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The Pivotal Role of Mössbauer Spectroscopy in the Characterization of Prussian Blue and Related Iron Cyanide Complexes

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Abstract

For 50 years, ^{57}Fe Mössbauer spectroscopy has played a pivotal role in the characterization of Prussian blue complexes and many related iron cyanide complexes, a pivotal role that is extensively illustrated in this paper. For the benefit of the young Mössbauer spectroscopists, the successes, the failures, and the pitfalls reported in the literature are discussed. The successes include the unquestionable distinction of iron oxidation and spin states in Prussian blue and the determination that Prussian blue and Turnbull's blue are the same. The failures include the distinction between low-spin Fe^{II} and high-spin Fe^{III}cations in Berlin green. The pitfalls include many, sometimes poorly determined, hyperfine parameters that have been reported for complexes whose stoichiometry is either unknown or unspecified and even sometimes incorrect.

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Fernande Grandjean obtained a Ph.D. in physics from the University of Liège, Belgium in 1973. She has pursued her scientific career at the University of Liège and was promoted to Chargé de Cours in 1983, Professor in 1992, and Ordinary Professor in 2002. She retired in 2008 and now holds an appointment as Adjunct Professor in Chemistry with the Missouri University of Science and Technology. In parallel with her teaching career, she pursued research in Mössbauer spectroscopy. Her 250 publications deal mostly with permanent magnet and thermoelectric materials, spin-transition and spin-crossover compounds, minerals, and various oxides.

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1. Introduction

Iron cyanide complexes form a challenging group of complexes for study by Mössbauer spectroscopists and were investigated [1-5] by ^{57}Fe Mössbauer spectroscopy as early as 1962, *i.e.*, only four years after Mössbauer's discovery of the effect. Indeed, since 1962, ^{57}Fe Mössbauer spectroscopy has played a pivotal role in the characterization of these complexes. Unfortunately, the challenges associated with both working on complexes of poorly defined stoichiometry and the problems of deconvoluting often partially or poorly resolved Mössbauer spectra have led to a good deal of confusion in the earlier literature dealing with Prussian blue and the many related iron cyanide complexes. Some of these problems will be discussed herein.

The emblematic representative of the iron cyanide complexes is Prussian blue, a mixed valence complex that can be either a ferric ferrocyanide, Fe^{III} hexacyanoferrate(II), complex with an ideal $Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot xH_2O$ composition, when in its so-called *insoluble* form, or a complex with the $AIFe^{III}[Fe^{II}(CN)_6] \cdot xH_2O$ composition, when in its so-called *soluble* form.

When Prussian blue is completely or partially oxidized, Prussian yellow or Berlin green are formed, respectively. Prussian yellow is ferric ferricyanide, Fe^{III} hexacyanoferrate(III), whereas Berlin green is a solid solution of Prussian blue and Prussian yellow. Further, when Prussian blue is reduced, Berlin white or Everitt's salt, is formed as a ferrous ferrocyanide, Fe^{II} hexacyanoferrate(II), complex. The oxidation process of Berlin white and the successive colors of the pigments are schematically represented in Scheme 1 where in (Fe^{n+}, Fe^{m+}) Fe^{n+} represents the $n+$ iron cation coordinated to six CN^- nitrogens and Fe^{m+} represents the $m+$ iron cation coordinated to six CN^- carbons.

These various Prussian blue related complexes offer a very lucrative field of investigation for ^{57}Fe Mössbauer spectroscopy, a technique that is an ideal and essentially unique method for determining both the oxidation state and the spin-state of iron ions in a solid, a determination that is often not possible by x-ray diffraction and is very difficult by iron *K*-edge x-ray absorption spectroscopy.

In addition to the variety of iron oxidation states that Prussian blue and its derivatives can provide, the iron cyanide complexes have many attractive physical properties. Their most obvious property is their color, a color that is of course evident from their common names and is a strong indicator of the nature of a reaction product.

Prussian blue was accidentally discovered [6,7] in 1704, a year that is often accepted but is still sometimes in dispute, by a Berlin dyemaker, Johann Jacob Diesbach. Subsequently, all of the variously colored iron cyanides have been used [8] extensively as artists' pigments or dyes and the study of their state of conservation in artwork is currently an active field of research [7].

Prussian blue has an open, non-compact, cubic structure, see Section 2, whose voids can host water molecules or monovalent cations and thus Prussian blue, with a channel diameter of ca. 3.2 Å, can be used [9,10] as a molecular sieve or an ion exchange complex.

Over the past twenty-five years or so, Prussian blue analogues have been synthesized and they offer a wide range of attractive physical properties. These properties include high Curie temperature molecular magnetism [11], photoinduced magnetism [12,13], photocontrolled pole reversal [14], photochromism and thermochromism [15], and spin-state transitions [16]. In the investigation of these attractive properties, ^{57}Fe Mössbauer spectroscopy has played an important role because of its ability to easily distinguish the different oxidation states and spin states of the iron ions. Finally, Prussian blue has not

$$\underset{\text{Berlin white}}{(Fe^{2+}, Fe^{2+})} <\!\!-\!\!\!-\!\!> \underset{\text{Prussian blue}}{(Fe^{3+}, Fe^{2+})} <\!\!-\!\!\!-\!\!> \underset{\text{Berlin green}}{[(1-\delta)\,(Fe^{3+}, Fe^{2+}) + \delta(Fe^{3+}, Fe^{3+})]} <\!\!-\!\!\!-\!\!> \underset{\text{Prussian yellow}}{(Fe^{3+}, Fe^{3+})}$$

Scheme 1. The iron cation oxidation states and colors of several iron cyanide complexes.

escaped use in the nano-world: both nanoparticles [17] and nanowires [18] derived from Prussian blue have been prepared and studied by ^{57}Fe Mössbauer spectroscopy.

In this paper, the pivotal role of ^{57}Fe Mössbauer spectroscopy in the characterization of iron cyanides and more specifically Prussian blue is reviewed through selected examples from the literature published between 1962 and 2012. The successes, the failures, and the drawbacks of the technique are examined for the benefit of the reader and especially for the younger members of the Mössbauer-effect community.

