

## Effect of Pressure on the Spin State of Iron in Ferrous Phenanthroline Compounds\*

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The effect of pressure to 175 kbar has been measured on the spin state of Fe(II) in bis- and trisphenanthroline complexes, using Mössbauer resonance and optical absorption. The bis complexes can be classified according to the degree of back bonding to the nonphenanthroline ligands. Compounds with halide ligands are high spin at low pressure. They convert to low spin with increasing pressure, but the rate of conversion with pressure decreases above 80 kbar. Compounds with intermediate back bonding (e.g., cyanates, thiocyanates, selenocyanates, or azides) are high spin at low pressure. With increasing pressure they tend to convert to low spin, but above  $\sim 30$ – $40$  kbar there is a net low-to-high spin conversion. The biscyanide is low spin at low pressure. At high pressure significant conversion to high spin is observed. All tris complexes are low spin at low pressure and exhibit measurable conversion to high spin at high pressure. The optical absorption data indicate large red shifts for the ligand  $\pi$ - $\pi^*$  transitions and smaller red shifts for the metal-to-ligand charge transfer peaks. These results are explained in terms of reduced back donation due to thermal occupation of the ligand  $n^*$  orbitals by ligand  $\pi$  electrons. The behavior is compared to that of the ferrocyanides. Similar experimental results are presented and briefly discussed for an intermediate-spin phenanthroline complex and for several bipyridyl compounds.

The compounds of ferrous iron with 1,10-phenanthroline have wide interest as prototypes for biologically active compounds and as analytical reagents, so their properties have been extensively studied.<sup>1-3</sup> Phenanthroline [(Fig. 1(a))] is a planar aromatic molecule with nitrogens at the one and ten positions, each of which can coordinate with a metal ligand. It forms two types of pseudo-octahedral complexes. In the bis compounds two phenanthrolines complex with iron, and the anions supply the other two ligands. In the tris complexes there are three phenanthrolines coordinated to the iron, and the anions are outside the coordination sphere.

In this paper we study the effect of pressure to 175 kbar on the spin state of iron in phenanthroline complexes. A few results are also presented on related complexes of bipyridyl [(Fig. 1(b))].

For a free atom or ion, or ionic compound the normal spin state is that of maximum multiplicity, in accordance with Hund's rule, however, for sufficiently large ligand field, one obtains a low-spin ground state. A large fraction of iron compounds which are low spin involve organic ligands or ligands such as  $\text{CN}^-$ . These have empty orbitals ( $\pi^*$  orbitals) which are not too high in energy above the ground state, and have the correct symmetry to bond with the occupied metal  $\pi^*(t_{2g})$  orbitals. This "back donation" of metal electrons into the ligand orbitals gives a strong bonding, a large ligand field,  $\Delta$ , and a decrease in interelectronic repulsion, as measured by the Racah parameters, due to delocalization of the  $t_{2g}$  electrons.

For a high-spin compound the effect of pressure is to increase the ligand field<sup>4,5</sup> (very crudely it varies as  $R^{-5}$ , where  $R$  is the metal-ligand distance), and to decrease the Racah parameters.<sup>4,5</sup> The increase in ligand field strength is due to increased electrostatic repulsion as well as stronger covalent bonding. The relative importance of these two causes varies widely

with the nature of the ligand. The decrease in the Racah parameters is associated with increased overlap of metal and ligand electrons, i.e., increased covalency, and consequent delocalization of the  $3d$  electrons (the "nephelauxetic effect" of Jorgensen<sup>6</sup>). The ligand field may increase as much as 15%–20% in 200 kbar. For high-spin systems with reasonably strong ligand

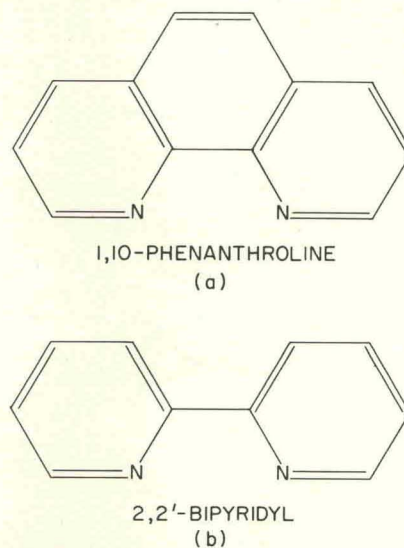


FIG. 1. Structure of 1,10-phenanthroline and 2,2'-bipyridyl.

fields a transition to low spin may be observed, e.g., for Fe(II) as a dilute substitutional impurity in  $\text{MnS}_2$ .<sup>7</sup>

In this paper we study the effect of pressure to 175 kbar on the spin state of Fe(II) in 12 phenanthroline complexes and four bipyridyl complexes. The compounds were synthesized using iron enriched to 75%–90% in  $^{57}\text{Fe}$ , using techniques from the literature.<sup>8-11</sup> Analyses for C, N, H, and Fe gave agreement generally



