Effect of Pressure on the C–Fe Bond in Ferrocyanides and Ferricyanides*

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High-pressure studies have been made on Fe–C bonding in ferrocyanides and ferricyanides using Mössbauer resonance. For the Cu, Ni, and Zn ferrocyanides a partial conversion to high-spin Fe(II) was observed at high pressure and elevated temperature. This is explained in terms of reduced metal-to-ligand back donation at high pressure. The ferricyanides reduced to ferrocyanides at modest pressure and room temperature. At high pressure and high temperatures all these salts showed extensive conversion to high-spin Fe(II). The process was reversible, but with considerable hysteresis. In prussian blue the high-spin Fe(III) and low-spin Fe(II) were separately tagged with Fe⁵⁷. The high-spin Fe(III) reduced strongly to high-spin Fe(II). The low-spin Fe(II) showed a partial conversion to low-spin Fe(III) at modest pressures. This conversion was independent of temperature. At higher pressures it converted to high-spin Fe(II) in an amount which increased sharply with temperature.

This paper discusses the effect of pressure to 200 kbar and temperature to 150°C on the C–Fe bonding in ferrocyanides and ferricyanides, largely through the use of Mössbauer resonance. Before discussing these compounds specifically, it is useful to review briefly the results of previous high-pressure studies on transition-metal complexes, especially those involving iron. We shall present our discussion in terms of an octahedral field, since these cyanide complexes are octahedral or nearly so.

The energy levels of a free transition-metal ion are separated by interelectronic repulsion, the magnitude of which can be expressed in terms of the Racah parameters A, B, and C. In an octahedral field the fivefold degenerate $3d$ levels are split into a threefold level (t_{2g}) and a doubly degenerate level (e_g) of higher energy. The size of this splitting is a measure of the field of the ligands called $10Dq$ or Δ. For many complexes these levels are filled according to Hund's rule, giving maximum multiplicity. A number of high-pressure optical studies[1] have shown that for these high-spin complexes Δ increases with increasing pressure, approximately as predicted by simple theory. The Racah parameters decrease with increasing pressure. This is explained in terms of spreading of the $3d$ orbitals due to interaction with the ligands, reducing interelectronic repulsion. Typically for a high-spin complex $\Delta \cong 9000$ cm⁻¹ at 1 atm and $B \cong \frac{1}{4}C \cong 900$ cm⁻¹. Δ may increase by about 15% in 150 kbar, and B may decrease by 8%–15% in the same pressure range.

Mössbauer resonance studies on high-spin ferrous compounds show a relatively high isomer shift (~ 1.3 mm/sec relative to iron metal) corresponding to a low-electron density at the nucleus, since there are six $3d$

electrons partially shielding the $3s$ orbitals. High-spin ferric compounds show isomer shifts of about 0.4 mm/sec. The higher electron density at the ferric nucleus is, in part at least, due to the reduced shielding since there is nominally one less $3d$ electron. With pressure the isomer shift decreases by a significant amount.[2] The primary cause is probably the spreading of the $3d$ orbitals mentioned above, decreasing the shielding of the $3s$ orbitals. It has been shown that Fe(III) reduces to Fe(II), with increasing pressure in a very wide variety of compounds[3] (both high spin and low spin). This has been explained rather conclusively in terms of an electron transfer from a ligand nonbonding level to the metal t_{2g} orbital. It is observed optically that the energy for charge transfer decreases with increasing pressure. The spreading of the $3d$ orbitals lowers their energy vis-a-vis the ligands causing iron to become more electrophillic.

With increasing ligand field, the balance between kinetic and potential energy may make it favorable to pair the spins in the t_{2g} level. The ferro- and ferricyanides are examples of tightly bound low-spin complexes. They exhibit values of $\Delta \sim 30$–$32\,000$ cm⁻¹ and $B \sim 400$ cm⁻¹. The structure and spectra of ferro- and ferricyanides have been discussed by a number of authors. The following are a few references pertinent to this work.[4–7] The isomer shift is very close to that of iron metal indicating a very high delocalization of the $3d$ electrons. The situation is explained in terms of pi bonding between the t_{2g} levels of the metal and the π^* orbitals of the ligand, indicated by the triple line on the

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[1] H. G. Drickamer in *Solids Under Pressure*, W. Paul and D. Waschauer, Eds. (McGraw-Hill Book Co., New York, 1963), pp. 357–385; H. G. Drickamer in *Solid State Physics*, F. Seitz and D. Turnbull, Eds. (Academic Press Inc., N. Y., 1965), Vol. 17, pp. 1–135. These reviews contain references to the original papers.