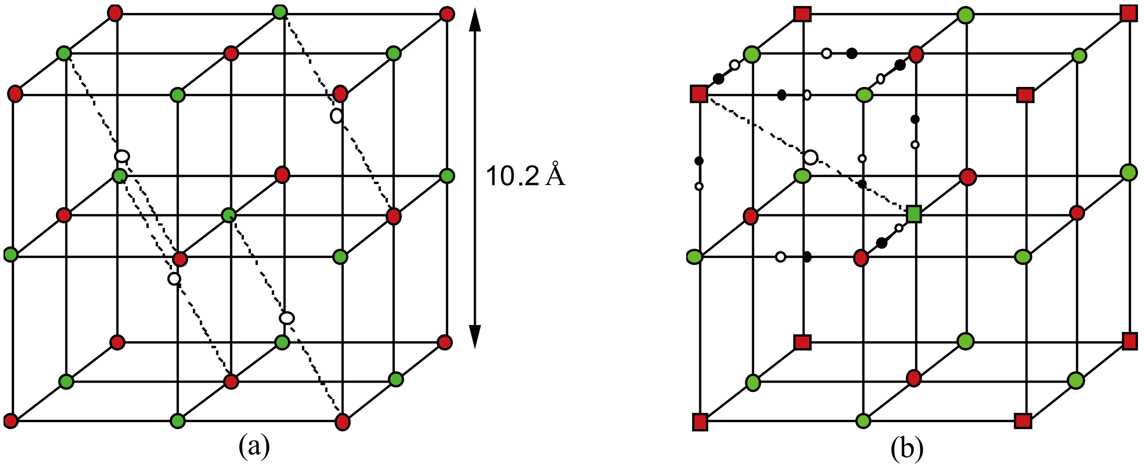
2. Crystallographic Structure of Prussian Blue

For many years both the detailed stoichiometric composition of Prussian blue and its crystallographic structure were unsolved problems. The colloidal character of Prussian blue led to much of this difficulty because Prussian blue frequently adsorbs impurities such as alkali cations or organic solvents into the open structure of its extremely fine particles. At this time Prussian blue is known to have a hydrated Fe^{III} hexacyanoferrate(II) anion, $\{Fe^{III}[Fe^{II}(CN)_6]\cdot x\text{H2O}\}^-$, with values of x that vary up to 16 and a cation that can be K^+, NH_4^+, or Na^+.

Any alkali-free $Fe_4^{III}[Fe^{II}(CN)_6]_3\cdot xH_2O$ Prussian blue must contain an increased amount of Fe^{III} to maintain charge balance; such an alkali-free Prussian blue is commonly referred to as an *insoluble* Prussian blue. In contrast, Prussian blues containing alkali cations are referred to as *soluble* Prussian blues. Even though all Prussian blues have a solubility product of ca. 1×10^{-41}, the *soluble* designation refers to the greater ease with which a *soluble* Prussian blue may be dispersed in water to form a colloidal suspension.

Keggin and Miles [19] by using powder x-ray diffraction, first reported in 1936 a structural study of soluble and insoluble Prussian blues. The soluble Prussian blue was reported to be cubic with $a = 10.2$ Å and to have an alternating arrangement of Fe^{II} and Fe^{III} ions with bridging CN$^-$ anions to yield a six-fold coordinated structure with the alkali metal ions found in the centers of some of the cubic lattice cavities; water was also located inside these cavities, see Fig. 1a. Keggin and Miles [19] also proposed a similar structure for the insoluble, $Fe_4^{III}[Fe^{II}(CN)_6]_3\cdot xH_2O$ Prussian blue, but one in which the additional Fe^{III} ions replaced the alkali metal cations.

In 1977 the single crystal x-ray structure of insoluble Prussian blue was solved by Buser et al. [20]. They reported a single crystal structure with a virtually ideal composition of $Fe_4^{III}[Fe^{II}(CN)_6]_3\cdot 15H_2O$. They developed a model consisting of a cubic Fe^{II}-CN-Fe^{III} framework in which some of the $[Fe^{II}(CN)_6]^{4-}$ sites were vacant, see Fig. 1b. In well formed single crystals these vacancies are crystallographically ordered and yield a primitive cubic cell with the *Pm3m* space group. In contrast, in very fine polycrystalline powders, the structure could be best approximated by a face-centered cubic cell with the *Fm3m* space



(a) (b)

Figure 1. (a) The structure [19] of soluble Prussian blue, $A\text{Fe}^{III}[Fe^{II}(CN)_6]$. The green and red circles represent Fe^{II} and Fe^{III} ions, respectively. The open circle represents the alkali metal cation, A^+. The CN$^-$ anions are not shown. (b) The unit cell of Prussian blue in the space group *Pm3m* [20]. The green and red symbols represent Fe^{II} and Fe^{III} ions, respectively, and the circle and square symbols indicate different crystallographic positions. The large open circle and the small open and closed circles represent oxygen, carbon, and nitrogen, respectively.

group. In the *Pm3m* structure the Fe^{III} completely occupies the 1*a* and 3*c* crystallographic sites, sites that are shown in Fig. 1*b* by the red squares and circles, respectively; the Fe^{II} partially occupy the 1*b* and 3*d* sites that are shown as the green squares and circles, respectively. In contrast, in the *Fm3m* structure Fe^{III} fully occupies the 4*a* crystallographic site and Fe^{II} randomly occupies the 4*b* site with a fractional occupancy of 0.75.

Because of the increased sensitivity of neutron diffraction to the water positions, in a neutron diffraction study of insoluble Prussian blue, Herren et al. [21] extended the earlier Buser et al. [20] model by refining two crystallographically independent water sites. They found that six water molecules are coordinated to Fe^{III} at the empty nitrogen positions and that eight water molecules either occupy the center of the Prussian blue unit-cell octants or are linked by hydrogen bonding to the coordinated water. Although this structural model of insoluble Prussian blue is now commonly accepted, the structure of soluble Prussian blue is still a matter of some debate. This debate is not central to the present paper and the interested reader is referred to ref. 7 and 22 for further details.

The crystallographic structures of the oxidized and reduced forms of Prussian blue have also been refined [23-25] in the face-centered cubic *Fm3m* structure. The various recently reported Prussian blue analogues often adopt crystallographic structures that are more complex than the simple cubic structures described above and shown in Figure 1. These complex structures are not discussed herein.

3. Mössbauer Spectral Studies of Prussian Blue

3.1. Prussian Blue versus Turnbull's Blue, a Success for Mössbauer Spectroscopy

For many years Prussian blue, a ferric ferrocyanide complex, prepared from an Fe^{III} salt solution and a potassium ferrocyanide solution was thought to be different from Turnbull's blue, a ferrous ferricyanide complex that may be prepared from an Fe^{II} salt and a potassium ferricyanide solution. Because both Prussian blue and Turnbull's blue exhibit [1-5,23] the same ^{57}Fe Mössbauer spectra and the same powder x-ray diffraction pattern, they were both finally recognized to be the same complex, ferric ferrocyanide, Fe^{III} hexacyanoferrate, a class 2 mixed-valence complex [26] Thus, Mössbauer spectroscopy was successfully used to show the equivalence of Prussian blue and Turnbull's blue, the equivalence of their mixed valency structure, and the equivalence of their iron ion electronic spin states.

