The Structure of the Titanium–Iron Cyanide Complexes[1]

Kemp Maer, Jr.,[2a] M. L. Beasley,[2b] R. L. Collins,[2a] and W. O. Milligan[2b,c]

Contribution from the Department of Physics, University of Texas, Austin, Texas 78712, and the Department of Chemistry, Baylor University, Waco, Texas 76703. *Received November 20, 1967*

Abstract: Mössbauer spectra at 77°K have identified the precipitated gel formed by the interaction of $TiCl_3$ and $H_3Fe(CN)_6$ solutions as a ferrocyanide, $Ti^{4+}[Fe(CN)_6]^{4-}$, resulting from a redox reaction. The isomer shift ($\delta = -0.06$ mm/sec) and quadrupole splitting ($\Delta \sim 0$) are identical (based on a computer curve-fit program) with those from a sample of $Ti^{4+}[Fe(CN)_6]^{4-}$ made by the direct interaction of $TiCl_4$ and $H_4Fe(CN)_6$ solutions. The precipitated gel formed from $TiCl_3$ and $[H_4Fe(CN)_6]$ gave $\delta = -0.01$ and $\Delta = 0$, and corresponds to $Ti^{3+}{}_4[Fe(CN)_6]^{4-}{}_3$, which is expected in the absence of a redox reaction. Mössbauer spectra for $Fe^{2+}{}_3[Co(CN)_6]^{3-}{}_2$ exhibited double quadrupole splitting. The peak for $\Delta = 2.81$ is attributed to four $Fe_I{}^{2+}$ ions in the 4b positions of Fm3m, whereas the peak for $\Delta = 1.82$ is attributed to two $Fe_{II}{}^{2+}$ ions statistically distributed in the 8c positions. For the first time it has been shown that the two kinds of Fe^{2+} ions are actually in a different environment. Mössbauer spectra of the so-called Prussian and Turnbull's blue, which have been aged under water for 10 min or more and selectively enriched in ^{57}Fe to obviate severely overlapping Mössbauer absorption peaks, have confirmed the work of earlier investigators on unenriched samples. Both of the blue gels which have contacted water for less than 30 min after the precipitation step have been found to be amorphous by electron diffraction, whereas longer aged samples are crystalline. It is suggested that Mössbauer spectra for such gels aged for periods much less than 10 min would throw light on this rapid aging phenomenon.

The addition of solutions of titanium tri- or tetrachloride to solutions of potassium ferro- or ferricyanide, in the presence of excess acid to avoid hydrolysis of the titanium salts, yields colloidal precipitates, the structure and morphology of which has been little studied. In 1942 it was reported[3] that the precipitates, formed by the interaction of titanium tetrachloride in hydrochloric acid with potassium ferro- and ferricyanides, were crystalline, and the X-ray diffraction patterns corresponded to a face-centered cubic structure (Fm3m) characteristic of an isomorphous series[3] of numerous metallic ferro- and ferricyanides (Figure 1). Titanium trichloride is a strong reducing agent, and its interaction with ferricyanides could involve a possible redox reaction which would obscure further studies, as has been the case in the corresponding Prussian and Turnbull's blue problem.

Mössbauer spectroscopy has been very successful in providing an elegant solution to the Prussian–Turnbull's blue problem,[4-8] except for certain considerations involving the "age" of the blue precipitates and possible air oxidation. However this method has not been applied to the companion problem of the titanium–iron cyanide complexes.

Recoil-free γ-ray fluorescence spectroscopy is a logical complementary tool with X-ray diffraction methods for structural studies, inasmuch as the former defines the charge states of the ions and the latter defines their positions.

The theory of the Mössbauer effect has been covered by several authors.[9] The isomer shift is the amount by which the spectrum is shifted relative to a fixed energy (which in turn is often chosen by the experimenter as the energy emitted by his own source when at rest, but is better chosen as the center of absorption of a standard substance such as iron or sodium nitroprusside). An increased electron density at the nucleus effects a negative isomer shift. The addition of an electron to ferric iron increases the isomer shifts, however, since an added "d" electron will shield the "s" electrons and lead to a positive isomer shift. Ferricyanide ions yield a small negative isomer shift relative to ferrocyanide, and this is part of the basis for differentiating the charged states. Shulman and Sugano[10] have performed MO treatments of these ions and concluded that the charge states are virtually identical. Another way of looking at it is to consider the nephelauxetic (or cloud-expanding) effect. The very strong cyanide ligands bond tightly to the iron nucleus, and this shields the nonbonding t_{2g} electrons. Consequently, the absence of one of these in Fe^{III} leads to much smaller effects than occur in Fe^{3+}. This nephelauxetic effect shows up clearly in the Mössbauer effect, both in the isomer shift and in the quadrupole splitting.

Quadrupole splitting in iron compounds is caused by the interaction of the electric field gradient with the nuclear quadrupole moment.[11] It is generally useless to try to visualize the electric field gradient as the gradient of the electric field at the nucleus. For one

---

[1] (a) Research supported, in part, indirectly by the Robert A. Welch Foundation (K. M. and R. L. C.); (b) the study was aided by a grant from the Office of Saline Water, U. S. Department of the Interior, and a grant from the M. D. Anderson Foundation of Houston (M. L. B. and W. O. M.).

[2] (a) University of Texas; (b) Baylor University; (c) Author to whom inquiries should be addressed: The Robert A. Welch Foundation, 2010 Bank of the Southwest Building, Houston, Texas 77002.

[3] H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, **46**, 99 (1942).

[4] M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

[5] L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962).

[6] E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 277 (1963).

[7] J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.*, 1120 (1963).

[8] K. Chandra, D. Raj, and S. P. Puri, *J. Chem. Phys.*, **46**, 1466 (1967).

[9] For surveys see: N. N. Greenwood, *Chem. Brit.*, **3** (2), 56 (1967); G. K. Wertheim, *Phys. Today*, 20, (7) 31 (1967).

[10] R. G. Shulman and S. Sugano, *J. Chem. Phys.*, **42**, 39 (1965).