[2] A. R. Champion, R. W. Vaughan, and H. G. Drickamer, J. Chem. Phys. **47**, 2583 (1967).

[3] H. G. Drickamer, G. K. Lewis, Jr., and S. C. Fung, Science **163**, 885 (1969). This review contains references to the original papers.

[4] W. P. Griffith, Quart. Rev. (London) **16**, 188 (1962).

[5] J. J. Alexander and H. B. Gray, Coord. Chem. Rev. **2**, 29 (1967).

[6] H. B. Gray and N. A. Beach, J. Am. Chem. Soc. **87**, 3340 (1965).

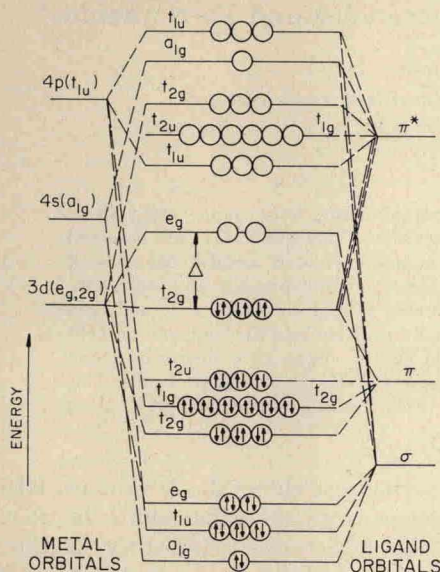[7] D. F. Schriver, Struct. Bonding (Berlin) **1**, 32 (1966).

FIG. 1. Molecular orbital diagram—ferrocyanides.

molecular-orbital diagram of Fig. 1. This "back donation" of electrons from metal to ligand stabilizes the t_{2g} levels, accounting for the high value of Δ, and reduces shielding of the $3s$ orbitals, which explains the high electron density at the nucleus. Shulman and Sugano[8] have given a semiquantitative discussion of this behavior. High-pressure Mössbauer resonance data on $K_4Fe(CN)_6$[9] shows a large decrease in isomer shift with pressure, probably associated with increased sigma bonding. The ferricyanide reduces rapidly to ferrocyanide with increasing pressure. There is some slight optical evidence that Δ may actually decrease somewhat with increasing pressure in the ferrocyanide.

The high-pressure Mössbauer resonance techniques used here have been presented elsewhere.[10] The results
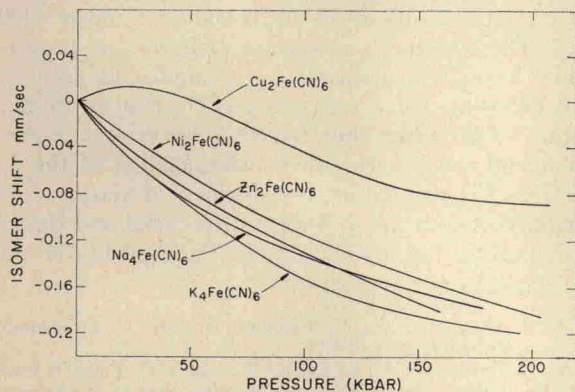

FIG. 2. Relative change in isomer shift with pressure— ferrocyanides.

TABLE I. Isomer shifts (I.S.) of ferrocyanides at 4 kbar and 23°C (relative to Fe metal).

Compound	I.S. (mm/sec)
$Cu_2Fe(CN)_6$	−0.037
$Ni_2Fe(CN)_6$	−0.052
$Zn_2Fe(CN)_6$	−0.073
$Na_4Fe(CN)_6$	−0.034
$K_4Fe(CN)_6$	−0.024

for ferrocyanides, ferricyanides, and for prussian blue are discussed separately.