3.2. Mössbauer Spectra of Various Commercial and Synthetic Prussian Blues

Several synthetic routes are described [7] in the scientific literature and in patents for the synthesis of bulk Prussian blue. One of the authors has successfully reproduced [7] many of these preparations, that originated from the eighteenth to the early twentieth century; The 295 K Mössbauer spectra of eight selected commercial and synthesized samples are shown in Fig. 2. Tables 1 and 2 give the expected composition and the Mössbauer spectral parameters resulting from a fit with one singlet and one symmetric doublet and a fit with two symmetric doublets, respectively. All the lines have a Lorentzian line shape profile.

Although all the spectra, shown in Figure 2 and fit with one singlet and one doublet, exhibit one line

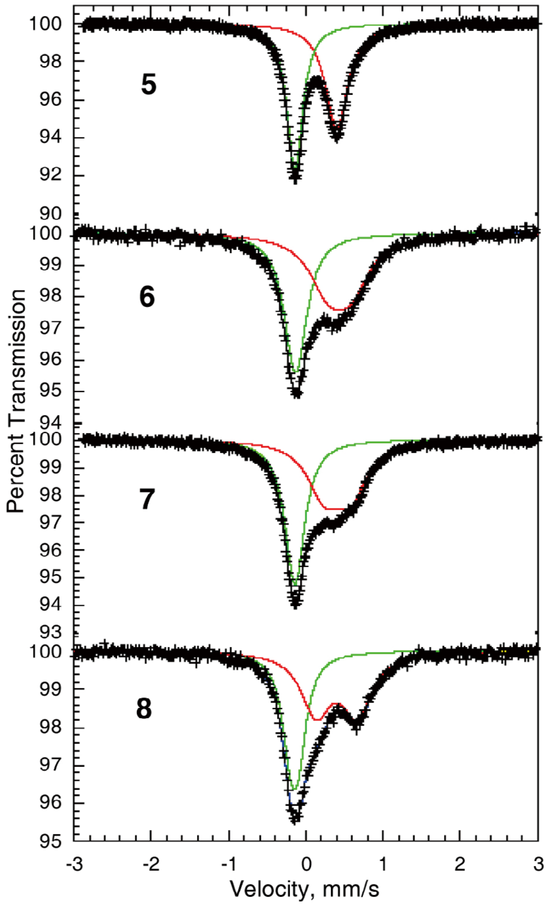


Figure 2. The 295 K Mössbauer spectra of selected Prussian blues prepared by various methods. The green and red solid lines represent the LS Fe^{II} and the HS Fe^{III} components in the fit.

in green at ca. –0.14 mm/s, assigned to the low-spin (LS) Fe^{II} ions and one doublet in red, with an isomer shift of ca. 0.4 mm/s, assigned to high-spin (HS) Fe^{III} ions, the overall shape of the spectra varies with sample preparation and composition. More specifically there is a rather wide range, from zero to 0.63 mm/s, of the Fe^{III} quadrupole splittings, see Table 1. A similar variety of Mössbauer spectra of Prussian blue complexes were also observed [27] by Reguera et al. The Fe^{II} ion in the strong ligand field of its six carbon near neighbors is indeed expected to be in the LS state and to exhibit an isomer shift that is close to zero relative to α-iron at 295 K. In contrast, the Fe^{III} ion in the weak ligand field of its six nitrogen near neighbors is expected to be in the HS state and to exhibit an isomer shift of ca. 0.4 mm/s relative to α-iron at 295 K.

Fits of Prussian blue Mössbauer spectra with one doublet and one singlet are commonly found in the literature. More accurately, it is commonly assumed that the LS Fe^{II} ion does not exhibit any quadrupole interaction because the electronic contribution is zero for a LS ion and the lattice contribution is zero in a perfectly cubic site. However, the experimental results shown in Fig. 2 and given in Table 1 indicate that the Fe^{II} singlet is broadened relative to the natural line width of 0.19 mm/s or to the experimental line width of ca. 0.24 mm/s. Hence, fits with two symmetric quadrupole doublets have been carried out and the resulting spectral parameters are given in Table 2. A close examination of Tables 1 and 2 indicate that the introduction of one additional parameter, the Fe^{II} quadrupole splitting, $\Delta E_Q{}^{II}$, does not significantly affect the isomer shifts, δ^{II} and δ^{III}, the Fe^{III} quadrupole splitting, $\Delta E_Q{}^{III}$, the Fe^{III} line width, Γ^{III}, and the Fe^{II} percent area, A^{II}. As expected, the Fe^{II} line width, Γ^{II}, decreases to a value close to the experimental line width. The Fe^{II} quadrupole splitting, $\Delta E_Q{}^{II}$, ranges from 0.042(1) to 0.114(1) mm/s, values that may be considered as an upper bound value in each spectrum. These small quadrupole splittings result from the presence of disordered vacancies and/or non-stoichiometric excess or deficiency in the A^+ cation. These defects may also result in a distribution of the Fe^{II} isomer shift but obviously the Fe^{II} line widths reported in Table 2 do not justify any more detailed fitting model. It is interesting to note, but may be fortuitous, that all the *soluble* Prussian blues exhibit a smaller Fe^{II} quadrupole splitting than the *insoluble* Prussian blues. The discussion below refers to the numbers given in Table 2.

Table 1. Mössbauer spectral parameters obtained from a singlet and doublet fit of Prussian blues^a

Expected Composition	δ^{II}, mm/s^b	$\Delta E_Q{}^{II}$, mm/s	Γ^{II}, mm/s	$A^{II,c}$, %	δ^{III}, mm/s^b	$\Delta E_Q{}^{III}$, mm/s	Γ^{III}, mm/s
KFe^{III}[Fe^{II}(CN)$_6$]·xH$_2$O, **1**^{d}	–0.138(1)	0	0.277(3)	50(1)	0.406(2)	0.08(3)	0.39(1)
Fe$_4{}^{III}$[Fe^{II}(CN)$_6$]$_3$·xH$_2$O, **2**	–0.139(1)	0	0.306(4)	49(1)	0.413(2)	0.227(5)	0.40(1)
Fe$_4{}^{III}$[Fe^{II}(CN)$_6$]$_3$·xH$_2$O, **3**	–0.154(1)	0	0.278(2)	48(1)	0.393(2)	0.622(3)	0.405(5)
NH$_4$Fe^{III}[Fe^{II}(CN)$_6$]·xH$_2$O, **4**	–0.151(1)	0	0.269(1)	47(1)	0.396(1)	0.545(2)	0.376(3)
KFe^{III}[Fe^{II}(CN)$_6$]·xH$_2$O, **5**	–0.140(1)	0	0.241(1)	46(1)	0.401(1)	0.000(5)	0.409(1)
NH$_4$Fe^{III}[Fe^{II}(CN)$_6$]·xH$_2$O, **6**	–0.131(2)	0	0.350(6)	47(1)	0.437(6)	0.30(1)	0.57(2)
KFe^{III}[Fe^{II}(CN)$_6$]·xH$_2$O, **7**	–0.141(1)	0	0.309(3)	46(1)	0.408(3)	0.339(4)	0.52(1)
Fe$_4{}^{III}$[Fe^{II}(CN)$_6$]$_3$·xH$_2$O, **8**	–0.148(1)	0	0.310(4)	44(1)	0.392(5)	0.545(6)	0.466(9)