[11] R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **28**, 1001 (1966); R. L. Collins and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2332 (1963); *J. Chem. Phys.*, **39**, 3433 (1963); R. L. Collins, K. Maer, Jr., and J. C. Travis, *J. Inorg. Nucl. Chem.*, 30, 113 (1968).

thing, the electric field at the nucleus is zero. If this were not so, the nucleus, being charged, would move to a position where the electric field was zero. Further, the gradient of a vector is a second rank tensor with nine components. It is useful to think of the electric field gradient (efg) tensor in terms of the shape of the charge distribution. If the charges are electrons, and hence negative, it is meaningful to specify that the equivalent ellipsoid of charge is spherical, football-shaped, or pancake-shaped. In terms of the elements of the efg tensor, this is equivalent to specifying V_{zz} as zero, negative, or positive. If axial symmetry is not present, an asymmetry parameter must be introduced. The quadrupole splitting in iron compounds is complicated by the two contributions to the efg tensor: the ligands which represent localized concentration of electrons, and the 3d electrons which are nonspherical. The ligand contribution to the efg tensor of the iron cyanides is zero, by symmetry. Further, the efg tensor is zero or small for low-spin Fe^{II} complexes and for high-spin Fe^{3+} complexes. Finally, the extent of the quadrupole splitting depends on thermal motion of the charge cloud. Most (probably all) quadrupole splittings increase at low temperatures. For this reason, it is advisable to measure the splitting at as low a temperature as feasible.

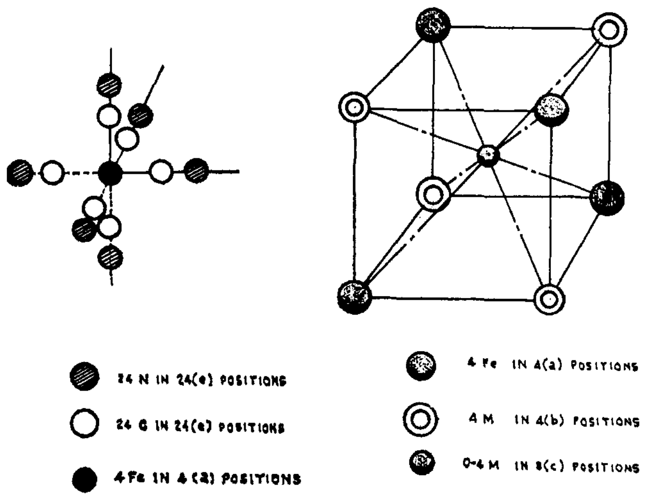

Figure 1. Diagram of one-eighth of the unit cell.

It is the purpose of this paper to report the results of an X-ray diffraction and Mössbauer spectroscopic study of the titanium-iron cyanide complexes, together with some observations on some closely related cobaltous, ferrous, ferric, and cobalticyanide compounds.

Experimental Section

Preparation of Samples. The heavy metal ferro-, ferri-, and cobalticyanides examined here were prepared at room temperature by the addition of a dilute solution (0.1 *N*) of metal salts (ACS reagent grade) to a dilute solution (0.1 *N*) of potassium ferrocyanide, ferricyanide, or cobalticyanide (ACS reagent grade), hydroferricyanic acid, or hydroferrocyanic acid (prepared as previously[12] described), employing a rapid mixing device.[12] The potassium ferrocyanide and hydroferrocyanic acid solutions were always prepared not more than 20 min prior to the precipitation step, in order to minimize possible air oxidation and decomposition by light. Possible contamination of potassium ferrocyanide by bacteria was also avoided by using only freshly prepared solutions. The dried hydroferrocyanic acid powder exhibited a pure white color when prepared and was stored in the dark in a desiccator to prevent the formation of blue decomposition products.

The resulting gels were always precipitated with a 5% excess of the metal salt, in order to minimize potassium ion contamination as well as to avoid excessive peptization[12] of the precipitates which renders washing more difficult.

Titanium Iron Cyanides. Titanium iron cyanides were prepared by quick mixing (0.1 *N*) titanium trichloride solutions with the corresponding (0.1 *N*) hydroferrocyanic and hydroferricyanic acids and the titanium tetrachloride with hydroferrocyanic acid. The titanium tri- and tetrachloride solutions contained a large excess of hydrochloric acid to avoid possible hydrolysis to form hydrous titanium oxides. After precipitation the resulting gels were placed in 250-ml polyethylene centrifuge bottles with close-fitting screw caps while in a nitrogen-filled glove box and then centrifuged at 3000 rpm. The samples in the centrifuge bottles were returned to the nitrogen atmosphere for each change of wash water (boiled to remove air and cooled) during the washing to minimize air oxidation. The first two washings were with 6 *N* hydrochloric acid instead of water, in an attempt to further avoid possible hydrolysis to form hydrous titanium oxides. The precipitates were then washed eight times with distilled water, filtered, and dried in a stream of nitrogen. This procedure resulted in an elapsed time of about 6 hr from the precipitation step to the nitrogen-dried powder.

Iron-Iron Cyanide Complexes. Iron-iron cyanide complexes were prepared by quick mixing (0.1 *N*) ferrous- and ferric sulfate solutions with the corresponding (0.1 *N*) potassium ferrocyanide and ferricyanide solutions. In order to minimize aging time in the Prussian and Turnbull's blue samples, the freshly precipitated gel was filtered and washed several times on filter paper until no positive test for excess ions was detectable in the filtrate. No attempt was made to dry these precipitates. The washed precipitates on the filter paper were attached to the copper "cold finger" of the Mössbauer spectrometer and were placed in liquid nitrogen. The entire preparation process required approximately 10 min. To minimize air oxidation, the precipitation and washing were done in a stream of nitrogen, similar to the procedure described in the preceding paragraph.

Ferrous ferrocyanide was prepared as previously described in a nitrogen atmosphere, washed in a centrifuge ten times with distilled water, and allowed to dry under nitrogen. (This was the same procedure as for the titanium compounds except for the hydrochloric acid.)

Ferric ferricyanide was prepared in air, washed ten times with distilled water in a centrifuge at 3000 rpm, filtered, and air-dried.