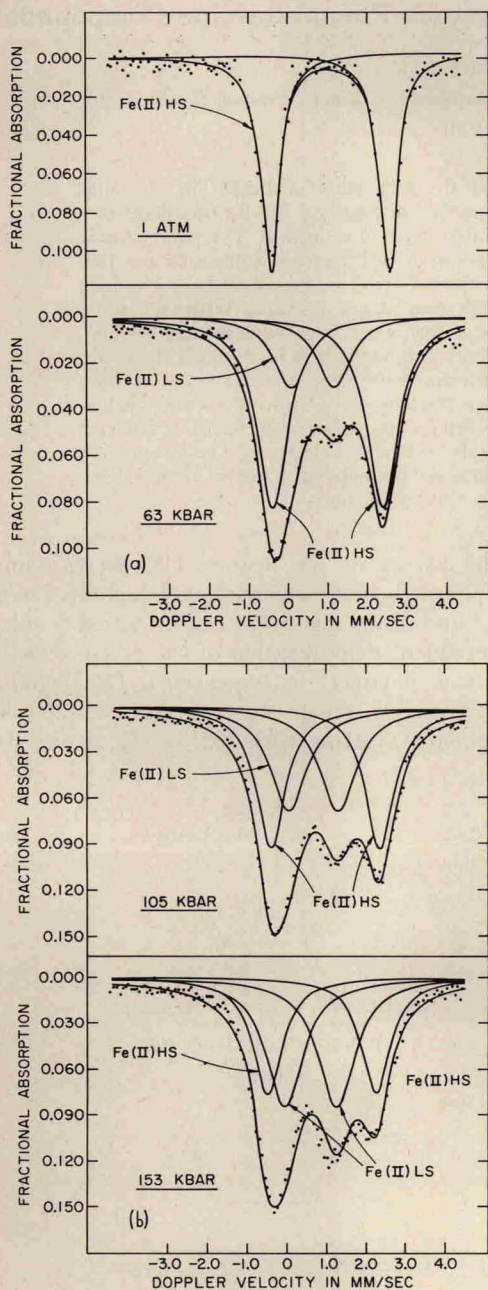


FIG. 2. Mössbauer spectra of  $\text{Fe}(\text{phen})_2\text{Cl}_2$ .

within 0.1% of the calculated values. The tools used in this investigation were Mössbauer resonance and optical absorption. The high-pressure techniques have been described elsewhere.<sup>12-14</sup>

Mössbauer resonance permits a determination of the spin states of ferrous iron. The parameters used are the isomer shift and quadrupole splitting. The isomer shift measures the *s*-electron density at the iron nucleus. High-spin ferrous iron exhibits a relatively large positive isomer shift (for high-spin phenanthroline complexes

0.95–1.05 mm/sec relative to iron metal). This corresponds to a relatively low electron density at the iron nucleus as there are six *3d* electrons shielding the *3s* electrons. Low-spin ferrous iron exhibits a markedly small isomer shift ( $\sim 0.1$ – $0.3$  mm/sec), primarily because the *t<sub>2g</sub>* electrons are delocalized into the ligand  $\pi^*$  orbitals by back donation reducing the shielding of the *3s* electrons. The quadrupole splitting results from the interaction of an electric field gradient at the iron nucleus with the nuclear quadrupole moment. A noncubic arrangement of the ligands can impose an electric field gradient. However, when present, an aspherical occupation of the *3d* shell usually gives a larger gradient. Since the high-spin ferrous configuration is not spherically symmetric, the high-spin ion exhibits a large quadrupole splitting (2.5–3.0 mm/sec), while the spherically symmetric low-spin state exhibits much smaller values (0.3–0.6 mm/sec). The relative amounts of the spin states present can be calculated from the areas under the Lorentzian peaks fitted to the experimental Mössbauer spectra.

The optical absorption peaks we shall be interested in include the visible peaks which measure electron transfer from the metal *t<sub>2g</sub>* orbitals to the ligand  $\pi^*$  orbital and the ultraviolet peaks involving excitation of an electron from the ligand  $\pi$  orbitals to the  $\pi^*$  orbitals. Both of these are useful in understanding the spin transitions.

The discussion is arranged as follows. First we present Mössbauer resonance and optical absorption results for

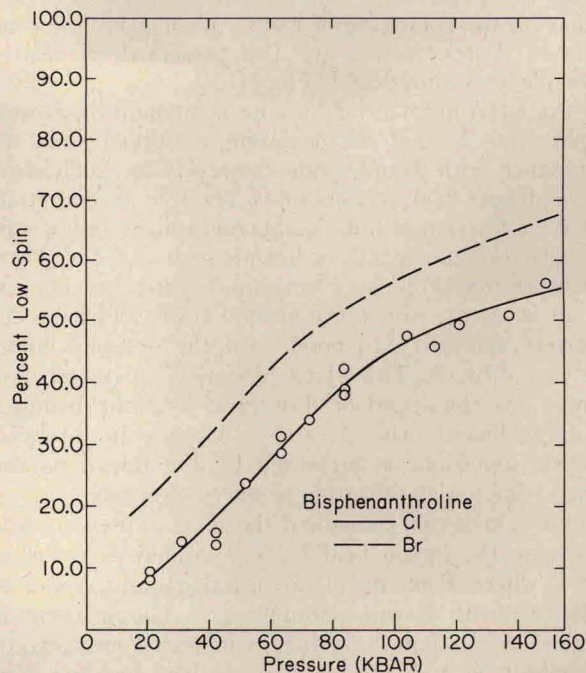


FIG. 3. Percent low spin vs pressure,  $\text{Fe}(\text{phen})_2\text{Cl}_2$  and  $\text{Fe}(\text{phen})_2\text{Br}_2$ .