested that Fe metal and Fe_3C result from high-temperature pyrolysis, and this was confirmed. The synthesis[1-3] of ferrous ferricyanide, $Fe_3{}^{2+}(Fe^{III}(CN)_6)_2$, by vacuum pyrolysis at lower temperature of Prussian Blue (ferric ferrocyanide, $Fe_4{}^{3+}(Fe^{II}(CN)_6)_3 \cdot xH_2O$) completes the preparation of the quartet of iron–iron cyanides. The valence of the iron ions in these two sites was not experimentally measurable, prior to Mössbauer spectroscopy. Using this technique, Prussian Blue, prepared by mixing the solutions containing ferric and ferrocyanide ions, and Turnbull's Blue, prepared by mixing solutions containing ferrous and ferricyanide ions, gave similar compounds.[4-7] An internal redox occurs in Turnbull's Blue and the electron moves spontaneously from cation to anion. Figure 1 illustrates the face-centered cubic structure of Prussian Blue.[5]

The ferric iron occupies two sites, termed metal I and metal II. Metal I is in the nitrogen hole of the cyanide ligands, while metal II sits randomly in the large cages together with water molecules.

Identification of the cation as high-spin ferrous (2+) or ferric (3+) iron, and of the iron cyanide as low-spin ferrous (II) or ferric (III) iron, is readily made by Mössbauer spectroscopy. These four kinds of iron yield distinctive patterns[8] as shown in Figure 2.

The concentration of ^{57}Fe in normal iron is 2.16%. Hence, by means of ^{57}Fe enrichment, selective enhancement of the cation and anion iron spectra could be made. This simplifies the otherwise overlapping spectra.

Preparation of Samples

Ferric ferrocyanide (Prussian Blue) was prepared by rapid mixing of aqueous solutions of ferric chloride and potassium ferrocyanide. The precipitated gel was filtered and washed three times in distilled water, and then dried in air. An optimum ferrous ferricyanide preparation involved a mild vacuum pyrolysis of ferric ferrocyanide. The conditions of pyrolysis were a vacuum of less than 1 mm and a temperature of 673°K for 10 min. The ferrous ferricyanide was allowed to cool *in vacuo*.

Selective enrichment of Fe^{3+} and Fe^{II} in the Prussian Blue was performed by the method described by Maer, *et al.*[5]

Turnbull's Blue (ferric ferrocyanide) was prepared by rapid mixing of aqueous solutions of potassium ferricyanide and ferrous chloride. The precipitated gel was filtered, washed three times in distilled water, and then air-dried. Mössbauer and ir spectra of Turnbull's Blue were identical with the spectra of Prussian Blue. Vacuum pyrolysis of Turnbull's Blue also produced ferrous ferricyanide.

Mössbauer Spectra

The Mössbauer spectra were obtained on a constant-acceleration spectrometer. A 50-mCi ^{57}Co-in-copper source was used at room temperature. The samples were supported between filter paper disks and mounted in a copper "cold finger" in a dewar with Mylar windows. Calibration was obtained by laser interferometry.[9] All velocities were reported relative to the center of the splitting of the inner lines of iron foil at room temperature.

Data

In the process of vacuum pyrolysis of Prussian Blue, DTA and TGA traces indicate the temperatures at which significant changes occur. In Figure 3, a gradual weight loss and endothermic DTA are observed until 175°C. A sharp exothermic peak occurs at 290°C with further weight loss. Along with a loss of water, small amounts of cyanogen were also noted by means of gas chromatography and ir.

A series of Mössbauer spectra were run on the Prussian Blue samples pyrolyzed at the temperatures indicated on the DTA in Figure 3. Figure 4 shows the Mössbauer spectra of the series of pyrolyzed Prussian Blue taken at 24°C, and Figure 5 shows the same series

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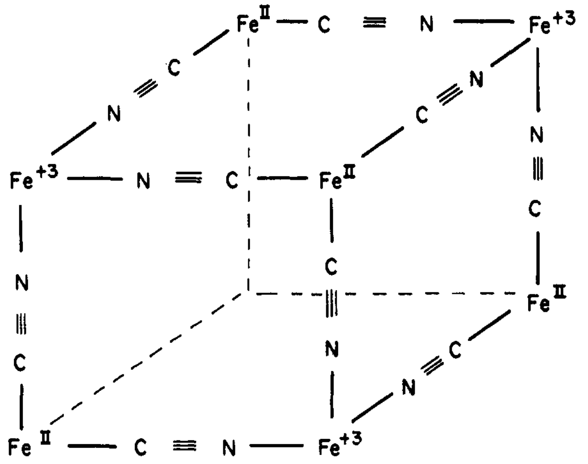

Figure 1. One-eighth unit cell of Prussian Blue.