Cobalt-Containing Complexes. Cobalt-containing complexes were prepared by quick mixing at room temperature dilute solutions (0.1 *N*) of ferrous sulfate (ACS reagent grade) with 0.1 *N* potassium cobalticyanide. The cobaltous ferro- and ferricyanide complexes were prepared by quick mixing at room temperature dilute solutions (0.1 *N*) of cobaltous chloride and the corresponding potassium ferro- and ferricyanide solutions. The resulting suspensions of the freshly precipitated cobalt-containing gels were washed ten times with distilled water in a centrifuge at 3000 rpm and allowed to age under water at room temperature. These samples were allowed to age for several weeks in the hope of growing larger crystals which would give sharper X-ray diffraction lines. However, little or no detectable change occurs after a period of 6 weeks, at which time the gels were then suction-filtered using Whatman No. 42 filter paper and allowed to air-dry.

Environment with ^{57}Fe. In order to separate the severely overlapping Mössbauer spectra of Prussian blue, Turnbull's blue, and ferric ferricyanide, selective enrichment of Fe^{3+} and Fe^{2+} ions in Prussian blue and Turnbull's blue, respectively, and $[Fe(CN)_6]^{3-}$ ion in the ferric ferricyanide was increased from its normal 2.17% ^{57}Fe to 92% ^{57}Fe, giving rise to well-defined nonoverlapping Mössbauer absorption peaks.

The enrichment was accomplished as follows. A 92% enriched $^{57}FeCl_3$ stock solution was prepared by dissolving 92% enriched

---

[12] H. B. Weiser and W. O. Milligan, *J. Phys. Chem.*, 40, 1074 (1936).

Table I. Preparation of Samples

Sample no.	Solutions mixed: 0.1 *N* (5% excess)	Solutions mixed: 0.1 *N*	Remarks		Mössbauer spectra in figure
$1^{a,b}$	$TiCl_3$	$H_4Fe(CN)_6$	Dried in N_2 atm		2
$2^{a,b}$	$TiCl_3$	$H_3Fe(CN)_6$	Dried in N_2 atm		3
$3^{a,b}$	$TiCl_4$	$H_4Fe(CN)_6$	Dried in N_2 atm		4
4^{c}	$Fe_2(SO_4)_3$	$K_4Fe(CN)_6$	"Prussian blue"	undried, washed ppt frozen at 77°K within 10 min after precipn step	5
$5^{c,d}$	$Fe_2(SO_4)_3$	$K_4Fe(CN)_6$	"Prussian blue"		6
$6^{c,e}$	$FeCl_2$	$K_3Fe(CN)_6$	"Turnbull's blue"		7
7^{b}	$FeSO_4$	$K_4Fe(CN)_6$	Dried in N_2 atm		8
8	$Fe_2(SO_4)_3$	$K_3Fe(CN)_6$	Air-dried		9
9^{f}	$Fe_2(SO_4)_3$	$K_3Fe(CN)_6$	Air-dried		10
10	$FeSO_4$	$K_3Co(CN)_6$	Air-dried		11,12
11	$CoCl_2$	$K_4Fe(CN)_6$	Air-dried		13
12	$CoCl_2$	$K_3Fe(CN)_6$	Air-dried		14

[a] In 6 *N* HCl to avoid possible hydrolysis to form hydrous titanium oxides. [b] Precipitated and transferred in nitrogen glove box to minimize possible air oxidation. [c] Partially protected from possible air oxidation by a nitrogen atmosphere. [d] Fe^{3+} enriched to 92% in ^{57}Fe. [e] Fe^{2+} enriched to 92% in ^{57}Fe. [f] $[Fe^{III}(CN)_6]^{3-}$ enriched to 92% in ^{57}Fe.

$^{57}Fe_2O_3$ in excess hot hydrochloric acid. Excess hydrochloric acid was removed by repeatedly evaporating almost to dryness at the boiling point and adding distilled water, until the resulting solution of $^{57}FeCl_3$ gave a pH value of about 3.

A $^{57}Fe_2(SO_4)_3$ solution was obtained by addition of H_2SO_4 to a portion of the stock solution and evaporating to near dryness. The resulting solution was then frozen in liquid nitrogen. The Mössbauer spectrum of the frozen solution revealed only Fe^{3+} ions.

A $^{57}FeCl_2$ solution was obtained by slow addition of hydrazine hydrate to portion of the stock solution and readjusting the pH with HCl to a value of about 3. The resulting solution was then frozen in liquid nitrogen. The Mössbauer spectrum of the frozen solution revealed only Fe^{2+} ions.

A sample of $K_3{}^{57}Fe(CN)_6$ was prepared by precipitation of hydrous ferric oxide from a portion of the stock $^{57}FeCl_3$ solution by addition of KOH giving a pH value in the range of 7. The precipitated hydrous ferric oxide will dissolve upon addition of a slight excess of KCN and refluxing for several hours. The resulting solution was then cooled and allowed to evaporate slowly at room temperature forming a low yield of small crystals of $K_3{}^{57}Fe(CN)_6$ which exhibited a Mössbauer spectrum corresponding to only $[Fe(CN)_6]^{3-}$ ions.[11]

The ^{57}Fe-enriched solutions were utilized to prepare samples of Prussian blue, Turnbull's blue, and ferric ferricyanide by the methods already described for the unenriched materials.

The preparations of the 12 samples reported here are summarized in Table I.

Mössbauer Spectra. The Mössbauer spectra are obtained on a constant-acceleration spectrometer. A 40-mCi ^{57}Co-in-chromium source was used at room temperature. Narrower line widths may be achieved in thin samples exhibiting a low degree of absorption. The excellent signal-to-noise ratio obtained by use of our improved data gathering and handling system[13] made it possible to employ thin samples ranging from 5 to 15 mg/cm². The samples were supported between filter paper disks and mounted in a copper "cold finger" in a dewar flask with Mylar windows. The very fast data-gathering and -handling system[13] permitted data acquisition rates of 30–50 kHz. The number of counts per channel varied from 0.5 to 8×10^6 and was based on the attainment of an adequate signal-to-noise ratio. The largest number of counts was taken with the unenriched samples. Calibration spectra were taken of 0.0005-in. iron foil, and all isomer shifts are referred to the center of these spectra. The 50% probable errors for isomer shifts (δ) and quadrupole splittings (Δ) are given by δ ±0.01 mm/sec and Δ ±0.02 mm/sec.

X-Ray Analysis. Standard X-ray diffraction patterns were obtained with Fe Kα X-radiation (manganese β filter). Debye-Scherrer photographs were taken using a camera of diameter 114.6 mm, with the samples in 0.5-mm diameter Mark tubes. Intensity measurements were obtained with a Norelco diffractometer. Calibration of interplanar spacings was based on sodium chloride and silicon standards in accordance with the usual practice.

