

changes in the sigma orbitals. The zinc salt shows a little smaller decrease, the nickel salt appreciably less, while the copper salt, which showed the maximum conversion, exhibits an actual *increase* in isomer shift with pressure in the low-pressure region. Evidently the relocation of t_{2g} electrons due to reduced back donation, more than overcomes the usual spreading of the sigma orbitals.

The effect of the cation on the conversion is of interest. There is a difference in crystal structure between the alkali ferrocyanides and the heavy metal ferrocyanides which may be a factor. The order of the electronegativities as determined from the electrode potentials is $K^+ > Na^+ > Zn^{++} > Ni^{++} > Cu^{++}$. This is the inverse order of the conversion. Evidently the copper, which forms the most covalent bond with the nitrogen end of the ferrocyanide, perturbs the electron distribution on the cyanide most strongly in a fashion to reduce iron-to-carbon back donation. On the other hand, the potassium, which forms a strongly ionic bond with the molecular ion, offers the least perturbation.

It is of interest to investigate the effect of strain and distortion on the low- to high-spin conversion. A strained ferrocyanide site is produced by the pressure-induced reduction of ferricyanides. All of the ferricyanides reduce easily with increasing pressure, so that by 40–50 kbar at 23°C, they are 80–90% converted to the ferrocyanide. In Fig. 8, one observes the spin state as a function of pressure for the five ferrocyanides so produced. The order of the cations is essentially preserved, but in each case there is more low- to high-spin conversion at a given pressure than one observes for the corresponding ordinary ferrocyanide. Even the potassium, sodium, and zinc salts show significant conversion at 110°C.

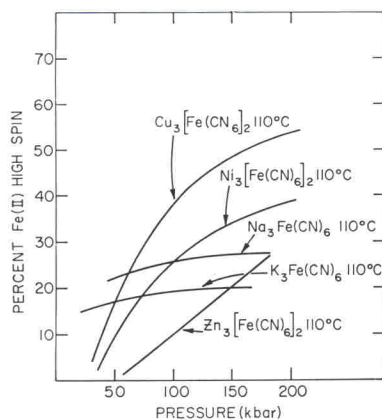


FIG. 8. Percent high-spin Fe(II) versus pressure—ferrocyanides made from ferricyanides.

The difference between these compounds and ordinary ferrocyanides is that here one has a hole either circulating among the six cyanide ions, or isolated on one of them to form a free radical. Evidently the back donation is significantly weakened by the presence of the hole.

A distortion in local symmetry at the iron site is produced by substituting for one of the cyanide ligands. The most widely studied systems are the nitroprussides, where an NO replaces the CN^- ion. The arrangement consists nominally of a low-spin ferrous ion surrounded by five CN^- ions and an NO^+ , although the actual electron distribution must be more complex (12). The Fe–NO bond length is only 1.63 Å compared with the Fe–CN distance of 1.91 Å. This strong distortion accounts for the high quadrupole splitting shown in Table I. The nitroprusside ion exhibits a very strong ligand field and even larger delocalization of the $t_{2g}(\pi)$ orbitals than does ferrocyanide. Other substitutions for a CN^- are possible. The substitution of NH_3 results in considerably less distortion, less quadrupole splitting, and a smaller degree of back donation.

Figure 9 shows the low- to high-spin conversion for a series of nitroprussides, as well as for the NH_3 substituted cyanide (13). The nitroprussides exhibit a very high degree of spin conversion, the NH_3 substituted complex shows markedly less. Evidently the distortion introduced by the substituent has an important effect on the change of bonding with pressure. Figure 10 shows the change of isomer shift with pressure for the low-spin ferrous ion. Again, those complexes which exhibit most high spin

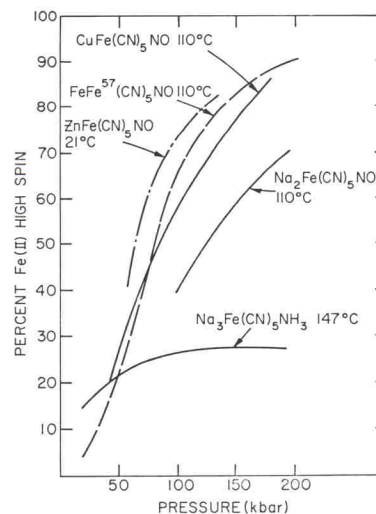


FIG. 9. Percent high-spin Fe(II) versus pressure—substituted cyanides.