FERROCYANIDES

The ferrocyanides studied include $K_4Fe(CN)_6$, $Na_4Fe(CN)_6$, $Zn_2Fe(CN)_6$, $Ni_2Fe(CN)_6$, and $Cu_2Fe(CN)_6$. (As mentioned previously, room-temperature data were already available for the first compound.) The latter three compounds have a cubic structure with the CN⁻ bridging the iron to the cation.[11,12] The first two have more complex structures[13] with the cations arranged interstitially. In all cases the iron is coordinated to the carbon. The compounds were synthesized using 90% Fe^{57} by known techniques[11,14] and gave satisfactory analyses. The initial isomer shifts at 23°C are given in Table I. Figure 2 exhibits the relative change in isomer shift with pressure. The potassium and sodium salts show a large decrease in isomer shift with pressure. The zinc salt shows measurably less, the nickel salt still less, and the copper salt actually exhibits

TABLE II. Quadrupole splittings in ferrocyanides mm/sec.

A. Low-spin Fe(II)—23°C

Compound	Pressure (kbar)				
	0	50	100	150	175
$Cu_2Fe(CN)_6$	0.36	0.55	0.62	0.66	···
$Ni_2Fe(CN)_6$	0.38	0.45	0.52	0.59	0.62
$Zn_2Fe(CN)_6$	0.18	0.30	0.39	0.48	0.53
$Na_4Fe(CN)_6$	0.29	0.39	0.45	0.49	0.50

B. High-spin Fe(II) formed under pressure

Compound	Pressure (kbar)				
	50	100	150	200	
$Cu_2Fe(CN)_6$	1.95	2.08	2.20	2.25	(110°C)
$Ni_2Fe(CN)_6$	···	2.40	2.39	2.41	(110°C)
$Zn_2Fe(CN)_6$	1.44	1.35	1.30	1.30	(147°C)

[8] R. G. Shulman and S. Sugano, J. Chem. Phys. **42**, 39 (1965).
[9] A. R. Champion and H. G. Drickamer, J. Chem. Phys. **47**, 2591 (1967).
[10] P. DeBrunner, R. W. Vaughan, A. R. Champion, J. Cohen, J. Moyzis, and H. G. Drickamer, Rev. Sci. Instr. **37**, 1310 (1966).

[11] H. B. Weiser, W. O. Milligan, and J. B. Bates, J. Phys. Chem. **46**, 99 (1962).
[12] A. K. Van Bever, Rec. Trav. Chim. **57**, 1259 (1938).
[13] A. J. C. Wilson, Struct. Rept. **9**, 209 (1942–44); **11**, 421 (1947–48).
[14] J. N. Friend, *A Textbook of Inorganic Chemistry* (C. Griffin & Co., London, 1925), Pt. 2, p. 212.
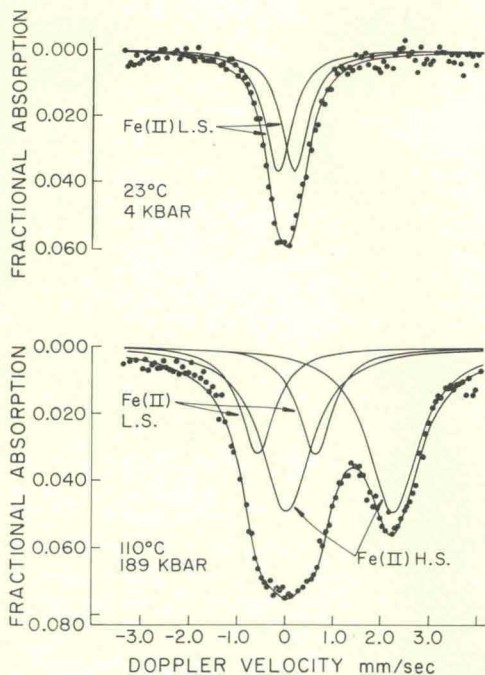
FIG. 3. Mössbauer spectra of copper ferrocyanide.

FIG. 5. Conversion to high-spin Fe(I) vs pressure at 110°C and 147°C—nickel ferrocyanide.

a maximum in the isomer shift at about 30 kbar. The significance of these differences will be clear a little later. Table II shows the change of quadrupole splitting with pressure. [With the techniques available to us in 1967 it was not possible to resolve the quadrupole splitting for $K_4Fe(CN)_6$.]