^{a}Statistical errors are reported; more realistic errors are ±0.005 mm/s for the isomer shifts, δ, and ±0.01 mm/s for the quadrupole splittings, ΔE_Q, and line widths, Γ. ^{b}The isomer shift, δ, is referred to α-iron powder at 295 K. $^c A^{II}$ is the percent area of the Fe^{II} singlet and $A^{III} = 100 - A^{II}$. ^{d}The composition is unknown but is probably as given.

The commercial Prussian blue complex, **1**, and the synthetic complex, **5**, have ca. zero Fe^{III} quadrupole splitting, whereas the commercial Prussian blue complex, **2**, has a small Fe^{III} quadrupole splitting and the synthetic complexes **3**, **4**, **6**, **7**, and **8** have large Fe^{III} quadrupole splittings. In the case of complexes **3** and **4**, complexes that are well crystallized with large crystallites with dimensions of a few microns [7] as has been shown by scanning electron microscopy, the large Fe^{III} quadrupole splitting may well result from the ordering of vacancies in the crystal structure, an ordering that increases the non-sphericity of the charge distribution around the Fe^{III} ion. In the case of samples **6**, **7**, and **8**, the origin of the large Fe^{III}

Table 2. Mössbauer spectral parameters obtained from a two-doublet fit of Prussian blues[a]

Expected Composition	δ^{II}, mm/s[b]	ΔE_Q^{II}, mm/s	Γ^{II}, mm/s	A^{II},[c] %	δ^{III}, mm/s[b]	ΔE_Q^{III}, mm/s	Γ^{III}, mm/s
$KFe^{III}[Fe^{II}(CN)_6]\cdot xH_2O$, **1**[d]	–0.138(1)	0.076(8)	0.251(7)	48(1)	0.404(2)	0.07(3)	0.40(1)
$Fe_4^{III}[Fe^{II}(CN)_6]_3\cdot xH_2O$, **2**	–0.141(1)	0.114(4)	0.247(6)	46(1)	0.408(3)	0.230(5)	0.41(1)
$Fe_4^{III}[Fe^{II}(CN)_6]_3\cdot xH_2O$, **3**	–0.153(1)	0.106(2)	0.226(3)	47(1)	0.400(2)	0.606(3)	0.401(5)
$NH_4Fe^{III}[Fe^{II}(CN)_6]\cdot xH_2O$, **4**	–0.151(1)	0.088(2)	0.233(2)	47(1)	0.399(1)	0.538(2)	0.372(3)
$KFe^{III}[Fe^{II}(CN)_6]\cdot xH_2O$, **5**	–0.140(1)	0.042(1)	0.237(1)	47(1)	0.400(1)	0.000(5)	0.400(1)
$NH_4Fe^{III}[Fe^{II}(CN)_6]\cdot xH_2O$, **6**	–0.132(2)	0.07(2)	0.33(1)	48(1)	0.435(7)	0.30(1)	0.57(2)
$KFe^{III}[Fe^{II}(CN)_6]\cdot xH_2O$, **7**	–0.141(1)	0.06(1)	0.294(5)	45(1)	0.404(3)	0.340(4)	0.52(1)
$Fe_4^{III}[Fe^{II}(CN)_6]_3\cdot xH_2O$, **8**	–0.146(1)	0.110(6)	0.263(7)	43(1)	0.400(5)	0.530(6)	0.466(9)

[a]Statistical errors are reported; more realistic actual errors are ±0.005 mm/s for the isomer shifts, δ, and ±0.01 mm/s for the quadrupole splittings, ΔE_Q, and line widths, Γ. [b]The isomer shift, δ, is referred to α-iron powder at 295 K. [c]A^{II} is the percent area of the Fe^{II} doublet and $A^{III} = 100 - A^{II}$. [d]The composition is unknown but is probably as given.

quadrupole splitting is not obvious and can only be elucidated through a detailed study of their powder x-ray diffraction patterns as is discussed below.

Our results [7] do not support the oversimplified conclusion reached by Reguera et al. [27] that the Fe^{III} quadrupole splitting was related to the width of the powder x-ray diffraction peaks. A more advanced analysis of the powder x-ray diffraction peaks of the Prussian blue complexes obtained with the Williamson-Hall method [28] yields a *strain* parameter that is related to the presence of lattice defects in the crystallites. As may be seen in Fig. 3, there is a linear, strain, % = 2.07 ΔE_Q + 0.11, correlation between the Fe^{III} quadrupole splitting and the strain in six of the seven Prussian blue complexes; complex **7** is an unannealed form of complex **5** that exhibits a very large strain parameter. As expected, a large Fe^{III} quadrupole splitting is associated with a large strain, indicating the presence of lattice defects in the crystallites.

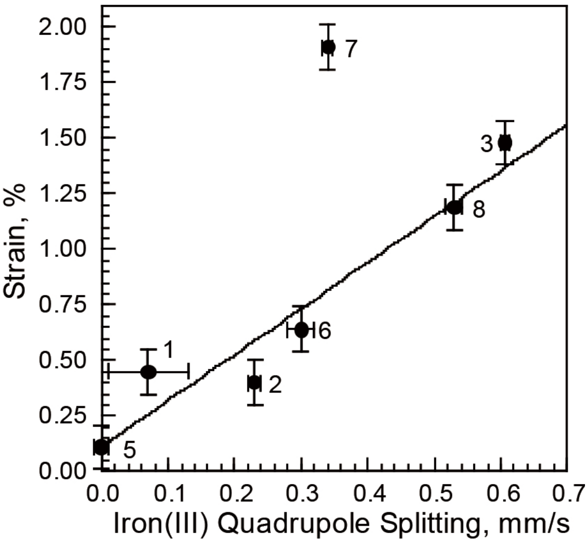


Figure 3. The correlation, *strain*, % = 2.07 ΔE_Q + 0.11, between the Fe^{III} quadrupole splitting and the strain as determined by the Williamson-Hall method for seven Prussian blue complexes. Complex **7** has not been included in the linear correlation. The error on the strain is estimated to be ±0.1 and the error on the quadrupole splitting is twice the statistical error reported in Table 2.

