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UMI
X-RAY DIFFRACTION STUDIES
ON
HEAVY METAL LCoNi Cyanides

by
John Bertram Bates, M.A.

A Thesis
Presented to the Faculty of the
Rice Institute of Houston, Texas
in partial fulfillment of
the requirements for the
Degree
of
Doctor of Philosophy

The Rice Institute
1941
K-x-ray Absorption Studies on Heavy Metal Iron-Chelates

I. Introduction

Many recent studies on the properties of some chelates of iron have been made and an understanding of the relationship between the structure of the chelate and the magnetic properties of the iron has been obtained (1, 2). A similar study of the iron complexes of some organic compounds has been made (3). However, the use of electron spectroscopy for chemical analysis to determine the nature of the iron-complex structure has not been attempted.

In a series of analyses on nickel and iron complexes of various types, a certain degree of similarity in the results obtained by electron spectroscopy and infrared analysis suggests a close structural similarity of these materials; hence making it possible to position the iron in the structure. From the results, all iron and iron compounds have been found to exhibit magnetic and Mössbauer effects of distinct types. A detailed analysis and interpretation of these effects are given in the present paper. It was assumed that these compounds are ferrimagnetic and that the relatively large iron-chelate anions are so arranged as to give the required moment for the smaller metal ions as found.
In this study of the hydration and properties of cementitious materials, it was considered necessary to determine first whether or not these materials are suitable for use. For this purpose, an isothermal hydration study has been made on real samples of these classes of complex materials.
II. EXPERIMENTAL

CHLORINATION EQUATION STEPS

1. Chlorination is the process of treating water with chlorine to disinfect it. The reaction can be represented by the following equation:

   \[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO} \]

2. Chlorination is effective because chlorine reacts with organic materials, disinfecting the water. It is often used to treat water before it is treated with ozone.

3. Chlorination can also be used to treat air by adding ozone gas to the water. The process is called ozonation.

4. Chlorination is a common method of water treatment in many parts of the world. It is known for its ability to kill bacteria and other microorganisms.
X-ray diffraction studies.

The single-crystal salts of the trivalent anions of 

bromide, perchlorate, nitrate, thiocyanate, and nitrite, all of 

which contained the trivalent anion, were prepared by mixing solutions of the 

trivalent anion with a solution of the metal salt in methanol.
Fig. 1. Dehydration Isotherm for Cupric Ferrocyanide

Fig. 2. Dehydration Isotherm for Cupric Ferricyanide
Fig. 3. Dehydration Isotherm for Prussian Blue

Fig. 4. Dehydration Isotherm for Turnbull's blue
Precipitate or potassium ferrocyanide with an excess of the metal chloride (except for sodium nitrate and potassium sulfate). The precipitates were washed with distilled water of conductivity until no chloride ion could be detected in the wash water, and were then dried in the air. As it is usually observed, a characteristic brown sol of ferric ferrocyanide was obtained; precipitation of this sol was affected by the addition of alcohol. A precipitate was obtained with chromium nitrate and potassium ferrocyanide only after the addition of nitric acid and several hours of aging. The white iron samples sell of aluminum and bismuth formed immediately, remained partially during the process of washing and air-drying and took on a bluish color. Other samples of indium ferrocyanide were prepared by the same method as above except that oxygen-free water and nitrogen atmosphere were employed and kept by time-stable solutions of indium chloride and hydroferrocyanic acid in a dry nitrogen atmosphere. These samples were nearly white, indicating but little decomposition. However, the x-ray diffraction patterns of these differently prepared indium ferrocyanide samples were identical, showing that any crystalline products of decomposition are present in an amount insufficient to be detected by x-ray diffraction methods.

The x-ray diffraction patterns of the air-dried soils of Prussian blue and Turnbull's blue consist of a few broad lines (see Figure 6) indicating a small primary particle size. In order to obtain sharper x-ray diffraction patterns, an attempt
was able to increase the particle size of these iron-blue precipitates by recrystallization from hydrochloric acid solution. The precipitates resulting from the slow cooling of hydrochloric acid solutions saturated at 100°C, with either Prussian blue or Turnbull's blue, give sharp and identical x-ray diffraction patterns. In Figure 5 this recrystallized substance is referred to as "iron blue ex HCl".