At high pressure and at temperatures above 100°C an unexpected phenomenon occurs. A new pair of peaks appears in the spectrum and increases in amount with pressure at the expense of the original spectrum. Figure 3 shows typical spectra for $Cu_2 \cdot Fe(CN)_6$. The new peaks have a center of gravity of 1.00–1.20 mm/sec and a quadrupole splitting of $\sim$2.0 mm/sec. The isomer shift decreases with increasing pressure (about 0.1 mm/sec in 100 kilobars). The quadrupole splittings are tabulated in Table II. In Fig. 4 conversions are shown as a function of pressure for the copper and nickel salts at 110°C and the zinc salt at 147°C. There was only a small conversion for zinc at 110°C; on the other hand, the copper salt showed measurable conversion at 23°C at the highest pressures. Figure 5 demonstrates the effect of temperature on conversion for $Ni_2Fe(CN)_6$. (All conversions were obtained from the areas under Lorentzian peaks fit to the data. They are nominal in the sense that there may be a difference in f number at the different sites.) The process is reversible, but quite

FIG. 4. Conversion to high-spin Fe(II) vs pressure—ferrocyanides.
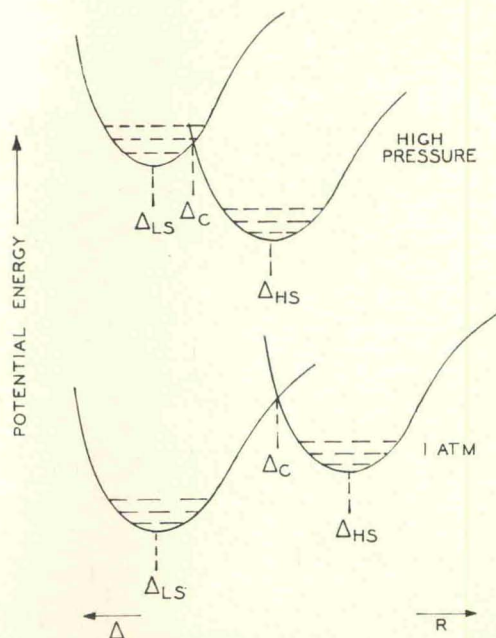

FIG. 6. Schematic potential-energy diagram.

TABLE III. Isomer shifts (I.S.) for ferricyanides and prussian blue at 4 kbar and 23°C (relative to Fe metal).

Compound	I.S. (mm/sec)	
$Cu_3[Fe(CN)_6]_2$	−0.076	(+0.28 at 147°C and 11 kbar)
$Ni_3[Fe(CN)_6]_2$	−0.112	
$Zn_3[Fe(CN)_6]_2$	−0.074	
$Na_3Fe(CN)_6$	−0.061	
$K_3Fe(CN)_6$	−0.093	
$Fe_4[^{57}Fe(CN)_6]_3$	−0.169	
$^{57}Fe_4[Fe(CN)_6]_3$	+0.384	

sluggishly so. When the sample was powdered by grinding, it returned completely to the low-spin Fe(II) state.

There appear to be two possible explanations for the observed phenomenon. Either low-spin Fe(I) or high-spin Fe(II) is being formed. It is known that $(CN)^-$ is a ligand with some tendency to stabilize low oxidation states, and one would expect an increase in isomer shift due to increased shielding of the $3s$ electrons, as well as a large quadrupole splitting with Fe(I). On the other hand, it is difficult to see how there would be energy available to transfer an electron from the ligands to the e_g levels, and the t_{2g} levels are full in low-spin Fe(II).

There is a considerable body of evidence that indicates the formation of high-spin Fe(II). The isomer shift is a little low, but not unlike some high-spin ferrous-phenanthroline complexes. The quadrupole splitting is in the usual range except possibly for zinc. As indicated above, there is considerable hysteresis on release of pressure. Using an apparratus developed to study organic reactions at high pressure, we quenched a sample from 200 kbar and 110°C, obtaining 5.1 mg of product containing 18% of the "high-spin" material according to its Mössbauer spectrum.

A very sensitive Faraday balance indicated that this material had a susceptibility 1.75 times that of unpressed material. This would indicate 15%–21% of high-spin Fe(II) depending whether one calculates on a "spin-only" basis or ratios between susceptibilities of known high- and low-spin ferrous materials. It was possible to get reasonable ir, visible, and uv spectra in a KBr pellet. The cyanide stretching frequency is at

TABLE IV. Quadrupole splittings high spin Fe(II) formed under pressure from ferricyanides.