Another interesting spectral parameter is the Fe^{II} percent area, A^{II}, that is expected to be 50 % for the soluble Prussian blue with an Fe^{II} to Fe^{III} ratio of one and is expected to be 3/7 or 43 % for an insoluble Prussian blue complex with an Fe^{II} to Fe^{III} ratio of 3/4. As is shown in Tables 1 and 2, the observed A^{II} values differ significantly from these expected values. Because the recoil-free fractions for LS Fe^{II} and HS Fe^{III} may be different at 295 K and thus affect the Fe^{II} to Fe^{III} ratio obtained from their respective Mössbauer spectral areas, Mössbauer spectra have been obtained between 85 and 295 K and they do not show any significant changes in the Fe^{II} percent area with decreasing temperature. Similar discrepancies between the expected and observed A^{II} values are present but not discussed in ref. 27.

The above discrepancies are obviously related to an actual chemical composition that differs from the expected composition. Indeed, chemical analyses [7] show that almost all of the commercial and synthesized Prussian blue complexes have a higher iron weight percent content than expected whereas the potassium containing Prussian blue complexes have a lower potassium weight percent content than expected. Thermogravimetric analyses [7] also reveal a variable amount, *x*, of water molecules. Hence, for instance, if only iron, potassium, and cyanide anions and water molecules are present, the actual compositions of **1** and **5** are $K_{0.6}Fe_{2.2}(CN)_6·0.8H_2O$ and $K_{0.8}Fe_{2.1}(CN)_6·0.7H_2O$, respectively, with the expected A^{II} area values of 54 and 52 %, respectively. Unfortunately, the observed A^{II} area values of 48(1) and 47(1) % for **1** and **5**, see Table 2, do not agree with these expected values and one must conclude that the recoil-free fraction of LS Fe^{II} ions is smaller than that of HS Fe^{III} ions between 85 and 295 K. This difference reveals that one of the drawbacks of Mössbauer spectroscopy is its inability, at least on the basis of only one 295 K spectrum, to yield a reliable value of the percentage of Fe^{II} actually present in a complex. Hence, the discussion of the Fe^{II} to Fe^{III} ratio reported [27] in the case of the Turnbull's blue must be approached with caution in the absence of a corresponding chemical analysis.

On the basis of a Mössbauer spectral study of 26 Prussian blue complexes of different provenances, Reguera, et al. [27] have suggested several, somewhat unexpected, correlations between the Mössbauer spectral parameters, *i.e.*, correlations between the Fe^{III} isomer shift and quadrupole splitting, the Fe^{II} isomer shift and Fe^{III} quadrupole splitting, and the Fe^{II} and Fe^{III} isomer shifts. The unexpected observation of such correlations might be an indication of synergistic structural interactions within the cubic lattice framework of a Prussian blue. In order to further evaluate the validity, if any, of such correlations, we have tried to complement the 26 sets of hyperfine parameters obtained at 295 K and given in Tables 1 and 2 by Reguera, et al. [27] and shown in their Figs 5, 6, and 7, with the additional 25 sets of parameters obtained for the commercial and synthetic Prussian blue complexes given herein in Table 1 and also in ref. 7 and 29. Unfortunately, with the 51 sets of parameters only one rather poor linear correlation, $\delta^{II} = -0.063\ \Delta E_Q^{III} - 0.123$ mm/s, with a correlation factor of only 0.73, between the Fe^{II} isomer shifts, δ^{II}, and the Fe^{III} quadrupole splittings, ΔE_Q^{III}, was found to have a possible if marginal validity [30]. In these fits the Reguera, et al. [27] isomer shifts were all adjusted to the α-iron reference standard at 295 K. Hence we are forced to conclude that such correlations are highly questionable and may well be purely fortuitous in the absence of supplementary information, such as detailed x-ray structural analyses and chemical analyses.

4. Mössbauer Spectral Study of the Oxidized and Reduced Forms of Prussian Blue

The partially [7] and fully oxidized [23,25,31] and reduced [23,31] forms of Prussian blue have also been studied by Mössbauer spectroscopy.

The fully reduced complex, the ferrous ferrocyanide, is commonly called Berlin white or Everitt's salt and corresponds to either the $K_2Fe^{II}[Fe^{II}(CN)_6]$ or the $Fe_2^{II}[Fe^{II}(CN)_6]$ composition, in its *soluble* or *insoluble* form. The Mössbauer spectrum of $Fe_2^{II}[Fe^{II}(CN)_6]$ obtained [23] at 77 K is shown in Fig. 4, where the solid line results from a fit with a doublet with a small quadrupole splitting of 0.132(6) mm/s assigned to the LS Fe^{II}, the green solid line, and a quadrupole doublet with a large splitting of 3.203(3) mm/s assigned to the HS Fe^{II}, the blue solid line. A weak singlet was added in the fit to account for the weak absorption at ca. 1 mm/s. It is not clear why a HS Fe^{II} quadrupole splitting of 3.02 mm/s was reported by Maer et al. [23] because the quadrupole splitting is obviously greater than 3 mm/s in their Fig. 8. The spectral parameters reported by Maer et al. [23] and our parameters are given in Table 3. The ratio of the HS Fe^{II} to LS Fe^{II} areas in our fit is 2.47(5), a ratio that is rather close to 2:1 in agreement with the $Fe_2^{II}[Fe^{II}(CN)_6]$ composition reported by Maer et al. [23] in their Table III.

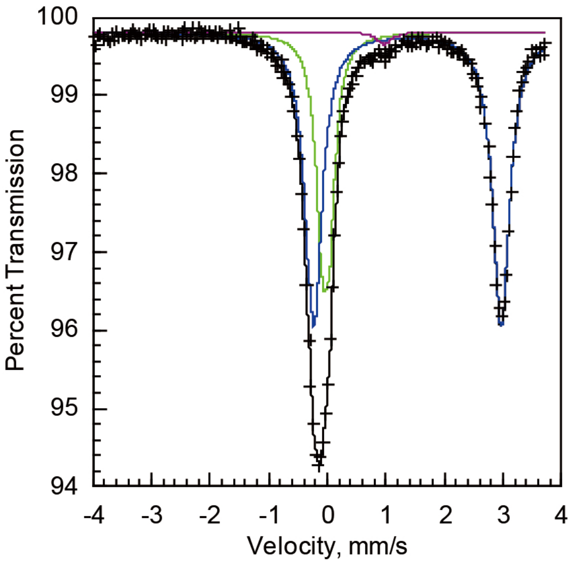


Figure 4. The Mössbauer spectra of Berlin white, $Fe_2^{II}[Fe^{II}(CN)_6]$, obtained [23] at 77 K. The green and blue solid lines represent the LS Fe^{II} and HS Fe^{II} components in our fit. The purple solid line is a weak singlet accounting for the weak absorption at ca. 1 mm/s.