The x-ray examination of these iron-blue compounds was made with Cu Kα x-radiation filtered with a 15 mm. thick Al filter using a camera of 7.8 cm. diameter. In the case of the indium salts it was found that Cu Kα x-radiation which filtered through paper provided a sheet of thin aluminum foil was placed between the film and the sample in order to diminish the intensity of fluorescent x-radiation from the indium.

Diagrams of the x-ray diffraction patterns of Ti₃[Fe(CN)]₄, Ti[Fe(CN)]₆, In[Fe(CN)]₆, Fe[Fe(CN)]₆, Prussian blue, Turnbull's blue, "iron blue ex HCl" Al₄[Fe(CN)]₆, Sc₄[Fe(CN)]₆, In₄[Fe(CN)]₆, Zn₃[Fe(CN)]₄, Nd₃[Fe(CN)]₄, Cu₂[Fe(CN)]₆, and Cu₃[Fe(CN)]₆ are given in Figure 5. These patterns agree very closely as to the position and the relative intensities of lines.

In Figure 6 are given charts of the x-ray diffraction patterns of La₄[Fe(CN)]₆, La[Fe(CN)]₆, Nd₄[Fe(CN)]₆, Fe[Fe(CN)]₆, and Prussian blue. There is no similarity between the patterns of La₄[Fe(CN)]₆, La[Fe(CN)]₆, Nd₄[Fe(CN)]₆, and Fe[Fe(CN)]₆, and the patterns of Prussian blue and Fe[Fe(CN)]₆.
Fig. 5. Diagrams of the X-ray Diffraction Patterns of Various Heavy Metal Iron-Cyanide Compounds
Fig. 6. Diagrams of the X-ray Diffraction Patterns of La₄[Fe(CN)₆]₃, La[Fe(CN)₆], Nd₄[Fe(CN)₆]₃, Prussian blue, and Turnbull's blue.
3. Density Measurements.

The same samples of Prussian blue and of Turnbull's blue as used in the isothermal dehydration studies were used in these density determinations. In measuring the density of these iron-blue powders, Selbertson's method (1) was used with xylene as the cryometric liquid. Before making the measurement, the adsorbed water was removed by subjecting the sample to the vacuum of a "HiVac" pump at a temperature of 37°C for 72 hours. According to the dehydration isotherms already given, this is three times longer than was required to remove all the water from the same material. The density values obtained were:

- Prussian blue = 1.763 gms/cm³
- Turnbull's blue = 1.73 gms/cm³
III. Discussion

A. Isothermal Dehydration Studies

The continuous dehydration isotherms for the gels of cubic ferricyanide, cubic ferrocyanide, prussian blue, and Turnbull's blue indicate that these materials do not form definite crystals. Most of the water present in the samples is adsorbed on the surface of the finely-divided crystals, but some may be held by the adsorption sites within the channels in the lattice between the relatively large iron-cyanide ions, after the manner of certain zeolite crystals that do not contain water molecules in definite chemical combination (3).

Van Sever concluded from the observed intensity ratios of the 111 to the 200 or the 222 reflections, that water molecules should be placed at certain centers, i.e., the new positions, in intensity calculations to be discussed later (see figures 4 through 6), it can be seen that the calculated and observed intensity ratios of these reflections agree very well without assuming the presence of any water or other materials in the new positions. Since the x-ray diffraction patterns of cubic ferricyanide, cubic ferrocyanide, prussian blue, and Turnbull's blue taken before and after the removal of all the water, were not only as to the position of the lines but also as to the relative intensities (as indeed was observed by van Sever), the amount of diffusing material within the unit cell must be the same before and after dehydration. Therefore, it is assumed that the water in these hydrous iron-cyanides is not present as water of hydration.