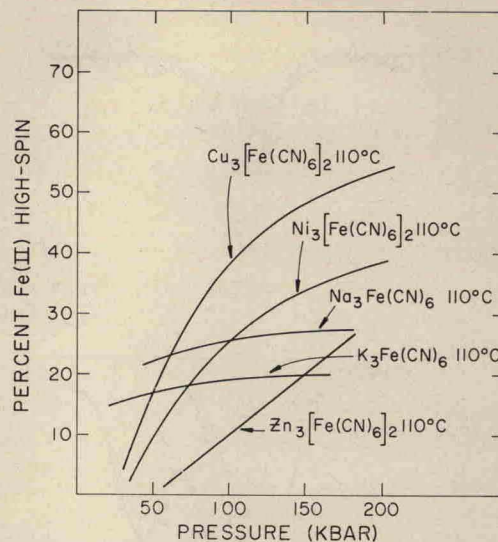| Original compound	Pressure (kbar)				
	50	100	150	200	
$Cu_3[Fe(CN)_6]_2$	2.14	2.22	2.28	2.31	(110°C)
$Ni_3[Fe(CN)_6]_2$	···	2.32	2.32	2.34	(110°C)
$Zn_3[Fe(CN)_6]_2$	1.60	1.43	1.30	1.21	(110°C)
$K_3Fe(CN)_6$	1.80	1.88	1.84	1.81	(110°C)
$Na_3Fe(CN)_6$	2.50	2.70	2.85	2.95	(110°C)

FIG. 7. Conversion of ferrocyanides made by reducing ferricyanides to high-spin Fe(II) vs pressure.

2090 cm^{-1} in ferrocyanides, which is considerably lower in energy than the free-cyanide value. This material exhibited a shoulder on the high-energy side at 2180 cm^{-1}. This would be consistent with reduced Fe–C binding. The Fe–C stretching frequency at 494 cm^{-1} had lost intensity and a new peak appeared at 467 cm^{-1}, again consistent with reduced Fe–C binding. A weak peak appeared in the near-ir at 11 800 cm^{-1}. This is a reasonable position for the $^5T_{2g} \rightarrow {}^5E_g$ transition measuring the crystal-field parameter Δ in a high-spin Fe(II) compound. The uv spectra were of poor quality but it
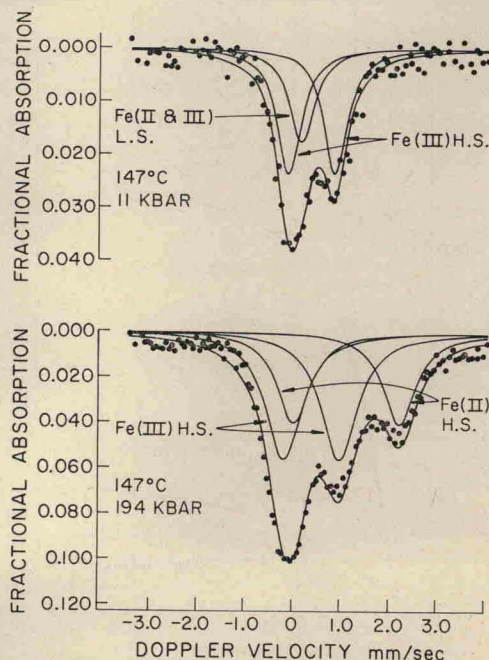

FIG. 8. Mössbauer spectra of copper ferricyanide.

appeared possible that the transitions measuring the low-spin crystal field were shifted to lower energy. This shift from low spin to high spin with increasing pressure at first appears paradoxical. One knows that the ligand field in high-spin complexes increases with decreasing metal–ligand distance.[1] There is a critical value of Δ of about 14 000–15 000 cm^{-1}, wherein a transition from high spin to low spin is expected. This has been observed as a function of temperature[15] and in this laboratory as a function of pressure in phenanthroline complexes.[16]

However, the conversion of Fe(III) to Fe(II) with pressure indicates that iron has an increased affinity for electrons with increasing compression, and that the $3d$ levels lower in energy with respect to the ligand levels. These factors would tend to reduce the back donation and weaken the pi bonding, increasing the energy of the low-spin state. The situation is illustrated schematically
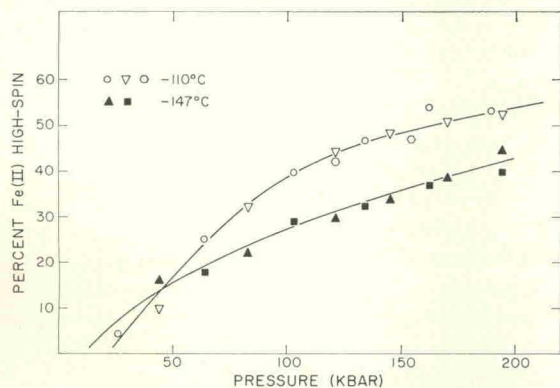
FIG. 9. Conversion to high-spin Fe(II) at 110°C and 147°C—copper ferricyanide.