While studying the electrochemistry of Prussian blue, Itaya et al. [31] obtained a room temperature Mössbauer spectrum of a reduced film, a spectrum that exhibits the HS Fe^{II} doublet characteristic of the ferrous ferrocyanide or Berlin white. The decrease in quadrupole splitting from 3.20 to 1.13 mm/s between 77 and 295 K may be explained by the Ingalls model [32] as a result of a changing population with increasing temperature of the three t_{2g} orbitals, whose degeneracy has been removed by a low symmetry component of the HS Fe^{II} coordination environment.

The Mössbauer spectra of two partially reduced Prussian blue complexes, the Berlin green, $\{KFe^{III}[Fe^{II}(CN)_6]\}_x\{Fe^{III}[Fe^{III}(CN)_6]\}_{1-x}$, are shown in Fig. 5. One sample, Fig. 5 top, was prepared [7] under a nitrogen atmosphere, whereas the other, Fig. 5 bottom, was prepared in air, following the synthesis described in ref. 25. The two spectra are very similar and they have been analyzed with two doublets with the spectral parameters given in Table 3. The doublet with the negative isomer shift, green solid line in Fig. 5, is assigned to a combination of the LS Fe^{II} and Fe^{III} ions; because the isomer shift of LS Fe^{II} and Fe^{III} ions are virtually the same within experimental accuracy and it is not possible to distinguish between these components in the presence of their strong overlap, see in Fig. 5. This doublet is rather broad with a line width of ca. 0.45 mm/s, a line width that is indicative of the presence of both LS Fe^{II} and Fe^{III} ions. The spectral parameters for the two samples are not significantly different. On the basis of their hyperfine parameters, it would be extremely difficult to distinguish Berlin green from some Prussian blue complexes, for instance see the parameters of complex **4** in Tables 1 and 2.

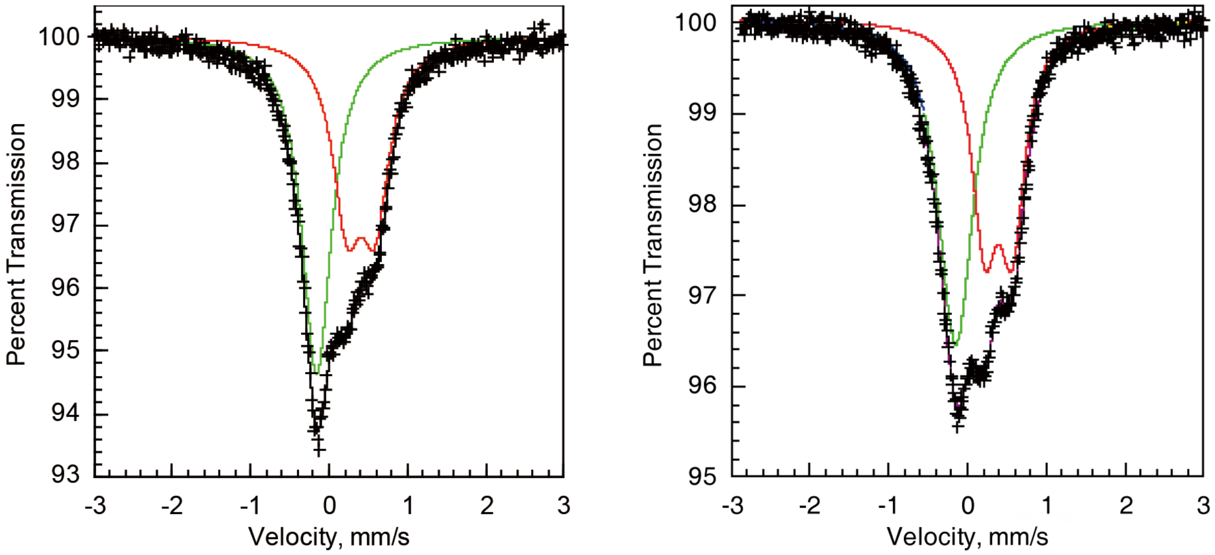


Figure 5. The 295 K Mössbauer spectra of Berlin green, $\{KFe^{III}[Fe^{II}(CN)_6]\}_x\{Fe^{III}[Fe^{III}(CN)_6]\}_{1-x}$, prepared in a nitrogen atmosphere, left, and prepared in air, right. The green and red solid lines represent the LS Fe^{II} and Fe^{III} and HS Fe^{III} components in the fit.

The fully oxidized form of Prussian blue is known as Prussian yellow, a ferric ferricyanide with the $Fe^{III}[Fe^{III}(CN)_6]$ composition. Because of the presence of both LS and HS Fe^{III} ions in this complex, strong overlap is both expected and observed [23] between the components in the Mössbauer spectrum, see Fig. 6. Indeed, in their early work, Maer et al. [23] had to use an ^{57}Fe enriched salt, $K_3{}^{57}Fe(CN)_6$, to enhance and thus characterize the LS Fe^{III} component of the spectrum with an isomer shift of –0.06 mm/s and a quadrupole splitting of 0.43 mm/s. Our fit of their published spectrum, Fig. 10 in ref. 23, yields an isomer shift of –0.043(2) mm/s, a quadrupole splitting of 0.42(1) mm/s, and a line width of 0.39(1) mm/s. Larger error bars are quoted here to account for digitalizing the published figure and estimating the velocity scale. Although the quadrupole splitting of 0.42(1) mm/s is not significantly different from the published [23] value of 0.43 mm/s, the isomer shift of –0.043(2) mm/s is somewhat different from the published value of –0.06 mm/s but the difference is less than one channel in the experimental spectrum and may well result from the inaccuracy introduced in digitalizing the data. Maer et al. [23] argue that the LS doublet can be identified within the Mössbauer spectrum