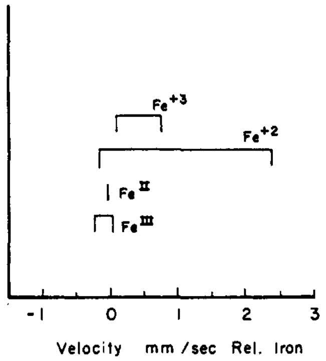

Figure 2. Typical line positions for different oxidation states of Fe.

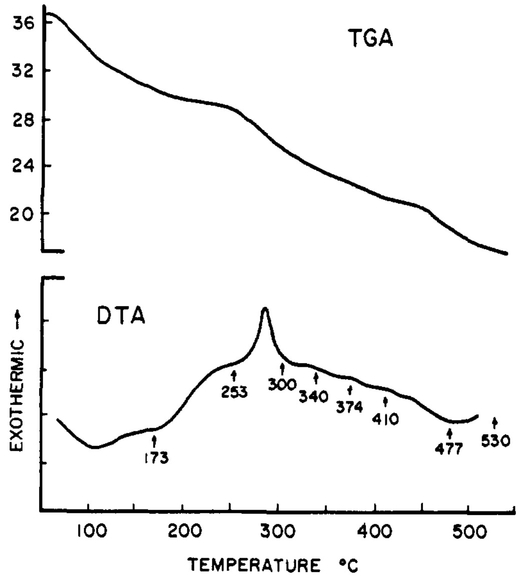

Figure 3. DTA and TGA of Prussian Blue.

at 77°K. In the 253°C pyrolyzed material, there first appears a trace of high-spin Fe^{2+}. The high-spin Fe^{2+} peaks are quite evident in material pyrolyzed at 300°C. As the temperature of pyrolysis is increased, it can be seen that ferrous iron occupies two sites, termed metal I and metal II. In Figure 6 of Mössbauer spectra taken at 77°K, 24°C, and 100°C, the quadrupole splittings of the metal I and metal II ferrous iron decrease with temperature. The metal II iron splitting decreases faster than the splitting of metal I.

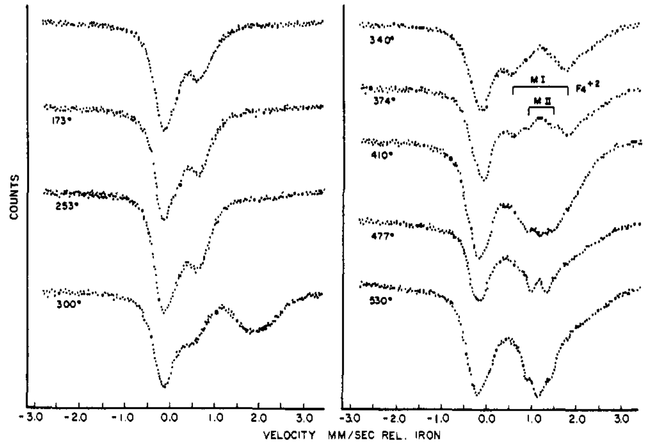

Figure 4. Mössbauer spectra at 24°C of pyrolyzed Prussian Blue.

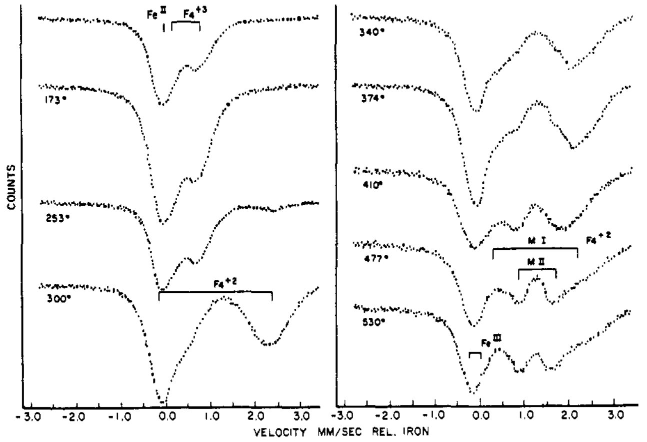

Figure 5. Mössbauer spectra at 77°K of pyrolyzed Prussian Blue.