in Fig. 6. Movement to the left in the figure represents increasing Δ and decreasing R(Fe–C distance). The decreased back donation has the effect of moving the low-spin potential well up, and possibly to the right. The high-spin potential well moves to left, until one arrives at a state where electrons can transfer thermally from the low-spin to the high-spin state. It is clear that high-pressure–high-temperature optical studies would be very helpful. The combined temperature–pressure wavelength range is beyond the reach of our old single-beam high-pressure optical apparatus, but a double-beam system is being developed, and eventually such measurements should be possible.

The dependence of conversion on the cation is of interest. It is consistent with the isomer-shift data of Fig. 1. The K+ and Na+ salts which showed no conversion exhibit large decreases in isomer shift due to increased sigma bonding. In the Cu+2 salt the increased

[15] E. König and K. Madeja, Inorg. Chem. 6, 48 (1967).
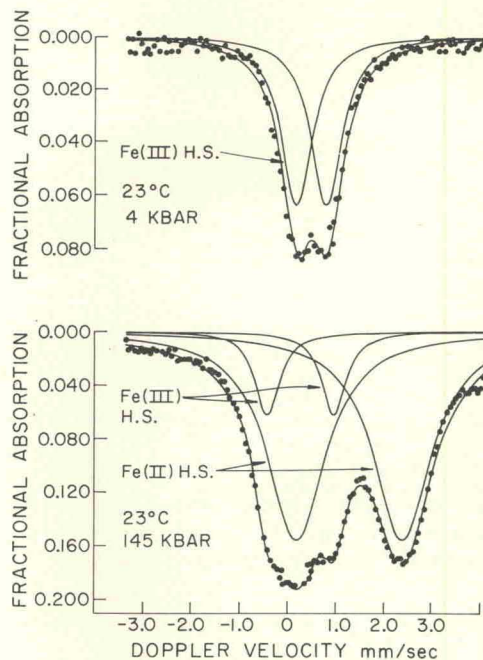[16] D. C. Fisher (personal communication, 1968).

FIG. 10. Mössbauer spectra of $Fe_4^{47}[Fe(CN)_6]_3$.

shielding due to decreased back bonding actually overcomes the first effect. The other salts are intermediate. The order of electronegativity as determined from electrode potentials is K > Na > Zn > Ni > Cu. Evidently the metal with the greatest tendency for covalency has the greatest effect in decreasing back donation. The difference in crystal structure between heavy metal and alkali salts may also be a factor. The possibility exists
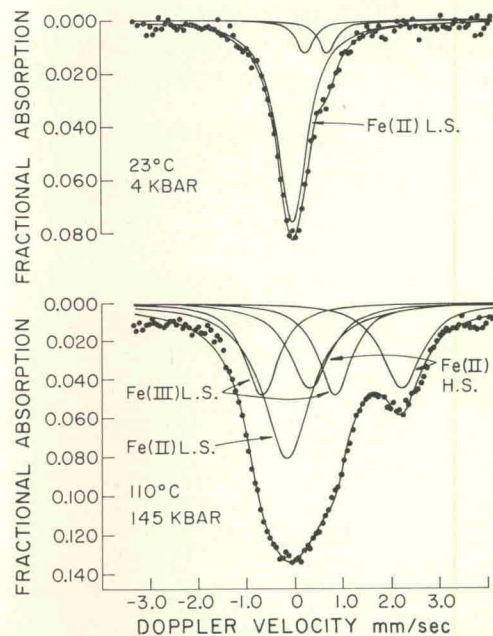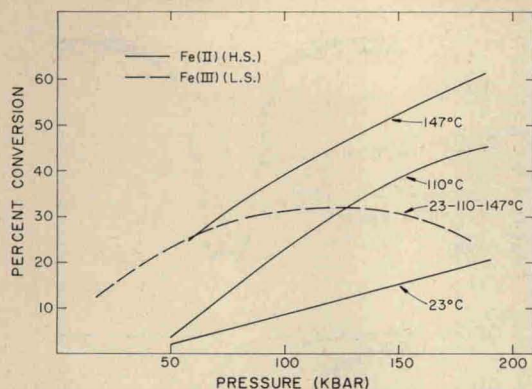
FIG. 11. Mössbauer spectra of $Fe_4[Fe^{57}(CN)_6]_3$.

