

## 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 Fe<sup>57</sup>. 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  $\Delta$ . For many complexes these levels are filled according to Hund's rule, giving maximum multiplicity. A number of high-pressure optical studies<sup>1</sup> have shown that for these high-spin complexes  $\Delta$  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  $\Delta \cong 9000 \text{ cm}^{-1}$  at 1 atm and  $B \cong \frac{1}{4}C \cong 900 \text{ cm}^{-1}$ .  $\Delta$  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 ( $\sim 1.3$  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.<sup>2</sup> 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<sup>3</sup> (both high spin and low spin). This has been explained rather conclusively in terms of an electron transfer from a ligand non-bonding 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 electrophilic.

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  $\Delta \sim 30\text{--}32\ 000 \text{ cm}^{-1}$  and  $B \sim 400 \text{ cm}^{-1}$ . 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.<sup>4-7</sup> 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  $\pi^*$  orbitals of the ligand, indicated by the triple line on the

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<sup>1</sup> 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.

<sup>2</sup> A. R. Champion, R. W. Vaughan, and H. G. Drickamer, *J. Chem. Phys.* **47**, 2583 (1967).

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

<sup>4</sup> W. P. Griffith, *Quart. Rev. (London)* **16**, 188 (1962).

<sup>5</sup> J. J. Alexander and H. B. Gray, *Coord. Chem. Rev.* **2**, 29 (1967).

<sup>6</sup> H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.* **87**, 3340 (1965).

<sup>7</sup> D. F. Schriver, *Struct. Bonding (Berlin)* **1**, 32 (1966).



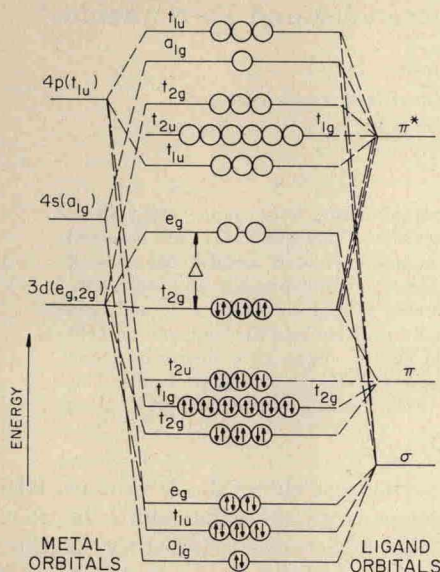


FIG. 1. Molecular orbital diagram—ferrocyanides.

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  $\Delta$ , and reduces shielding of the  $3s$  orbitals, which explains the high electron density at the nucleus. Shulman and Sugano<sup>8</sup> have given a semiquantitative discussion of this behavior. High-pressure Mössbauer resonance data on  $K_4Fe(CN)_6$ <sup>9</sup> 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  $\Delta$  may actually decrease somewhat with increasing pressure in the ferrocyanide.

The high-pressure Mössbauer resonance techniques used here have been presented elsewhere.<sup>10</sup> The results

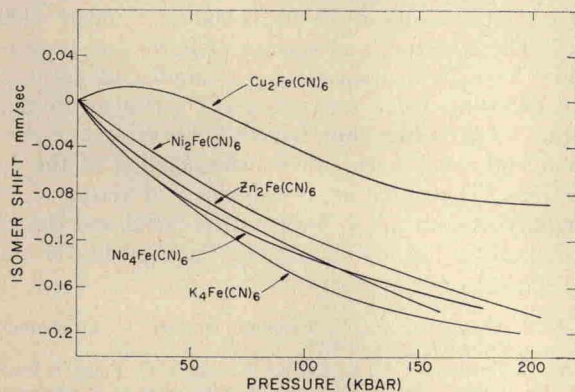


FIG. 2. Relative change in isomer shift with pressure—ferrocyanides.

<sup>8</sup> R. G. Shulman and S. Sugano, *J. Chem. Phys.* **42**, 39 (1965).

<sup>9</sup> A. R. Champion and H. G. Drickamer, *J. Chem. Phys.* **47**, 2591 (1967).

<sup>10</sup> P. DeBrunner, R. W. Vaughan, A. R. Champion, J. Cohen, J. Moyzis, and H. G. Drickamer, *Rev. Sci. Instr.* **37**, 1310 (1966).

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.<sup>11,12</sup> The first two have more complex structures<sup>13</sup> 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<sup>11,14</sup> 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.

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

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)

<sup>11</sup> H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.* **46**, 99 (1962).

<sup>12</sup> A. K. Van Bever, *Rec. Trav. Chim.* **57**, 1259 (1938).

<sup>13</sup> A. J. C. Wilson, *Struct. Rept.* **9**, 209 (1942-44); **11**, 421 (1947-48).

<sup>14</sup> J. N. Friend, *A Textbook of Inorganic Chemistry* (C. Griffin & Co., London, 1925), Pt. 2, p. 212.