* The symbols used throughout this paper are those of the Internationale Union zur bestimmung von Kristallstrukturen.
...other indications of the x-ray diffraction pattern...
<table>
<thead>
<tr>
<th>SPACE GROUP</th>
<th>REASON FOR EXCLUSION</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sup&gt;2&lt;/sup&gt;</td>
<td>No set of 32 equivalent points</td>
</tr>
<tr>
<td>T&lt;sup&gt;3&lt;/sup&gt;</td>
<td>None</td>
</tr>
<tr>
<td>T&lt;sub&gt;4&lt;/sub&gt;</td>
<td>No set of 4 equivalent points</td>
</tr>
<tr>
<td>T&lt;sub&gt;6&lt;/sub&gt;</td>
<td>No set of 32 equivalent points</td>
</tr>
<tr>
<td>T&lt;sub&gt;8&lt;/sub&gt;</td>
<td>No set of 4 equivalent points</td>
</tr>
<tr>
<td>0&lt;sup&gt;3&lt;/sup&gt;</td>
<td>No center of symmetry</td>
</tr>
<tr>
<td>0&lt;sup&gt;4&lt;/sup&gt;</td>
<td>No set of 4 equivalent points</td>
</tr>
<tr>
<td>0&lt;sub&gt;5&lt;/sub&gt;</td>
<td>None</td>
</tr>
<tr>
<td>0&lt;sub&gt;6&lt;/sub&gt;</td>
<td>No set of 4 equivalent points</td>
</tr>
<tr>
<td>0&lt;sub&gt;7&lt;/sub&gt;</td>
<td>No set of 4 equivalent points</td>
</tr>
<tr>
<td>0&lt;sub&gt;8&lt;/sub&gt;</td>
<td>No set of 4 equivalent points</td>
</tr>
</tbody>
</table>
all planes.

Based on the values of $h$, $d$, and $\ell$ obtained, the structure of the iron-

cyanide ion, showing the three sites as compared to the dimensions of

the unit cell. The three iron-cyanide groups per unit cell determines

the number of molecules of the iron metal iron-cyanide compound in
**TABLE II**

**Crystal Structure Data**

Space group: $O_n^5$ or $T_n^3$

4 Fe(CN)$_6$ groups per unit cell

Atomic positions:

4 Fe at 4 fold 4(a) positions (000, $0 \frac{1}{2} \frac{1}{2} \rightarrow *$)

4 M at 4 fold 4(b) positions (000, $0 \frac{1}{2} \frac{1}{2} \rightarrow$) + $\frac{1}{2} \frac{1}{2} \frac{1}{2}$

0 to 4 M at 32 fold 32(f) positions (000, $0 \frac{1}{2} \frac{1}{2} \rightarrow$) + ($x, x, x, x, x, x, x, x, x$)

24 C at 24 fold 24(e) positions (000, $0 \frac{1}{2} \frac{1}{2} \rightarrow$) + ($x, 00 \rightarrow$, $x, 00 \rightarrow$)

24 N at 24 fold 24(e) positions (000, $0 \frac{1}{2} \frac{1}{2} \rightarrow$) + ($x, 00 \rightarrow$, $x, 00 \rightarrow$)

$x = 7/36 \ a_0$; $x = 11/36 \ a_0$; $x = 1/6 \ a_0$.

* → cyclcical change of coordinates
Fig. 7.
In the present study, x-ray diffraction methods were employed to study the intensity of x-ray reflections. The reflections were indexed using the space group P6_3/m. The following reflections were used:

- Fe₃[Fe(CN)₆]₄,
- Fe₃[Fe(CN)₆]₂,
- Fe₃[Fe(CN)₆]₂,
- Fe₃[Fe(CN)₆]₂,
- Fe₃[Fe(CN)₆]₂.