FIG. 12. Conversion to low-spin Fe(III) and high-spin Fe(II) vs pressure—$Fe_4[^{57}Fe(CN)_6]_3$.

that one is observing isomerization, i.e., that the cyanide ion is flipping so that the nitrogen bonds to the iron. The prussian-blue spectra discussed later in this paper, and the spectra of $Fe^{57}Fe(CN)_5NO$ discussed in the following paper effectively eliminate this possibility.

FERRICYANIDES

The ferricyanides of the same five cations were studied in high pressure and high temperature. In a previous paper[9] we showed that $K_3Fe(CN)_6$ reduced to the ferrous state very rapidly with increasing pressure at room temperature until a first-order phase transition intervened. All of the other four salts also reduced very rapidly with pressure at 23°C but with no sign of a phase transition. The ferrous and ferric isomer shifts are superimposed, and only in the sodium salt could we get any quantitative measure of the amount of reduction. The quadrupole splitting of the ferric ion in the heavy metal salts was too small to permit a fit to be made. The initial isomer shifts are listed in Table III. The reduction of sodium ferricyanide could be discribed by the relation

$$K = C_{II}/C_{III} = 0.12P^{1.57}, \qquad (1)$$

where C_{II} and C_{III} are the concentrations of ferrous

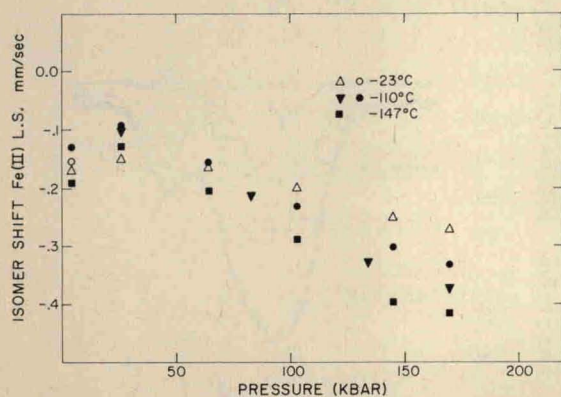FIG. 13. Isomer shift vs pressure—low-spin Fe(II) in $Fe_4[^{57}Fe(CN)_6]_3$.

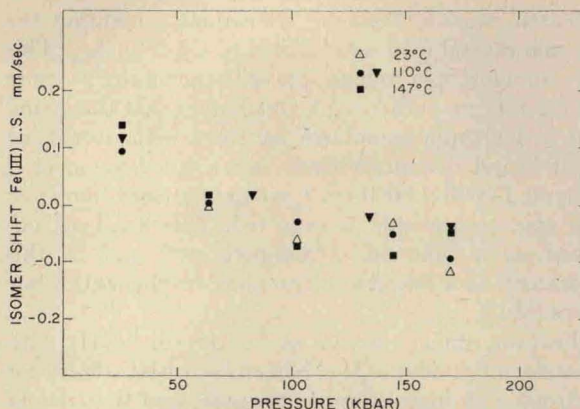FIG. 14. Isomer shift vs pressure—low-spin (Fe(III) in $Fe_4[^{57}Fe(CN)_6]_3$.

and ferric sites with their ligands, and P is the pressure in kilobars. At 110°C and high pressure all of these materials exhibited high-spin Fe(II) peaks which increased in size with pressure. The isomer shifts were in the same range as for the ferrocyanides. The quadrupole splittings appear in Table IV. The conversions at 110°C are shown in Fig. 7. For every salt except the copper the conversion to high-spin Fe(II) is substantially higher than for the ferrocyanides. Even the K^+ and Na^+ salts show measurable conversion. There are some differences in crystal structure—the heavy metals involve both bridged and interstitial cations. However, we believe that the main difference is the following. At the reduction we have a low-spin Fe(II) surrounded by six $(CN)^-$ ions plus a hole. This hole serves to weaken the bonding and move the low-spin potential well up and to the right in Fig. 6. Again, high-pressure optical studies will be helpful.