Lattice constants are based on the average of several microphotometer tracings of several separate photographs employing Fe Kα X-radiation (manganese β filter) and corrected according to Cohen's difference method[14] of least squares.

Results and Conclusions

X-Ray Analysis. The crystal structure of various iron cyanide complexes was first reported in the 1936 classic paper by Keggin and Miles,[15] who proposed a face-centered cubic unit cell. In 1938 van Bever[16] extended these results to a series of isomorphous ferricyanides, placing 4 Fe atoms in the 4a positions of Fm3m, 4 M_I atoms in the 4b positions, 24 C atoms and 24 N atoms in the 24e positions, varying numbers of water molecules (4 to 6) distributed statistically in the 8c positions, and 2 M_{II} atoms distributed statistically in the 32f positions. Weiser, Milligan, and Bates[17] suggested on the basis of continuous dehydration isotherms that no definite hydrates were formed. Some of the water present in the samples was assumed to be adsorbed on the surface of the finely divided crystals, but some also was considered to be held by adsorption forces within the channels[3] in the lattice between the relatively large ferrocyanide or ferricyanide ions, after the manner of certain zeolites that do not contain water molecules in definite crvstallographic positions.

---

(13) J. G. Page, J. W. Jagger, and R. L. Collins, Proceeding of the 2nd Symposium on Low Energy X and Gamma Sources and Applications, Oak Ridge Isotope Information Center, ORNL-IIC-10, 142–156, 1967.

(14) M. U. Cohen, *Rev. Sci. Instr.*, **6**, 70 (1935).

(15) J. F. Keggin and F. D. Miles, *Nature*, **137**, 577 (1936).

(16) A. K. van Bever, *Rec. Trav. Chim.*, **57**, 1259 (1938).

(17) H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, **45**, 701 (1941).

Table II. X-Ray Diffraction Results

Sample no.[c]	Compn (based on Mössbauer spectra)	Cubic Fm3m a_0	Fe–C or Co–C	C–N	Remarks
1	$Ti^{3+}_4[Fe(CN)_6]^{4-}_3$	10.171 (3)	1.873	1.153	*b*
2	$Ti^{4+}[Fe(CN)_6]^{4-}$	10.164 (4)	*a*	*a*	No detectable differences in intensities
3	$Ti^{4+}[Fe(CN)_6]^{4-}$	10.164 (4)	*a*	*a*	
4, 5	$Fe^{3+}_4[Fe(CN)_6]^{4-}_3$	10.116 (3)	*a*	*a*	No detectable differences in intensities
6	$Fe^{3+}_4[Fe(CN)_6]^{4-}_3$	10.116 (3)	*a*	*a*	
7	$Fe^{2+}_2[Fe(CN)_6]^{4-}$	10.184 (2)	1.870	1.156	*b*
8, 9	$Fe^{3+}[Fe(CN)_6]^{3-}$	10.151 (2)	*a*	*a*	
10	$Fe^{2+}_3[Co(CN)_6]^{3-}_2$	10.271 (2)	1.887	1.149	*b*
11	$Co^{2+}_2[Fe(CN)_6]^{4-}$	10.193 (2)	1.872	1.151	*b*
12	$Co^{2+}_3[Fe(CN)_6]^{3-}_2$	10.287 (2)	1.886	1.153	*b*

[a] Parameter values not available. [b] Details to be published elsewhere. [c] See Table I.

Table III. Mössbauer Parameters[a]

Sample no.	Compound (based on Mössbauer Spectra)	Fe^{III} δ	Fe^{III} Δ	Fe^{II} δ	Fe^{II} Δ	Fe^{3+} δ	Fe^{3+} Δ	Fe^{2+} δ	Fe^{2+} Δ
1	$Ti^{3+}_4[Fe(CN)_6]^{4-}_3$	...	...	−0.01	0	...	...	...	...
2	$Ti^{4+}[Fe(CN)_6]^{4-}$	...	...	−0.06	~0	...	...	...	...
3	$Ti^{4+}[Fe(CN)_6]^{4-}$	...	...	−0.06	~0	...	...	...	...
4, 5	$Fe^{3+}_4[Fe(CN)_6]^{4-}_3$	...	...	−0.08	0	+0.49	0.57	...	...
6	$Fe^{3+}_4[Fe(CN)_6]^{4-}_3$	...	...	−0.07	0	+0.49	0.51	...	...
7	$Fe^{2+}_2[Fe(CN)_6]^{4-}$	...	...	−0.09	0	...	...	+1.42	3.02
8, 9	$Fe^{3+}[Fe(CN)_6]^{3-}$	−0.06	0.43	...	...	+0.50	0.52	...	...
10	$Fe^{2+}_3[Co(CN)_6]^{3-}_2$								
	(M_I)	...	...	...	...	...	...	+1.27	2.81
	(M_{II})	...	...	...	...	...	...	+1.23	1.82
	298°K (M_I)	...	...	...	...	...	...	+1.13	1.76
	298°K (M_{II})	...	...	...	...	...	...	+1.11	0.97
11	$Co^{2+}_2[Fe(CN)_6]^{4-}$	...	...	−0.01	~0	...	...	...	...
12	$Co^{2+}_3[Fe(CN)_6]^{3-}_2$	−0.08	0.85	...	...	...	...	...	...

[a] Isomer shifts (δ) and quadrupole splitting (Δ). The isomer shift is with respect to the center of the six-line spectrum of natural iron at room temperature. The numerical values of δ and Δ are based on a computer curve-fit program and are expressed in mm/sec. Except when noted, all samples were examined at 77°K.

In 1942, Weiser, Milligan, and Bates[3] examined numerous heavy metal ferro- and ferricyanides, and proposed in space group $Fm3m/O_h^5$ that 4 Fe atoms were located in the 4a positions, 4 M_I atoms were located in the 4b positions, and 24 C and 24 N atoms were located in the 24e positions, in agreement with Keggin and Miles and van Bever, but that 0 to 4 M_{II} atoms were distributed statistically in the 8c positions in contrast to other hypotheses. Intensity calculations for several ferrocyanides and ferricyanides gave reasonably good agreement with experiment for approximate parameter values of $x_C = 0.194$ and $x_N = 0.306$. These same parameter values were found by van Bever to be suitable for his divalent ferricyanides. The general features of the 1942 structures have been found acceptable[18–21] for numerous divalent hexacyano complexes such as $M_3^{2+}[X(CN)_6]_2^{3-}$, where M = Mn, Fe, Co, Ni, Zn, Cd, Cu, or Cr, and X = Co, Cr, Mn, Rh, or Ir.