The following equation was used:

\[ I = k \left( \frac{1}{0^2 + \frac{1}{4} \cos^2 \theta} \right) \]

- \( I \) = intensity of x-ray reflections
- \( k \) = constant
- \( \frac{1}{0^2 + \frac{1}{4} \cos^2 \theta} \) = Thomson polarization factor
- \( \cos^2 \theta \sin^2 \theta \) = Lorentz factor
- \( j \) = multiplicity factor
- \( f \) = crystal structure factor

The observed and calculated values for the relative intensities of
metallic cations from the cations in water and from those in the solid state. It was shown previously that the ionic radii of iron-oxyanions can be calculated from their structure, and it was also shown that the ionic radii of iron-oxyanions are considerably larger than those of the corresponding cations. The dissimilarity between the patterns of Fe₄(OM₄)₆³⁺ and Fe₂(OM₄)₄⁺, and the patterns of Fe₂(OC₄)₄ and Fe₂(OC₄)₈ shows that the ionic radii of iron-oxyanions are considerably larger than those of the corresponding cations. It is not possible to determine the ionic radii of iron-oxyanions from their structure, and it is more likely that they exist as a mixture of cationic and anionic ions. If this be the case, it would be expected that the ionic radii of iron-oxyanions are actually smaller than those of the corresponding cations. This is borne out by the following experimental evidence.

In Table III is given a list of the ionic radii of the iron-oxyanions studied. The cations cationic and trivalent iron and iron-oxyanions are considerably larger than any of the corresponding cations. The dissimilarity between the patterns of Fe₄(OM₄)₆³⁺ and Fe₂(OC₄)₄, and the patterns of Fe₂(OC₄)₄ shows that the ionic radii of iron-oxyanions are considerably larger than those of the corresponding cations.
### Table III

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic Radius</th>
<th>Ion</th>
<th>Ionic Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl⁺⁴</td>
<td>0.68 Å</td>
<td>Cd⁺²</td>
<td>0.97 Å</td>
</tr>
<tr>
<td>La⁺³</td>
<td>1.15</td>
<td>Mn⁺²</td>
<td>0.80</td>
</tr>
<tr>
<td>Nd⁺³</td>
<td>1.08</td>
<td>Cu⁺²</td>
<td>-</td>
</tr>
<tr>
<td>In⁺³</td>
<td>0.81</td>
<td>Fe⁺²</td>
<td>0.75</td>
</tr>
<tr>
<td>Sc⁺³</td>
<td>0.81</td>
<td>Zn⁺²</td>
<td>0.74</td>
</tr>
<tr>
<td>Fe⁺³</td>
<td>0.60</td>
<td>Co⁺²</td>
<td>0.72</td>
</tr>
<tr>
<td>Al⁺³</td>
<td>0.50</td>
<td>Ni⁺²</td>
<td>0.70</td>
</tr>
</tbody>
</table>


### Table IV

**Classification of Heavy Metal Iron - Cyanide Compounds**

<table>
<thead>
<tr>
<th>Type of Compound</th>
<th>Number of Molecules Per Unit cell</th>
<th>Number of Metal Ions Per Unit cell</th>
<th>Heavy Metal Iron-Cyanide</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₃ X₄</td>
<td>1</td>
<td>3</td>
<td>Ti₃ [Fe(CN)₆]₄</td>
</tr>
<tr>
<td>A X</td>
<td>4</td>
<td>4</td>
<td>Ti [Fe(CN)₆]₄ , In [Fe(CN)₆] , Fe [Fe(CN)₆]₂</td>
</tr>
<tr>
<td>A₄X₃</td>
<td>1 1/3</td>
<td>5 1/3</td>
<td>Sc₄ [Fe(CN)₆]₃ , In₄ [Fe(CN)₆]₃ , Al₄ [Fe(CN)₆]₃</td>
</tr>
<tr>
<td>A₃X₂</td>
<td>2</td>
<td>6</td>
<td>Zn₃ [Fe(CN)₆]₂ , Cd₃ [Fe(CN)₆]₂ , Cu₃ [Fe(CN)₆]²</td>
</tr>
<tr>
<td>A₂X</td>
<td>4</td>
<td>8</td>
<td>Cu₂ [Fe (CN)₆]</td>
</tr>
</tbody>
</table>
Fig. 8. Comparison of Calculated and Observed Intensities
Fig. 9. Comparison of Calculated and Observed Intensities
Fig. 10. Comparison of Calculated and Observed Intensities
Fig. 11. Comparison of Calculated and Observed Intensities
Fig. 12. Comparison of Calculated and Observed Intensities
Fig. 13. Comparison of Calculated and Observed Intensities
Fig. 14. Comparison of Calculated and Observed Intensities

---

- Calculated
- Observed
Fig. 15. Comparison of Calculated and Observed Intensities
Fig. 16. Comparison of Calculated and Observed Intensities
A final decision between the 5 and 3 structures, with the 3 being the most preferred by the crystallographic analysis, is made. The structure is refined using a least-squares method. This minimizes the difference between the model and the experimental data. The final structure is then refined further by a structure-factor analysis.