In order to separate the overlapping Mössbauer spectra, the Fe^{3+} and Fe^{II} ions in Prussian Blue were separately enriched in ^{57}Fe. Figure 7 illustrates the pyrolysis of the $^{57}Fe^{3+}$ enrichment. The labeled ferric iron clearly proceeds on pyrolysis to ferrous iron. The results of the enrichment of the ferrous iron are similar.

Contrary to our conclusion in *Nature*,[3] contact with humid air at room temperature causes the ferrous ferricyanide to be slowly converted to Prussian Blue. In Figure 8, the X-ray diffraction pattern for the ferrous ferricyanide exposed to humid air for 1 day shows traces of Prussian Blue. The ir spectra of Prussian Blue and ferrous ferricyanide were quite similar but not identical.

Reconstitution

That Prussian Blue can be readily reconstituted indicates that little lattice damage is done in vacuum pyrolysis below 450°C. In Figure 9, the original Prussian Blue is A. Ferrous ferricyanide prepared in a vacuum pyrolysis at 410°C is shown in Figure 9B. The ferric ferrocyanide can be promptly reconstituted by treating the ferrous ferricyanide with warm dilute HCl for 5 min. The Mössbauer spectrum of the reconstituted Prussian Blue is illustrated in Figure 9C. Treating the ferrous ferricyanide with warm dilute NaOH for 5 min produces a ferrimagnetic compound. Mössbauer spec-

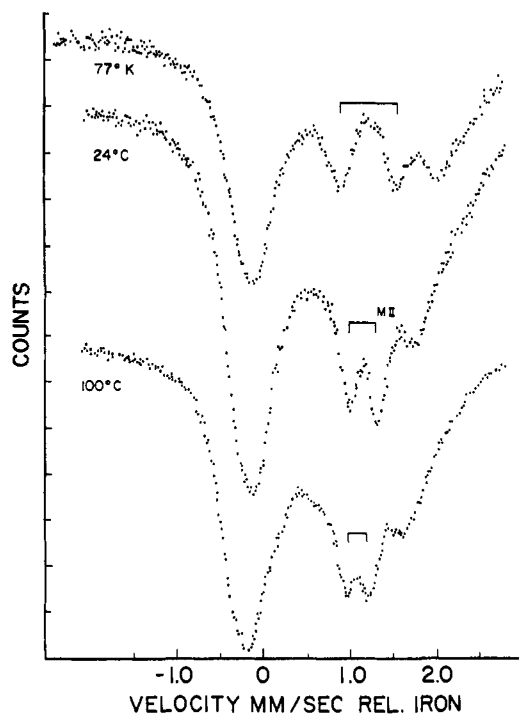

Figure 6. Mössbauer spectra of Prussian Blue pyrolyzed at 460 °C.

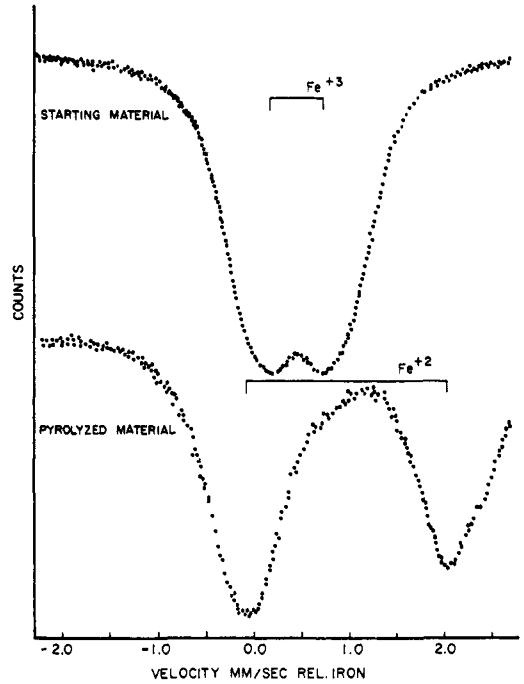

Figure 7. Ferric enrichment of Prussian Blue, pyrolysis at 400 °C.