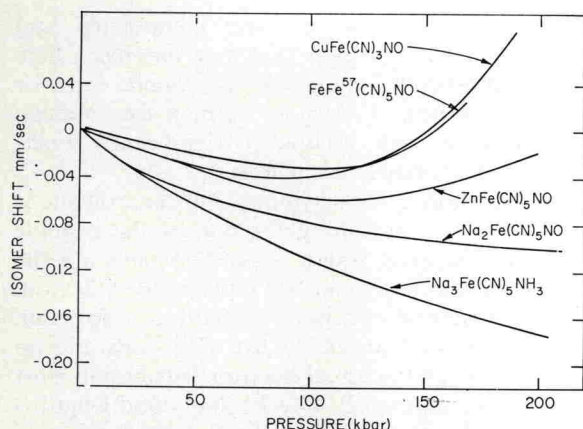


FIG. 10. Isomer shift (relative to 1 atm) versus pressure—substituted cyanides.

conversion show an actual decrease in electron density at the iron nucleus with pressure, while the NH_3 substituted complex exhibits less conversion and the usual increase in electron density with pressure.

In addition to these general studies, two compounds merit special discussion. These are Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, and ferrous nitroprusside $\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}]$. In each case, we find iron in two different oxidation and/or spin states. It is possible to tag each type of site separately with ^{57}Fe and look at its behavior. We have done this with both these compounds.

Prussian blue is ferric ferrocyanide. It consists of a low-spin $\text{Fe}(\text{II})$ ion coordinated to six cyanides through the carbon, and a high-spin $\text{Fe}(\text{III})$ ion coordinated to the nitrogen (14). From Fig. 11 one observes that the high-spin $\text{Fe}(\text{III})$ transforms to high-spin $\text{Fe}(\text{II})$ very strongly with increasing pressure. As we shall see in a moment, the disappearance of $\text{Fe}(\text{III})$ high spin involves both the direct reduction and a second process. The fact that

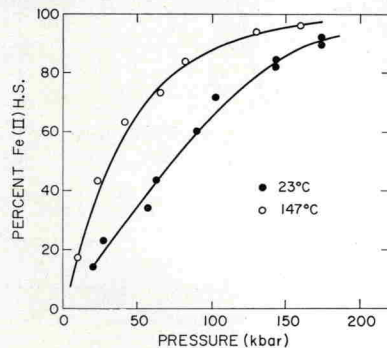


FIG. 11. Yield of high-spin $\text{Fe}(\text{II})$ from $^{57}\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

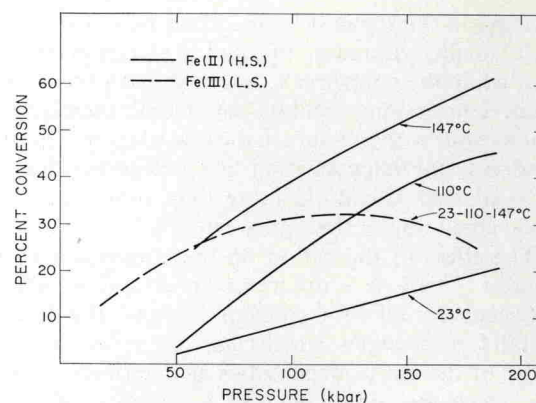
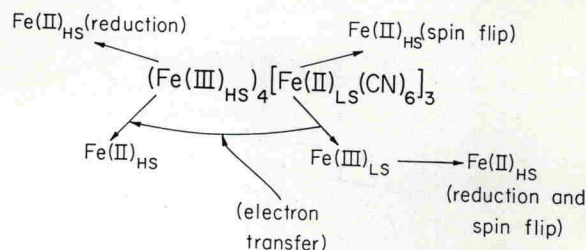


FIG. 12. Conversion versus pressure— $\text{Fe}_4[^{57}\text{Fe}(\text{CN})_6]_3$.

no low-spin iron appears in this spectrum eliminates the possibility that the change of spin state is due to isomerization of the CN^- ion. The data on $^{57}\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}]$ confirm this conclusion.

In the spectra of $\text{Fe}_4[\text{Fe}^{57}(\text{CN})_6]_3$ two features appear. At moderate pressures, low-spin $\text{Fe}(\text{III})$ appears. This indicates the transfer of an electron from the low-spin $\text{Fe}(\text{II})$ of the ferrocyanide to the high-spin $\text{Fe}(\text{III})$ cation. At higher pressures the low- to high-spin transformation of the $\text{Fe}(\text{II})$ dominates. As can be seen from Fig. 12, the electron distribution between iron sites is independent of temperature, but the spin flip is not. It is of interest that the energies of the t_{2g} levels on the cation coordinated to the nitrogen lower with increasing pressure with respect to those on the iron coordinated to the carbon. At 1 atm in the ground state, the electron is on the ferrocyanide ion. From Figs. 11 and 12, one can see that at 150°C and 160 kbar, over 90% of the ferric ions present are low-spin ions (coordinated to the carbon); that is, there is over 90% probability that the electron has transferred to the cation. The processes that occur under pressure are illustrated by the following diagram.



In this diagram *reduction* refers always to ligand to metal electron transfer.

In $\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}]$ the cation is a high-spin ferrous ion. With pressure, one observes for