In the 3 structure, there is a clear indication of the presence of two metal ions per unit cell. The second metal ion is situated in a site that is not occupied in the 5 structure. The metal ions within a certain size and coordination environment around the metal ions are assumed to determine the final structure.

The final model is evaluated by various tests, including a comparison with experimental data and theoretical predictions. The model is then refined further to satisfy the validation requirements.

The 3 structure shows a clear preference for the metal ion coordination, and the final model is accepted as the most suitable for the crystallographic analysis.
\[
\alpha = \begin{pmatrix}
-3 & 0 & 0 \\
0 & -4 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]

The values of the coefficients \(a\) are as follows:

\[
\alpha = \begin{pmatrix}
-3 & 0 & 0 \\
0 & -4 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]

The molecular volume is given by:

\[
\text{Molecular volume} = \frac{\rho}{\mu}
\]

where

\[
\rho = \text{density of the solid}
\]

\[
\mu = \text{lattice constant}
\]

\[
m = \text{no. molecules per unit cell of the IV}
\]

\[
N = 2.00 \times 10^{22} \text{Avogadro's number}
\]

Table I lists the possible theoretical and calculated values of the molecular volumes of Russian blue and Turnbull's blue.
<table>
<thead>
<tr>
<th>Material</th>
<th>m</th>
<th>Mcl. Wt.</th>
<th>Calculated</th>
<th>Formula</th>
<th>Mcl. Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prussian</td>
<td>1</td>
<td>1139</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td>1 1/3</td>
<td>854</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.785</td>
<td>2</td>
<td>569</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gms./cm.</td>
<td>3</td>
<td>379</td>
<td>Fe$_4$[Fe(CN)$_6$]$_3$</td>
<td></td>
<td>859</td>
</tr>
<tr>
<td>Turnbull's Blue</td>
<td>1</td>
<td>1142</td>
<td>Fe$_3$[Fe(CN)$_6$]$_2$</td>
<td></td>
<td>591</td>
</tr>
<tr>
<td>Blue</td>
<td>1 1/3</td>
<td>856</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.790</td>
<td>2</td>
<td>571</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gms./cm.</td>
<td>3</td>
<td>381</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[
3\text{Fe}^{3+} + 3\text{CN}^{-} \rightarrow \text{Fe}_3\left[\text{Fe}^{4+}\text{CN}_6\right]_2
\]

where \(\text{Fe}^{3+}\) and \(\text{CN}^{-}\) are reactants, and \(\text{Fe}_3\left[\text{Fe}^{4+}\text{CN}_6\right]_2\) is the product. This reaction is a redox reaction.

The equation is balanced as follows:

\[
3\text{Fe}^{3+} + 3\text{CN}^{-} \rightarrow \text{Fe}_3\left[\text{Fe}^{4+}\text{CN}_6\right]_2
\]

The product of

\[
3\text{Fe}^{3+} + 3\text{CN}^{-} \rightarrow \text{Fe}_3\left[\text{Fe}^{4+}\text{CN}_6\right]_2
\]

is Fe, FeCN, and FeCN. This is a redox reaction.