The $Cu_3[Fe(CN)_6]_2$ ion exhibited an additional feature of interest. At 110 C it behaved like the other salts. At 147° and low pressure, before any significant reduction appeared, it exhibited considerable conversion of low-spin Fe(III) to high-spin Fe(III), as can be seen in the upper spectrum of Fig. 8. With increasing pressure the high-spin Fe(III) reduced to high-spin Fe(II) as in the lower spectrum. Figure 9 shows that the amount of high-spin Fe(II) at a given pressure was actually less at 147°C than at 110°C. The shape of the conversion-pressure curve is also different. The reduc-

TABLE V. Yield of high-spin Fe(II) from $^{57}Fe_4[Fe(CN)_6]_3$.

Pressure (kbar)	Percent 23°C	Fe(II) H.S. 147°C
20	12	35
60	40	73
100	67	88
140	83	95
180	92	97

TABLE VI. Quadrupole splittings in high pressure products from prussian blue.

Material	Pressure (kbar)					
	25	50	100	150	175	
Low-spin Fe(III)	1.20	1.25	1.42	1.60	1.67	(23–110–147°C)
High-spin Fe(II)	⋯	2.00	2.1	2.10	2.10	(23°C)
	⋯	1.78	1.90	1.92	1.95	(110–147°C)

tion of high-spin Fe(III) to high-spin Fe(II) could be fit by the equation

$$K = C_{II}/C_{III} = 1.98 \times 10^{-3} P^{1.12}. \qquad (2)$$

PRUSSIAN BLUE

The structure of prussian blue has been elucidated by Robin.[17] Insoluble prussian blue has the formula $Fe_4[Fe(CN)_6]_3$, it is a ferric ferrocyanide. A low-spin Fe(II) is coordinated to the carbon, and a high-spin Fe(III) to the nitrogen. It offers the possibility of combining ordinary ferrocyanide with a ferric salt enriched to 90% in ^{57}Fe, and also of using an ordinary (2% ^{57}Fe) ferric salt with enriched ferrocyanide. Both these possibilities were exploited. The initial isomer shifts appear in Table III. Figure 10 shows spectra of $^{57}Fe_4[Fe(CN)_6]_3$ at atmosphere and at high pressure. There is a large decrease in high-spin Fe(III) and a large increase in high-spin Fe(II). The disappearance of the Fe(III) involves both direct reduction and the electron-transfer process described below. Conversions appear in Table V.

There was no sign of low-spin Fe(III) in the spectrum. This makes isomerization (reversal of the CN⁻ ion) very unlikely as an explanation of the low-spin to high-spin transformation

In the spectra of $Fe_4[Fe^{57}(CN)_6]_3$ two features appear. (See Fig. 11.) At low pressure and low temperature a low-spin Fe(III) spectrum appears and grows with pressure at first. This indicates an electron transfer from the Fe(III) cation to the ferrocyanide. As can be seen from the dashed curve of Fig. 12, this equilibration is independent of temperature. Robin

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

and Day[18] have given a thorough discussion of mixed-valence compounds and electron transfer. It is of interest that the probability that the electron will appear on the iron bonded to the carbon decreases with pressure. At higher pressures, the conversion to Fe(II) high spin begins to dominate. As can be seen from Fig. 12, this conversion increases markedly with increasing temperature. The high-spin Fe(II) comes in part from the process described earlier in this paper, but at the highest pressures there is actually a reduction in the amount of Fe(III) low spin present. Figure 13 and 14 show the change in isomer shift with pressure for the low-spin Fe(II) and the low-spin Fe(III) formed by electron exchange. The Fe(II) shows a maximum at low pressure consistent with a large decrease in back donation. It should be kept in mind that the isomer shifts at elevated temperature should contain a small correction since source and absorber were at slightly different temperature. This would in no way affect the conclusions. Table VI exhibits the quadrupole splittings of the low-spin Fe(III) and high-spin Fe(II) produced under pressure.

This work reinforces the earlier work on the reduction of iron with pressure in illustrating the increase of affinity of iron for electrons with increasing compression.

ACKNOWLEDGMENTS

[18] M. B. Robin and P. Day, Advan Inorg. Chem. Radiochem. 10, 247 (1967).