Currently, Milligan and Beasley[22] have determined the structure of a series of 30 ferrocyanides, ferricyanides, and cobalticyanides in which redox reaction complications are unlikely. The lattice constants varied systematically from 9.966 (6) to 10.657 (1) Å. All of the metal–carbon distances were in the range of 1.870 to 1.899 Å. The C–N distances were in the range of 1.148 to 1.160 Å. Although only Debye–Scherrer data were available, the *R* values were in the range of 0.034 to 0.099. Preliminary X-ray studies have now been extended to some of the compounds reported here which may involve redox reactions. Some of the results are given in Table II. It will be noted that the lattice constants fall in line with those reported for the 30

---

(18) A. Ferrari, M. E. Tani, and G. Magnano, *Gazz. Chim. Ital.*, **89**, 2512 (1959).

(19) A. Ferrari and M. E. Tani, *ibid.*, **90**, 1565 (1960).

(20) A. Ferrari, M. E. Tani, and E. Morisi, *Acta Cryst.*, **17**, 311 (1964); **14**, 695 (1961); **15**, 90 (1962).

(21) A. Vaciago and A. Mugnoli, *Atti Accad. Nazl. Lincei Rend., Classe Sci. Fis. Mat. Nat.*, **25**, 531 (1958); **26**, 517 (1959).

(22) W. O. Milligan and M. L. Beasley, submitted for publication.

isomorphous structures. Although, it is evident that X-ray structural calculations cannot be expected to distinguish clearly between structures differing only as the result of a possible redox reaction, the present X-ray results are consistent with the Mössbauer spectra to be discussed in the next section of this paper.

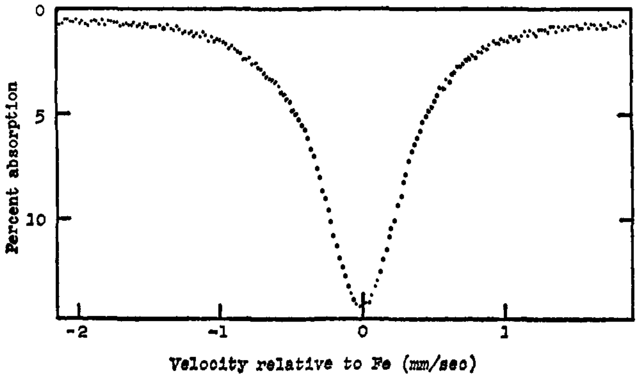

Figure 2. Mössbauer spectrum at 77°K for $Ti^{3+}{}_4[Fe^{II}(CN)_6]^{4-}{}_3$: sample no. 1, $TiCl_3 + H_4Fe(CN)_6$.

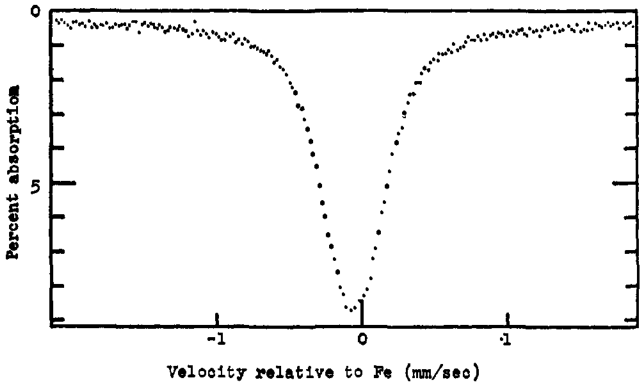

Figure 3. Mössbauer spectrum at 77°K for $Ti^{4+}[Fe^{II}(CN)_6]^{4-}$: sample no. 2, $TiCl_3 + H_3Fe(CN)_6$.

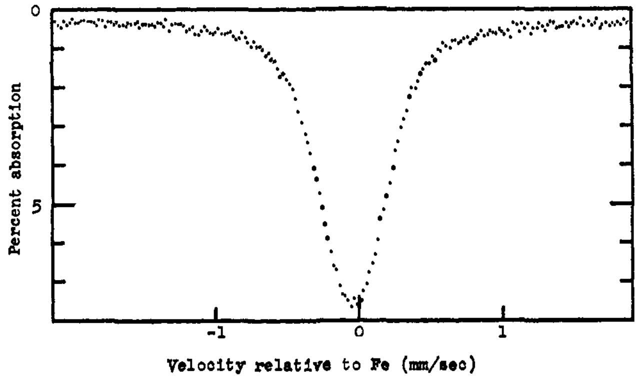

Figure 4. Mössbauer spectrum at 77°K for $Ti^{4+}[Fe^{II}(CN)_6]^{4-}$: sample no. 3, $TiCl_4 + H_4Fe(CN)_6$.

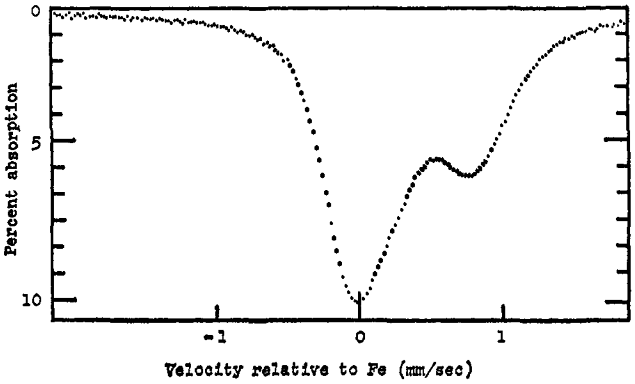

Figure 5. Mössbauer spectrum at 77°K for $Fe^{3+}{}_4[Fe^{II}(CN)_6]^{4-}{}_3$: sample no. 4, $Fe_2(SO_4)_3 + K_4Fe(CN)_6$, "Prussian blue."