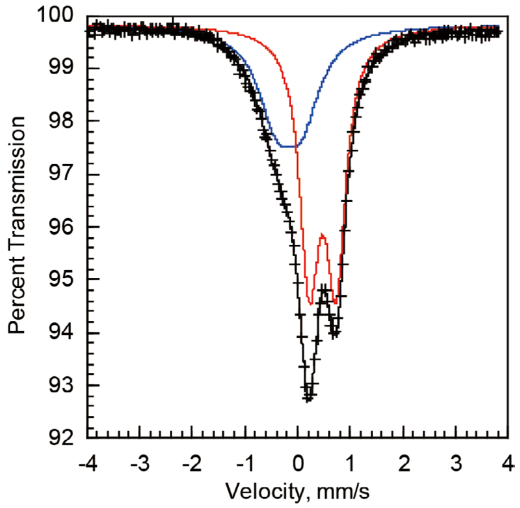


Figure 6. The Mössbauer spectrum of Prussian yellow, $Fe^{III}[Fe^{III}(CN)_6]$, obtained [23] at 77 K. The blue and red solid lines represent the LS and HS Fe^{III} components in the fit.

of Prussian yellow shown in Fig. 6. An attempt to fit this spectrum with one free HS Fe^{III} doublet and a LS Fe^{III} doublet, the isomer shift, quadrupole splitting, and line width of which were constrained to –0.043, 0.42, and 0.39 mm/s, has lead to a very poor fit. A statistically satisfactory fit could be obtained if the line width is refined but this yields a very large value of line width of 1.1 mm/s. Hence, the spectrum shown in Fig. 6 was fit with two free symmetric doublets and the resulting spectral parameters are given in Table 3. The isomer shift of –0.16 mm/s at 77 K is somewhat more negative than expected for a LS Fe^{III} ion and the line width of 0.83 mm/s is large. Both of these parameters may indicate that the sample studied by Maer et al. was not as pure as indicated. The very significant departure from one of the LS to HS percent area ratio may also be indicative of some impurity. Another possibility that cannot be excluded is the easy partial reduction of $Fe^{III}[Fe^{III}(CN)_6]$ and hence the presence of both LS Fe^{II} and Fe^{III} ions, see below the discussion of ref. 25.

In their study of the electrochemistry of Prussian blue, Itaya et al. [31] obtained the room temperature Mössbauer spectrum of an oxidized film, a doublet with an isomer shift of 0.37(2) mm/s and a quadrupole splitting of 0.41(2) mm/s assigned to HS Fe^{III} ions. However, they mistakenly compared this doublet with that of LS FeIII ions observed by Maer et al. [23] in their Fig. 10.

Table 3. Mössbauer spectral parameters of reduced and oxidized Prussian blues[a]

Complex	T, K	Assign-ment	δ, mm/s[b]	ΔE_Q, mm/s	Γ, mm/s	*Area*, %	Ref.
Berlin white							
$Fe_2^{II}[Fe^{II}(CN)_6]$	77	LS Fe^{II}	–0.09	0	-	-	23
		HS Fe^{II}	1.42	3.02	-	-	
	77[c]	LS Fe^{II}	–0.033(2)	0.132(6)	0.250(9)	28.4(6)	this work
		HS Fe^{II}	1.367(1)	3.203(3)	0.349(4)	70.3(4)	
$K_2Fe^{II}[Fe^{II}(CN)_6]$	RT	HS Fe^{II}	1.14(2)	1.13(2)		100	31
Berlin green							
$\{KFe^{III}[Fe^{II}(CN)_6]\}_x$-	295[d]	LS Fe	–0.158(2)	0.00(2)	0.45(1)	51(1)	7
$\{Fe^{III}[Fe^{III}(CN)_6]\}_{1-x}$		HS Fe^{III}	0.407(4)	0.355(1)	0.44(1)	49(1)	
	295[e]	LS Fe	–0.149(5)	0.11(1)	0.48(1)	51(1)	7
		HS Fe^{III}	0.397(5)	0.35(1)	0.39(1)	49(1)	
Prussian yellow							
$Fe^{III}[Fe^{III}(CN)_6]$	RT	HS Fe^{III}	0.37(2)	0.41(2)			31
	77	LS Fe^{III}	–0.06	0.43			23
			–0.16(1)	0.49(1)	0.83(3)	39(1)	this work
		HS Fe^{III}	0.50	0.52			23
			0.479(2)	0.503(3)	0.444(4)	61(1)	this work
	RT[f]	LS Fe^{III}	–0.168(1)	0.119(3)	0.384(3)	50(1)	25, 33
		HS Fe^{III}	0.381(1)	0.448(2)	0.447(3)	50(1)	

[a] Statistical errors are reported; more realistic errors are ±0.005 mm/s for the isomer shifts and ±0.01 mm/s for the quadrupole splittings and line widths. [b] The isomer shift, δ, is referred to α-iron at 295 K. [c] This fit includes a weak singlet with a δ of 0.97(3) mm/s, a fixed Γ of 0.3 mm/s, and an area of 1.3(2) %. [d] Prepared in a nitrogen atmosphere. [e] Prepared in air. [f] Although reported to be for $Fe^{III}[Fe^{III}(CN)_6]$, the results correspond more closely to $\{KFe^{III}[Fe^{II}(CN)_6]\}_x\{Fe^{III}[Fe^{III}(CN)_6]\}_{1-x}$.

Unfortunately, more confusion in the characterization of the ferric ferricyanide, Prussian yellow, $Fe^{III}[Fe^{III}(CN)_6]$, the fully oxidized form of Prussian blue, has been added to the literature by the work of Kumar et al. [25,33] The perceptive reader of ref. 25 will immediately note that the reported hyperfine parameters cannot correspond to those of the spectrum [25] shown in Fig. 3; an isomer shift of –0.17 mm/s is reported for a line observed at ca. 0.5 mm/s. From a private communication [33] with S. M. Yusuf, we learned that indeed several mistakes occurred throughout ref. 25. In spite of stating that a constant acceleration Mössbauer spectrum was used in their study, [25] a sinusoidal velocity scale was mistakenly used in the fitting program and in Fig. 3. In addition, the spectral parameters were mixed up in the published paper and hence all the published parameters should be ignored. The correct spectrum provided in the private communication [33] with S. M. Yusuf is shown in Fig. 7 and its hyperfine parameters from a fit with two symmetric quadrupole doublets are given in Table 3. The statistical error bars were estimated from our fit of the data. It should be noted that the 15 percent absorption at ca. zero mm/s is too large and indicates that the absorber was too thick and hence, the lines may not be Lorentzian and may be broadened. Indeed, a close examination of the residuals of the fit indicates non-Lorentzian lines. All attempts to fit the spectrum shown in Fig. 7 with more than two doublets failed, most likely because of the broadened non-Lorentzian lines.