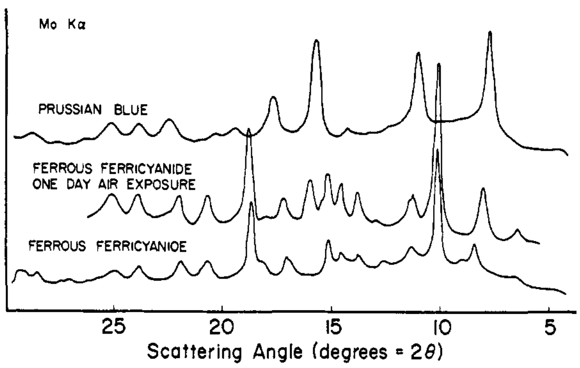

Figure 8. X-Ray diffraction patterns.

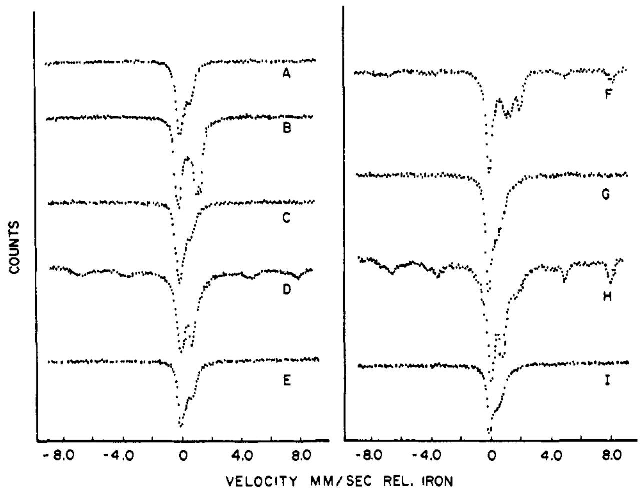

Figure 9. Reconstitution of Prussian Blue.

trum Figure 9D indicates that the compound contains some Fe_3O_4. However, with acid treatment, the Fe_3O_4 is dissolved and ferric ferrocyanide is reconstituted. Note Figure 9E.

Pyrolysis of Prussian Blue at atmospheric pressure in air for 10 min at 410°C produces a mixture of ferrous ferricyanide and Fe_3O_4 as shown in Figure 9F. The Fe_3O_4 forms on the outside of the particles from visual examination of fractured granules. Again with acid treatment, in Figure 9G, the Fe_3O_4 is dissolved and the ferric ferrocyanide is reconstituted. Base treatment of the air-pyrolyzed material, Figure 9H, produces a similar compound to that of the base-treated vacuum-pyrolyzed material. On acid treatment of the base-treated material, the Fe_3O_4 is dissolved and the Prussian Blue is reconstituted. This is illustrated in Figure 9I.

Infrared spectra and X-ray diffraction patterns of Prussian Blue and the reconstituted material are the same.

Conclusion

Vacuum pyrolysis of Prussian Blue produces ferrous ferricyanide, the valences of the iron being clearly identified in the selectively enriched Mössbauer data. The effect of the mild vacuum pyrolysis is primarily that of forcing out the trapped water in the cages. As illustrated in Figure 1, the metal II sits randomly in the cages with the water. As the water is driven out, and the volume available increases, the thermal motion of metal II increases relative to metal I, and the quadrupole splitting diminishes. Figure 6 of Mössbauer spectra taken at 77°K, 24°C, and 100°C supports this conclusion. In the TGA, there is a 40% weight loss. This loss of water presumably relieves the internal pressure and so reduces the lattice distance and leads to the reversal of the redox process. Fung and Drickamer[10] have reported that with external pressures of 145 to 200 kbars, much of the high-spin Fe^{3+} was reduced to high-spin Fe^{2+}, and at an external pressure of 4 kbars the low-spin Fe^{II} showed partial conversion to low-spin Fe^{III}. At 145 kbars, not

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only is there a conversion to low-spin Fe^{III}, but there appears high-spin Fe^{2+}. The process was reversible with a decrease in applied pressure. However, when water is removed by vacuum pyrolysis, we find that the conversion is reasonably stable.