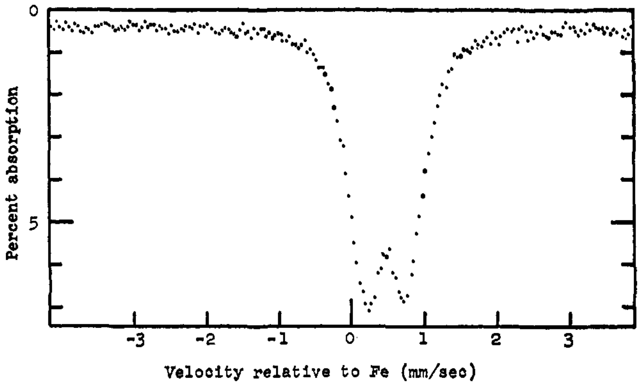

Figure 6. Mössbauer spectrum at 77°K for $Fe^{3+}{}_4[Fe^{II}(CN)_6]^{4-}{}_3$: sample no. 5, $^{57}Fe_2(SO_4)_3 + K_4Fe(CN)_6$, "Prussian blue."

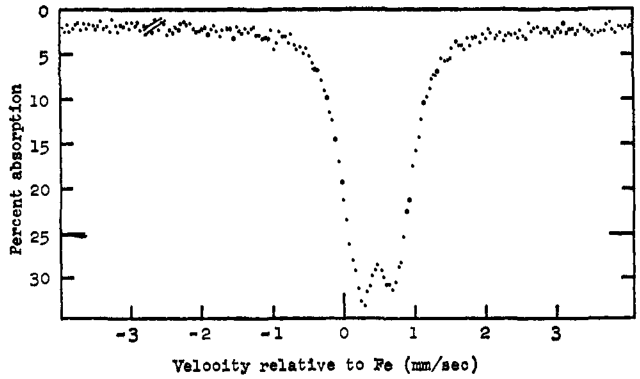

Figure 7. Mössbauer spectrum at 77°K for $Fe^{3+}{}_4[Fe^{II}(CN)_6]^{4-}{}_3$: sample no. 6, $^{57}FeCl_2 + K_3Fe(CN)_6$, "Turnbull's blue."

Mössbauer Spectra. There are given in Figures 2–14 Mössbauer spectra for the 12 samples listed in Table I. The isomer shifts (δ) and quadrupole splittings (Δ) are given in Table III and were determined by a computer-curve-fit program and are expressed in millimeters/second. From the Mössbauer spectrum shown in Figure 2 it may be deduced that when (sample no. 1) $TiCl_3$ is mixed with $H_4Fe(CN)_6$, the precipitate obtained is a ferrocyanide, $Ti^{3+}{}_4[Fe(CN)_6]^{4-}{}_3$, giving a δ shift of -0.01 relative to iron. Although this reaction appears to be straightforward, this is not the case when (sample no. 2) $TiCl_3$ is mixed with $H_3Fe(CN)_6$, as shown in the Mössbauer spectrum (Figure 3) of the resulting precipitate. Instead of obtaining the characteristic quadrupole splitting and isomeric shift for ferricyanides, the spectrum indicated ferrocyanide with no detectable ferricyanide present. This suggests a redox reaction has taken place, converting the compound to $Ti^{4+}[Fe(CN)_6]^{4-}$. The titanium(IV) ferrocyanide complex was then synthesized (sample no. 3) and its Mössbauer spectrum (Figure 4) was identical with that obtained from mixing (sample no. 2) $TiCl_3$ with $H_3Fe(CN)_6$.

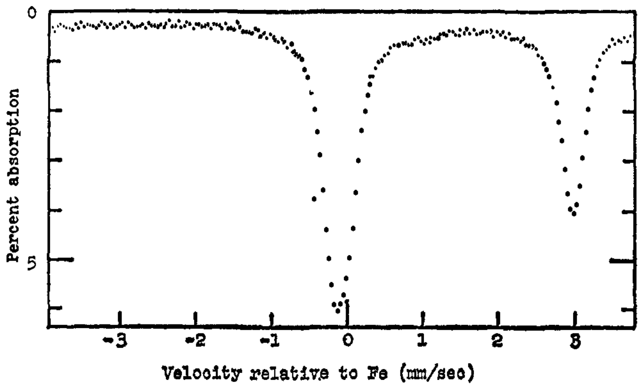

Figure 8. Mössbauer spectrum at 77°K for $Fe^{2+}{}_2[Fe^{II}(CN)_6]^{4-}$: sample no. 7, $FeSO_4 + K_4Fe(CN)_6$.

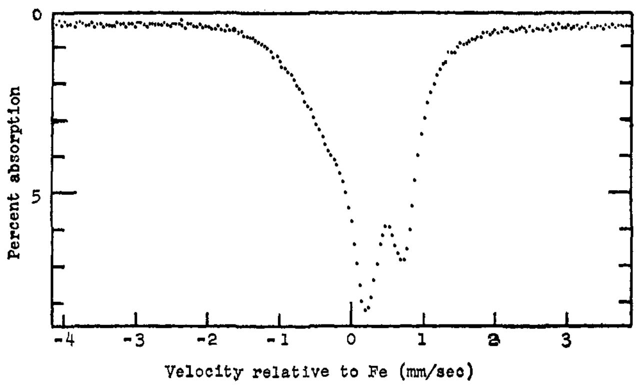

Figure 9. Mössbauer spectrum at 77°K for $Fe^{3+}[Fe^{III}(CN)_6]^{3-}$: sample no. 8, $Fe_2(SO_4)_3 + K_3Fe(CN)_6$.

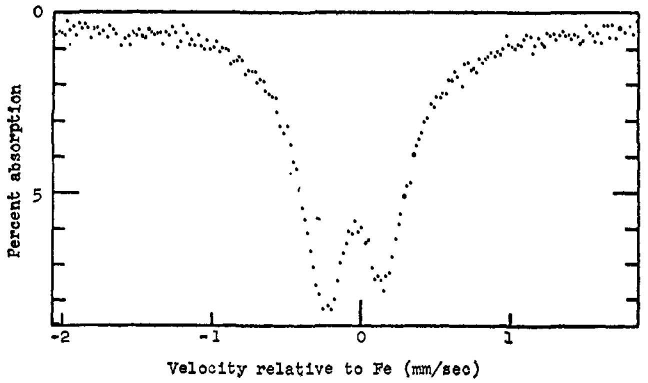

Figure 10. Mössbauer spectrum at 77°K for $Fe^{3+}[Fe^{III}(CN)_6]^{3-}$: sample no. 9, $Fe_2(SO_4)_3 + K_3{}^{57}Fe(CN)_6$.

