

excellent basis for a systematic study of electronic properties, because it is possible to vary the field at the iron in a controlled manner by varying the extra ligands on the bis complexes or by substituting different groups (e.g. CH_3 , Cl , NO_2) at various positions on the phenanthrolines. Two such studies have recently been published (3, 74). With increasing pressure, the high spin bis complexes tend to convert to low spin, as can be seen in Figure 6. The pressure at which conversion initiates correlates with the size of the ligand field at 1 atm, as one might expect. The surprising feature is that at 40–80 kbar the high spin to low spin conversion stops and at higher pressures there may actually be a net low spin to high spin conversion with increasing pressure. Similarly, the low spin tris complexes convert partially to high spin at high pressure.

At first a low to high spin transition seems difficult to understand either on electronic or thermodynamic grounds. It is normal for the ligand field to increase with pressure, which should increase the probability of the low spin state. For most compounds the effective ionic radius of a low spin Fe(II) ion is smaller than that of the high spin ion.

The bonding of phenanthroline to iron has a component common to many ligands which have empty orbitals of π symmetry lying not too far above metal d_π orbitals. The metal tends to donate electrons into these π^* orbitals, which increases the bonding and tends to stabilize the metal d_π orbitals and thus to increase the ligand field. The difference in ligand field between the tris and bis complexes and within each group are primarily associated with differences in backdonation. If the π^* orbitals tend to be occupied by ligand π

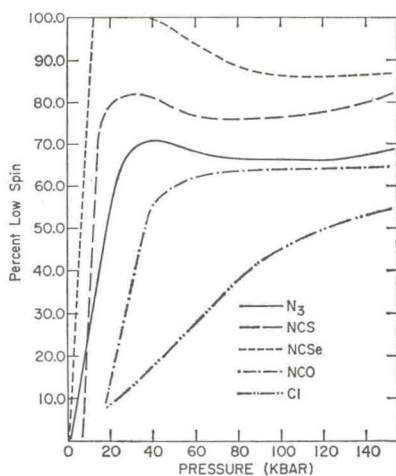


FIGURE 6. Conversion to low spin vs pressure—ferrous bis phenanthroline complexes.

electrons at high pressure they are less available for backdonation. Any reduction in backbonding would reduce the size of the ligand field and, therefore, the probability of the low spin state.

To the extent that the π orbital is emptied by π - π^* transfer it becomes available for metal d_π to ligand π backdonation. This form of backdonation would, however, tend to destabilize the d_π orbitals and thus to reduce the ligand field.

The lowest allowed π - π^* optical transitions lie in the range 2–4 eV. They shift rapidly to lower energy with increasing pressure. While the red shift implies increased occupation of the π^* orbital at high pressure, the shift is still only a small fraction of ν_{\max} . It appears that one must postulate a large difference between optical and thermal transition energies to obtain significant occupation of π^* orbitals with π electrons in the requisite pressure range. The difference between thermal and optical transitions are discussed in more detail in a later section.

It is also possible that the compressibility of the system is greater when the iron is high spin, or that the arrangement of the molecules when the iron is high spin allows a closer packing. It is important to remember that the criterion for increase of conversion with pressure is that the volume of the system as a whole decrease with increasing conversion at constant p and T . This may come about due to the shortening of bonds or the closer packing of the complexes due to changes in their electronic structure. It is, of course, not necessary that every bond in the system shorten to accomplish this objective.

As indicated above, the probability of the low spin state is related directly to the size of the ligand field. The low energy tail of the charge transfer peak tends to obscure the ligand field peaks. Since the charge transfer peak tends to shift red with pressure, it is not practical to measure the ligand field optically as a function of pressure. However, Erickson (67) has demonstrated an excellent correlation between the low spin isomer shift and the ligand field Δ ; the larger the ligand field the smaller the isomer shift. This is inherently reasonable, as the lower isomer shift results from larger backbonding, greater delocalization of the $3d$ electrons, and less shielding of the $3s$ electrons. In Figure 7, we see the very satisfactory correlation between low spin isomer shift and fraction low spin ferrous ion present for a series of substituted phenanthrolines (74). The data presented in the figure are for 100 kbar, but similar correlations apply at other pressures and for other groups of phenanthrolines, as discussed in the original papers.

A second group of low spin ferrous compounds where backdonation is important are the ferrocyanides (75). Since these involve relatively large ligand fields ($\Delta = 30$ – 35 kK), one would not anticipate a ready conversion to the high spin state. At room temperature indeed no conversion occurs, below 200 kbar, at least. However, at 110°C and 150 kbar $\text{Cu}_2\text{Fe}(\text{CN})_6$ exhibits 65%