The pyrolysis does not completely destroy the well-ordered structure of Prussian Blue. The X-ray diffraction patterns indicate the ferrous ferricyanide is also crystalline, different from Prussian Blue. The major peaks in ferrous ferricyanide have moved to larger diffraction angles which is consistent with considerable shrinkage in the lattice. A slow conversion occurs in humid air, ferrous ferricyanide to Prussian Blue. X-Ray diffraction patterns of reconstituted ferric ferrocyanide by acid treatment are identical with those of Prussian Blue. The X-ray spectrum of ferrous ferricyanide has not been satisfactorily interpreted. Attempts to index all lines to a cubic lattice have failed. Hence, either the lattice is noncubic or there are more than one lattice present. We expect that the structure of ferrous ferricyanide will be found to be very close to that of Prussian Blue, except that the lattice spacing will be less as a result of water loss and, of course, the valences of the iron ions differ.

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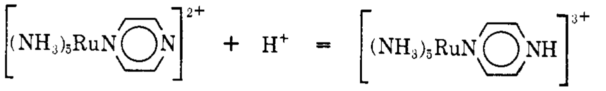
Binuclear Complexes of Ruthenium Ammines

Carol Creutz and H. Taube*

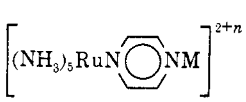
Contribution from the Chemistry Department of Stanford University,
Stanford, California 94305. *Received July 24, 1972*

Abstract: The preparation of the species $[(NH_3)_5Ru]_2pyr^{4+, 5+, or 6+}$ in solution is described, as is that of solid phases containing each of the three cations. The species of intermediate oxidation state with the ion bearing a charge of 5+ is shown to be stable in solution with respect to disproportionation to the 4+ and 6+ states. In addition to a band at 565 nm (ϵ 2.1 × 10^4), where the 4+ (but not the 6+ ion) also shows strong absorption, it shows absorption at 1560 nm. Neither the 4+ nor 6+ species shows absorption in this region of the spectrum. Following Hush, this absorption is assigned as an intervalence transition. The validity of this interpretation of the spectrum depends on the ion in the ground state conforming to the oxidation state description [2+, 3+] rather than to [2$^1/_2$, 2$^1/_2$]. The evidence in support of the "deeply trapped" description is reviewed. When the ruthenium atoms are made substitutionally nonequivalent, the near-ir absorption always shifts to shorter wavelengths, the shift corresponding in energy to the stabilization of one oxidation state relative to the other brought about by the substitutional changes. When the solvent is changed, only slight shifts in the ir absorption maximum are recorded (to 1580 in ethanol (D = 24), 1595 in formamide (D = 109)).

Physical properties of a number of ruthenium(II) pentaammine complexes with π-acceptor ligands (aromatic heterocycles,[1,2] organonitriles,[3] carbon monoxide,[4] and dinitrogen[5]) have been reported. The studies of Ford, *et al.*,[1] on the equilibrium



demonstrating the enhanced basicity of pyrazine when complexed to Ru(II), suggested to us the possibility of replacing the proton with another metal ion M^{n+} to give binuclear complex $[(NH_3)_5Ru(pyr)M]^{2+n}$ (pyr = pyrazine)



Such binuclear complexes are of interest in the further study of the Ru(II)–ligand backbonding interaction[1,6] and in studies of metal–metal interaction mediated by bridging ligands.

In the course of our experiments, we prepared a series of mixed-valence Ru(II)–Ru(III) complexes. The physical properties of these ions are of interest in the growing field of mixed valence compound studies.[7,8] In addition, the interpretation of their electronic spectra may lead to greater understanding of the energetic requirements of electron transfer processes.[9,10] Spectral and other physical properties of $[(NH_3)_5Ru]_2pyr^{n+}$ (n = 4, 5, 6) and related compounds are reported and discussed here.

Experimental Section

Spectra. Ultraviolet–visible range spectra were measured on a Cary 14 or Cary 15 recording spectrophotometer at room temperature. Extinction coefficients of binuclear Ru(II) complexes in the ultraviolet–visible region were measured as follows. An exactly weighed *ca.* 3-mg sample of the solid salt weighed into a weighing

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