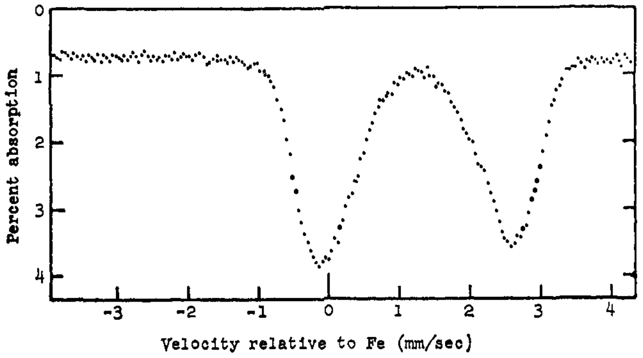

Figure 11. Mössbauer spectrum at 77°K for $Fe^{2+}{}_3[Co^{III}(CN)_6]^{3-}{}_2$: sample no. 10, $FeSO_4 + K_3Co(CN)_6$.

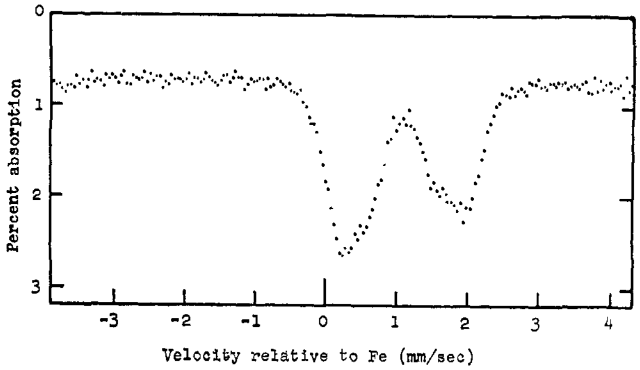

Figure 12. Mössbauer spectrum at 298°K for $Fe^{2+}{}_3[Co^{III}(CN)_6]^{3-}{}_2$: sample no. 10, $FeSO_4 + K_3Co(CN)_6$.

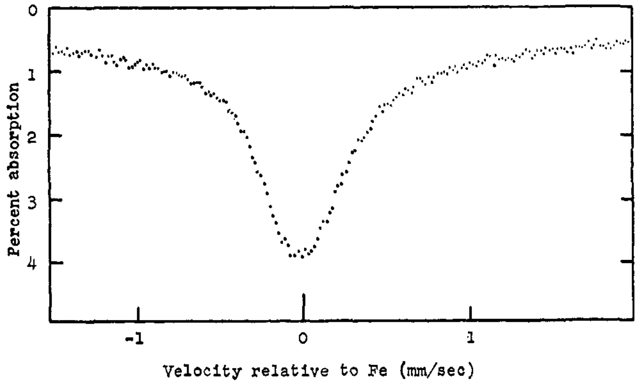

Figure 13. Mössbauer spectrum at 77°K for $Co^{2+}{}_2[Fe^{II}(CN)_6]^{4-}$; sample no. 11, $CoCl_2 + K_4Fe(CN)_6$.

The ferrocyanide spectra shown in Figures 3 and 4 are not caused by the $Ti^{3+}{}_4[Fe(CN)_6]^{4-}{}_3$ compound (Figure 2) since the isomer shift is different as well as the line width at half-height. The line width at half-height of $Ti^{3+}{}_4[Fe(CN)_6]^{4-}{}_3$ is appreciably larger than that of $Ti^{4+}[Fe(CN)_6]^{4-}$ (0.67 *vs.* 0.54 mm/sec). The origin of this difference is likely an unresolved quadrupole splitting which may be caused by the random filling of Ti^{3+} in the 8c positions surrounding each iron, and only 1.33 Ti^{3+} ions to fill them. The more positive isomer shift of the $Ti^{3+}{}_4[Fe(CN)_6]^{4-}{}_3$ compound remains unexplained as yet.

The Mössbauer spectrum obtained for (sample no. 4) Prussian blue, unenriched at either iron site, is shown in Figure 5. The overlapping spectrum of the iron sites makes interpretation extremely difficult without selective enrichment. The Fe^{3+} portion of the overlapping spectrum is shown in Figure 6 which was obtained by using (sample no. 5) enriched $^{57}Fe_2(SO_4)_3$ in the formation of Prussian blue. The results indicate sample no. 5 to be ferric ferrocyanide.

Turnbull's blue (sample no. 6) was prepared using enriched $^{57}FeCl_2$. The corresponding Mössbauer spectrum (Figure 7) shows a redox reaction has taken place with respect to the $^{57}Fe^{2+}$ ion since all of the $^{57}Fe^{2+}$ appears to have been oxidized to $^{57}Fe^{3+}$. The two Mössbauer spectra in Figures 6 and 7 are essentially superimposable.

The Mössbauer spectrum obtained from the precipitate (sample no. 7) formed by mixing $FeSO_4$ and $K_4Fe(CN)_6$ solutions is shown in Figure 8. The Fe^{2+} ion has a Mössbauer spectrum giving widely split lines. The ferrous ion spectrum is overlapped on the left peak with the single ferrocyanide peak. However, even with this overlap the spectrum is easily interpreted as that of ferrous ferrocyanide. In the case (sample no. 8) of Berlin green, or $FeFe(CN)_6$, the Mössbauer spectrum shown in Figure 9 suggests the two sharp peaks are due to the Fe^{3+} ion and that the $[Fe(CN)_6]^{3-}$ ion peak is hidden. This hidden ferricyanide ion peak is clearly revealed by the Mössbauer spectrum in Figure 10 where the precipitate (sample no. 9) is obtained by mixing $Fe_2(SO_4)_3$ and $K_3{}^{57}Fe(CN)_6$. The quadrupole splitting due to the ferricyanide ion is now quite visible, thus making it possible to conclude that the precipitate is ferric ferricyanide.

