

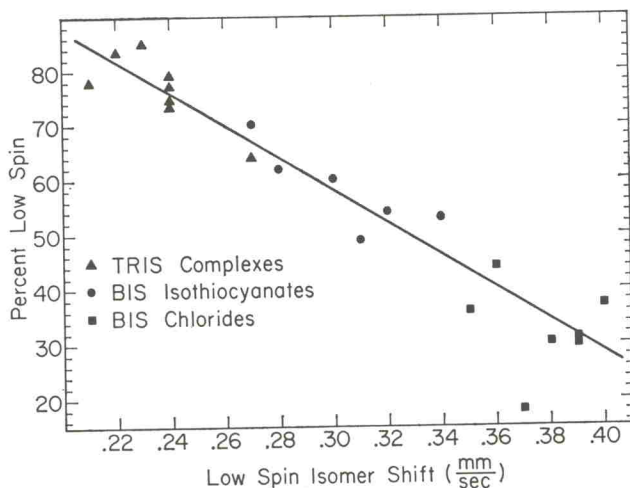


FIGURE 7. Low spin ferrous isomer shifts vs percent low spin at 100 kbar—phenanthrolines.

high spin ferrous ion, and $\text{Ni}_2\text{Fe}(\text{CN})_6$ exhibits 18–20%. The isomorphous $\text{Zn}_2\text{Fe}(\text{CN})_6$ and the sodium and potassium salts, with a slightly different structure, exhibit no conversion. At 150°C and high pressure the zinc salt exhibits ~25% conversion to high spin, and the sodium and potassium salts show small traces (<10%). Since the conversion depends so sharply on the cation it is apparent that the occupation of the ligand π^* orbitals at high pressure involves both cyanide and cation π electrons.

A third set of systems where one observes spin change is that involving substituted ferrous phthalocyanines (76). The planar molecule consists basically of four pyrrole rings bridged by nitrogens. The ferrous ion lies in the plane in a site of D_{4h} symmetry. The substitutions studied involve the axial addition of pyridine, substituted pyridines, or piperidine above and below the plane. The order of the orbitals is apparently (with increasing energy) $d_{xz}, d_{yz}(e_g)$; $d_{xy}(b_{2g})$; $d_{z^2}(a_{1g})$; and $d_{x^2-y^2}(b_{1g})$. In the unsubstituted molecule the splitting between d_{z^2} and $d_{x^2-y^2}$ is sufficient that one obtains an intermediate spin ferrous ion. The addition of axial ligands raises the energy of the d_{z^2} orbital sufficiently to give a low spin iron. For the pyridines and substituted pyridines this effect is reinforced by backdonation from the metal d_π orbitals to the ligand π^* orbitals. This is reflected in the order of the metal-to-ligand charge transfer peaks. The piperidine has no empty π^* orbitals but exhibits very strong σ bonding as exemplified by the very large acid dissociation constant of the piperidine derivative.

With increasing pressure the low spin compounds transform partially to intermediate spin, but the conversion levels off above ~ 100 kbar. For the pyridines and picolines the conversion to intermediate spin is primarily due to decrease in backdonation both to the axial and planar ligands, just as with the phenanthrolines and cyanides. This decrease in backdonation raises the energy of the metal d_{π} orbitals. This tendency is balanced by the spreading of the $3d$ orbitals which is accentuated by the thermal occupation of the π^* orbitals by ligand π electrons at high pressure. Since these π^* orbitals are concentrated farther out on the periphery of the molecule than the π orbitals this increases the possibility of $3d$ expansion. The piperidine complex, which exhibits backbonding only to the phthalocyanine nitrogens, converts only modestly to intermediate spin at low pressure, and the amount of intermediate spin actually decreases at high pressure.

Change of oxidation state.—The most general electronic transition discovered in compounds of iron is the reduction of ferric iron to the ferrous state. The mechanism involves the transfer of an electron from a ligand non-bonding level to the metal d_{π} orbitals. The first observations were published in 1967 (77), and since then reduction has been observed in perhaps 40–50 compounds including halides, cyanides, hydrates, salts of organic acids, and a variety of organometallic compounds. Higher oxidation states, as in the ferrates (78), also reduce with pressure. The optical absorption peaks corresponding to electron transfer from ligand to metal usually have maxima in the range 2–4 eV. They shift to lower energy by as much as 0.2–0.3 eV at 150 kbar. This red shift is associated with the spreading of the $3d$ electrons which is also reflected in the decrease of isomer shift and of the Racah parameters with increasing pressure. The data published up to 1970 have been summarized elsewhere (79). Much of the earlier data must be regarded as qualitative because of difficulties in perfecting experimental techniques. In any case, there is no easy way of comparing the electronic properties of many of the ligands. There are some general results. First, the reduction increases with pressure, but does not go to completion. For many compounds over a considerable range of pressure and conversion, the data can be approximated by the expression:

$$K = \frac{C_{II}}{C_{III}} = AP^M \quad 1.$$

where C_{II} and C_{III} are the concentrations of ferrous and ferric ions, P is the pressure, and A and M are constants. Second, the reduction generally increases with temperature. Third, the process is reversible in the sense discussed earlier.

We shall restrict our detailed discussion here primarily to a recent study of a series of substituted acetylacetonates (19). This study utilized refinements