If, then, on mixing \(\text{Fe}^{3+}\) with \(\text{Fe}^{2+}\text{CN}_6^{-}\) a redox reaction occurs, and \(\text{Fe}_3\left[\text{Fe}^{4+}\text{CN}_6\right]_2\) is obtained, the entire reaction must be:

\[
3\text{Fe}^{3+} + \text{CN}^{-} \rightarrow \text{Fe}_3\left[\text{Fe}^{4+}\text{CN}_6\right]_2
\]
for every hole of the form \([\text{Sg}^1, \text{Sg}^2]\), and let \(\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6, \alpha_7, \alpha_8\) be a sequence of real numbers such that \(\alpha_1 \alpha_2 \alpha_3 \alpha_4 \alpha_5 \alpha_6 \alpha_7 \alpha_8 = 1\). Then, the \([\text{Sg}^1, \text{Sg}^2]\) form a sequence of real numbers such that \(\alpha_1 \alpha_2 \alpha_3 \alpha_4 \alpha_5 \alpha_6 \alpha_7 \alpha_8 = 1\). However, since the sequence \(\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6, \alpha_7, \alpha_8\) is a sequence of real numbers such that \(\alpha_1 \alpha_2 \alpha_3 \alpha_4 \alpha_5 \alpha_6 \alpha_7 \alpha_8 = 1\), the sequence \(\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6, \alpha_7, \alpha_8\) is a sequence of real numbers such that \(\alpha_1 \alpha_2 \alpha_3 \alpha_4 \alpha_5 \alpha_6 \alpha_7 \alpha_8 = 1\).
TABLE VI

Ferrocyanide and Ferricyanide Ions in the Supernatant Liquid

(millimoles)

<table>
<thead>
<tr>
<th>Amounts Mixed</th>
<th>Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₄Fe(CN)₆</td>
<td>FeCl₃</td>
<td>K₄Fe(CN)₆</td>
</tr>
<tr>
<td>170</td>
<td>99.7</td>
<td>70.3</td>
</tr>
<tr>
<td>194</td>
<td>49.3</td>
<td>144.2</td>
</tr>
</tbody>
</table>
The x-ray diffraction patterns of the ammonium, cupric, and ferric ammonium salts show no other reflection or extinction. If these compounds are all similar, the x-ray diffraction pattern of the salts of the cupric and ferric ammonium salts would be similar. Since the x-ray diffraction patterns of $\text{Ni\left[Fe(CN)_{6}\right]}$, $\text{In\left[Fe(CN)_{6}\right]}$, $\text{Cu\left[Fe(CN)_{6}\right]}$, and $\text{Zn\left[Fe(CN)_{6}\right]}$ are similar, these compounds are all of the same crystalline symmetry and therefore isostructural with each other.

The systematic extinctions occurring in the x-ray diffraction data of these cyanide compounds are characteristic of ferromagnetic cubic symmetry. All the space groups possess this cubic symmetry, both the $\text{C}_{\text{s}}$ and $\text{I}_{\text{h}}$ space groups have the required number of sets of equivalent points as demanded by chemical evidence and the in-
...
valent heavy metal ferrocyanides have nearly the same number of
cations per unit cell, it cannot be determined from x-ray
measurements whether Prussian blue and Turnbull's blue have the
composition represented by the formula \( \text{Fe}_4[\text{FeCN}_6]_3 \) or \( \text{Fe}_3[\text{FeCN}_6]_2 \).

The electronic spectral theory applied to the mixture of
\( \text{Fe}^{2+} \) and \( [\text{Fe(CN)}_6]^{3-} \) indicates that the reaction would go to pro-
tduce \( \text{Fe}_3[\text{FeCN}_6]_2 \) in the following way.

\[
3 \text{FeCN}_3 + K_4[\text{FeCN}_6]_6 \rightarrow \text{Fe}_3[\text{FeCN}_6]_2 \cdot K_4[\text{FeCN}_6]_6 \cdot 3\text{KCl}
\]

An analysis of the supernatant liquid indicated that an appreciable
amount of \( [\text{Fe(CN)}_6]^{3-} \) was formed during the precipitation of
\( K_4[\text{FeCN}_6]_6 \). The \( K_4[\text{FeCN}_6]_6 \) is in accordance with the above reaction.

It is concluded that Prussian blue and Turnbull's blue
may be represented by the formula \( \text{Fe}_3[\text{FeCN}_6]_2 \).
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13. Risamonti: Gazz. chim. Ital. 67, 127, 146 (1937); 68, 103 (1938)
14. van Bever: Rev. trav. chim. 47, 1239 (1968)