Although Fe^{2+} ions in the 4b positions and Fe^{2+} ions in the 8c positions could not be distinguished in the ferrous ferrocyanide complex, they can be distinguished (sample no. 10) in $Fe^{2+}{}_3[Co(CN)_6]^{3-}{}_2$. The Mössbauer spectrum (Figure 11, at 77°K; Figure 12, at 298°K) shows a doublet with broad and asymmetric lines. Figure 12 shows plainly that there are two sets of doublets. Note that the quadrupole splittings given in Table III are considerably less than those at 77°K (Figure 11). It seems likely that the Fe^{2+} in the 4b positions and the Fe^{2+} (two atoms statistically distributed) in the 8c positions are susceptible to thermal averaging of their efg tensors, and this accounts for the dramatic drop in quadrupole splitting as the temperature is raised. It should also be pointed out that the Fe^{2+} in the 4b positions and Fe^{2+} in the 8c positions are not equally bound (*i.e.*, not in the same environment). Interpretation of the relative intensities of the four lines in Figures 11 and 12 suggests that the inner pair of lines corresponds to the Fe^{2+} (two atoms statistically) in the 8c positions, and the outer pair of lines corresponds to the Fe^{2+} atoms in the 4b positions.

The Mössbauer spectra in Figures 13 and 14 correspond to cobaltous ferrocyanide (sample no. 11) and cobaltous ferricyanide (sample no. 12), respectively. Interpretation of the Mössbauer spectrum of each indicates the precipitates to be the products expected from the reagents mixed.

The Mössbauer spectra demonstrate clearly that a redox reaction is involved when $TiCl_3$ solution is added to a $H_3Fe(CN)_6$ solution to yield a ferrocyanide, most likely $Ti^{4+}[Fe^{II}(CN)_6]^{4-}$. The X-ray diffraction patterns are consistent with this view. However, it is not entirely clear as to whether the redox reaction occurs in solution, $Ti^{3+} + [Fe^{III}(CN)_6]^{3-} \rightarrow Ti^{4+} + [Fe^{II}(CN)_6]^{4-} \rightarrow Ti^{4+}[Fe^{II}(CN)_6]^{4-}$, followed by precipitation of the insoluble $Ti^{4+}[Fe^{II}(CN)_6]^{4-}$, or whether $Ti^{3+}[Fe^{III}(CN)_6]^{3-}$ is precipitated directly from solution, followed by an internal redox reaction, $Ti^{3+}[Fe^{III}(CN)_6]^{3-} \rightarrow Ti^{4+}[Fe^{II}(CN)_6]^{4-}$. The titanium-iron cyanide complexes studied here had aged in contact with water for 6 hr prior to acquisition of the Mössbauer spectra. In the future work it is planned to attempt to examine samples that have aged for shorter periods of time.

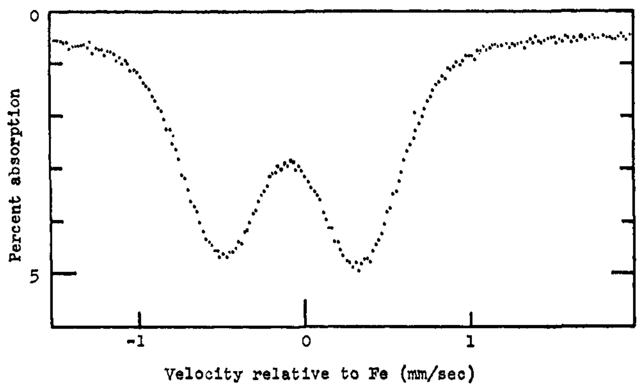

Figure 14. Mössbauer spectrum at 77°K for $Co^{2+}{}_3[Fe^{III}(CN)_6]^{3-}{}_2$: sample no. 12, $CoCl_2 + K_3Fe(CN)_6$.

Although there are obvious analogies between the titanium-iron cyanide complexes and the Prussian-Turnbull's blue system, the latter may be more complex. X-Ray and electron diffraction examination of Prussian blue and Turnbull's blue that have aged for several hours yields Debye-Scherrer patterns that are identical within the limits of observation.[3,15,23] However, the electron diffraction patterns of the two blue gels that have aged in contact with water for about 2 min are of the amorphous type. Conversion to crystalline-type patterns takes place in less than about 30 min. The Mössbauer spectra reported here (and which agree with those of earlier investigators[4-8]) are for samples that have aged for about 10 min or longer. In this connection, we have examined the two blue gels in a Cary Model 14 spectrophotometer, and, in general agreement with Bhattacharya,[24] the spectra are slightly different in samples less than 10 min old and become identical in about 30 min. These preliminary results suggest a difference in the gels when first precipitated.

One of us[3] concluded in 1942 that X-ray diffraction methods could not distinguish between the ferrocyanide and the ferricyanide hypotheses, but decided on the latter in view of the standard redox potentials of the $Fe^{2+}|Fe^{3+}$ and $[Fe(CN)_6]^{4-}|[Fe(CN)_6]^{3-}$ couples. However, Davidson[25] chose the ferrocyanide hypothesis on the grounds that ferric ferrocyanide would be precipitated from the solution containing the four ions in redox equilibrium on the assumption that this compound would be the least soluble of the four possible products. However, in 1 *M* acid solution the redox

---

[23] G. R. Levi, *Giorn. Chim. Ind. Applicata.*, 7, 410 (1925).

[24] A. K. Bhattacharya, *J. Indian Chem. Soc.*, 12, 149 (1935).

[25] D. Davidson, *J. Chem. Educ.*, **14**, 238 (1937); **15**, 277 (1937).

potentials for both couples are almost identical (−0.77 and −0.71 V).[26]

Furthermore, Chadwick and Sharp[27] have recently pointed out that considerations based on the formation of insoluble substances of high lattice energy and high charge may be more important than redox potentials arising from solution in determining the composition of the final product.

It appears highly desirable to develop a technique for measuring the Mössbauer spectra of the two blue gels where aging under water has been minimized.

Acknowledgment. The curve-fit program was a modification by James L. Gilchrist of J. Spijkerman's linearized least-squares curve-fit program.

---

[26] G. H. Hanania, D. H. Irvine, W. A. Eaton, and P. George, *J. Phys. Chem.*, **71**, 2016, 2022 (1967).

[27] B. M. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 119 (1966).