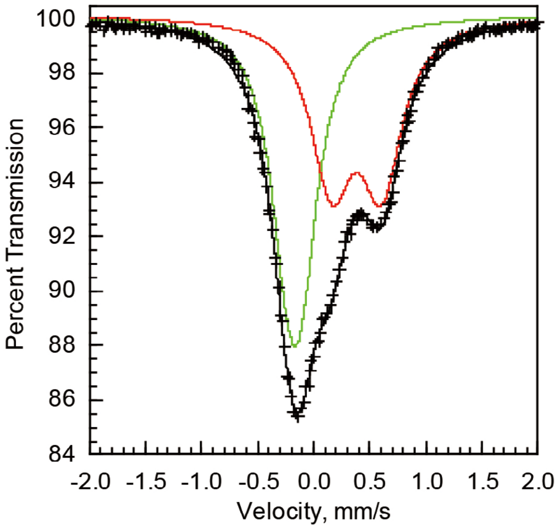


Figure 7. The Mössbauer spectrum of reported $Fe^{III}[Fe^{III}(CN)_6]$ obtained [33] at 295 K. The green and red solid lines represent the LS and HS Fe^{III} components in our fit. Note the similarity with the spectra of Berlin green, $\{KFe^{III}[Fe^{II}(CN)_6]\}_x\{Fe^{III}[Fe^{III}(CN)_6]\}_{1-x}$, shown in Figure 5.

It is clear that the spectra shown in Figs. 6 and 7 for so-called ferric ferricyanide or Prussian yellow are very different but that those shown in Figs. 5 and 7 are very similar. Hence, we are tempted to conclude that the sample of $Fe^{III}[Fe^{III}(CN)_6]$ studied in ref. 25 is not a pure Prussian yellow but is more probably close to Berlin green and contains some LS Fe^{II} ions that are not distinguishable in the Mössbauer spectrum. In addition, the authors clearly indicate that their sample was green, which is not possible for ferric ferricyanide, $Fe^{III}[Fe^{III}(CN)_6]$. It is well known that ferric ferricyanide readily reduces in air and forms at least in part ferric ferrocyanide, Prussian blue. Their synthesis protocol in air favors this reduction; as explained above even a preparation in a nitrogen atmosphere leads to Berlin green, see Fig. 5. Kumar et al. [25] support their claim that they have prepared ferric ferricyanide, $Fe^{III}[Fe^{III}(CN)_6]$ by magnetic susceptibility and neutron diffraction results. However, the magnetic susceptibility measurements were limited between 4.2 and 75 K and hence an estimate of the effective moment through the Curie-Weiss law is handicapped by the low temperature of the measurements. In addition, the magnetic scattering observed at 1.5 K by neutron diffraction is very weak and is likely to be rather insensitive to the presence of some LS Fe^{II} ions. We thus conclude that Kumar et al. have most likely studied a sample of Berlin green and not a pure ferric ferricyanide as they claim.

5. Prussian Blue in the Nano-world

Nanowires and nanoparticles of Prussian blue have been prepared and studied [17,18] by ^{57}Fe Mössbauer spectroscopy. The most striking observation is that the room temperature Mössbauer spectra of these samples are very similar or identical to those of Prussian blue pigments [7,29], shown in Fig. 2. Samples S and W are reported [18] to have mean particle diameters of 31 and 68 nm and yield Mössbauer spectra which are very similar to the spectra of complexes **2** and **7** shown in Fig. 2; their hyperfine parameters are indeed similar within experimental accuracy. The room temperature Mössbauer spectrum [17] of insoluble Prussian blue nanowires is very similar to the spectrum of complex **8** shown in Fig. 2. The reader must be careful in comparing the reported [17] spectral parameters with other values in the literature, because no isomer shift reference is given in ref. 17 but a reference to sodium nitroprusside may reasonably be assumed through a comparison with the isomer shifts quoted in ref. 27.

6. Conclusions

In the introduction, we promised to stress the successes, failures, and drawbacks of Mössbauer spectroscopy. The early and undisputable success is the recognition of the equivalence of Prussian blue and Turnbull's blue and their identification as a class-2 mixed valence complex. Another success is of course the distinction between LS iron ions and HS iron ions through their isomer shift and quadrupole splitting. This success is accompanied by a failure, the failure to distinguish between LS Fe^{II} and LS Fe^{III} ions because of the similarity of their isomer shift and quadrupole splitting. Because Prussian blue and its reduced and oxidized complexes have a complex crystallographic structure, a structure that can accommodate vacancies, trapped cations, and water molecules, their Mössbauer spectra vary accordingly and tend to exhibit rather broad lines that decrease the ability of the technique to distinguish different oxidation and spin states. We have also shown that the young Mössbauer scientists must be very careful in reading and referring to the literature, a literature that contains numerous mistakes – sadly many more than have been delineated above. Even today, 50 years after their first study by Mössbauer spectroscopy, Prussian blue and its analogues still form a rich field of investigation, the history of which is obviously not finished.

Acknowledgments

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[30] It is necessary to point out that the published [27] linear relationship shown in Fig. 6 [27] could not be reproduced herein because the datum point with coordinates (0.645 mm/s and 0.110 mm/s) in Fig. 6 could not be found in the Tables [27] 1 or 2. Further, unfortunately we find that the data points found in the Figs. [27] 5, 6, and 7 do not fully correspond to the values given [27] in Tables 1 and 2; in all three of these figures there are at least one or two missplotted or missing points. As a consequence we have been unable to reproduce the correlation parameters given [27] in Table 4.

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Future Conferences, Symposia, Workshops

July 13-16, 2015
Third International Conference on Advanced Complex Inorganic Nanomaterials (ACIN 2015)
Namur, Belgium
http://webapps.fundp.ac.be/acin2015/

July 26-29, 2015
7th International Gold Conference (GOLD 2015)
Cardiff, United Kingdom
http://sites.cardiff.ac.uk/gold2015/

August 30-September 3, 2015
Colloquium Spectroscopicum Internationale XXXIX (CSI 2015)
Figueira da Foz, Coimbra, Portugal
http://csi2015.fis.uc.pt/

September 13-18, 2015
International Conference on the Applications of the Mössbauer Effect (ICAME 2015)
University of Hamburg, Hamburg, Germany
http://www.icame2015hamburg.de/

December 15-20, 2015
Nuclear Probes in Nanoscale Characterization in the Pacifichem 2015 Conference (PACIFICHEM 2015)
Honolulu, Hawaii, USA
http://www.pacifichem.org/symposiadesc2015/c_symp_254.htm

July 3-8, 2016
16th International Congress on Catalysis (ICC 16)
Beijing, China
http://www.icc2016china.com/index.html

November 13-18, 2016
XV Latin American Conference on the Applications of the Mössbauer Effect (LACAME 2016)
Panama City, Panama
http://www.viceipup.up.ac.pa/Lacame2016/

September 3-8, 2017
International Conference on the Applications of the Mössbauer Effect (ICAME 2017)
Saint Petersburg, Russia