

TABLE VIII. Shift of higher energy metal-ligand charge transfer peak ($\Delta\nu$, cm^{-1}).

Compound	Pressure (kilobars)					
	20 (position)	50	75	100	120	140
Fe(phen) ₂ X ₂						
Cl	(19 020)	-530	-900	-1210	-1450	-1700
NCS	(18 880)	-560	-820	-980	-1050	-1080
NCS _e	(18 780)	-540	-760	-900	-970	-1000
N ₃	(19 550)	-650	-1020	-1320	-1520	-1710
NCO	(18 950)	-580	-880	-1090	-1220	-1330
Fe(phen) ₃ X ₂						
N ₃ (6H ₂ O) ^a	(18 850)	-660	-950	-1150	-1290	-1430
SCN(1H ₂ O)	(18 520)	-510	-790	-1000	-1150	-1300
NCO(<i>n</i> H ₂ O)	(18 980)	-750	-1140	-1430	-1630	-1840

^a Waters of hydration are indicated in parentheses.

compounds, as well as a large red shift of the optical transitions. The molecular orbital diagram of Fig. 17(b) represents the situation. In this region the dominant feature is the reduction of back bonding because of thermal occupation of the ligand π^* orbitals by ligand π electrons. The difference between thermal and optical transitions is illustrated in the schematic configuration coordinate diagram in Fig. 18. Optical transitions occur vertically on such a diagram according to the Franck-Condon principle. Thermal transfer is not subject to this restriction and therefore requires less energy, so that the π^* level becomes thermally accessible to the ligand π electrons at elevated pressure. One may consider this case as configuration interaction between the ligand π , $\Psi(\pi)$ and ligand π^* , $\Psi(\pi^*)$ states. The interaction can then be described by a function, $a\Psi(\pi) + b\Psi(\pi^*)$. At 1 atm the coefficient b is very small relative to a . However at high pressure, the coefficient b becomes comparable to a in magnitude and the occupation of the ligand π^* level is substantially increased. As the schematic diagram (Fig. 16) illustrates, there is substantial shift of the low energy tail of the π - π^* absorption to lower energy with only a moderate relative decrease in energy of the π - π^* absorption peak. This type of thermal electron transfer process has proven to be responsible for a pressure-

induced ferric to ferrous reduction¹⁸ although the peaks of the optical transitions associated with the process have energies on the order of 3-4 eV just as they have in this case.

The decrease in the amount of low spin present with increasing temperature adds verification to the interpretation involving a thermal electron transfer. A high-pressure isobar of the trisphenanthroline thiocyanate also indicated a decrease in the low-spin state at elevated temperature.

Normally the isomer shift decreases with increasing pressure, corresponding to an increase in electron density at the nucleus at high pressure.^{15,16} This is attributed to the delocalization of the $3d$ orbitals (nephelauxetic effect) which also accounts for the decrease in Racah parameters at high pressure. For bisphenanthroline complexes discussed above, there is an actual increase of isomer shift in the low pressure region. This corresponds to the relocation of t_{2g} electrons due to decreased back bonding, and leads to the tendency for low-spin to high-spin conversion.

Over a considerable range of pressure the two spin states exist in equilibrium. (Successive runs at the same pressure showed no change in conversion with time.) The fact that one sees both spin states rather than a mixed spin state indicates that the relaxation time

TABLE IX. Shift of lower energy metal-ligand charge transfer peak ($\Delta\nu$, cm^{-1}).

Compound	Pressure (kilobars)					
	20 (est. position)	50	75	100	120	140
Fe(phen) ₂ X ₂						
Cl	(15 950)	-330	-630	-930	-1170	-1410
NCS	(16 750)	-350	-530	-650	-720	-810
N ₃	(15 250)	-820	-1150	-1350	-1500	-1620
NCO	(15 950)	-580	-880	-1120	-1270	-1400

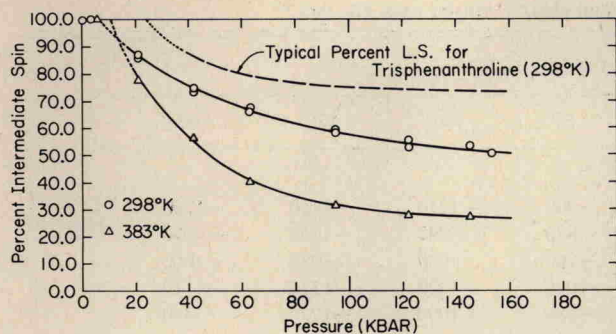


FIG. 19. Percent intermediate-spin Fe(II) vs pressure, $\text{Fe}(\text{phen})_2(\text{C}_2\text{O}_4) \cdot 5\text{H}_2\text{O}$.

is long compared with the Mössbauer decay. The two states of approximately the same energy are separated by an energy barrier large compared with the thermal energy. The barrier exists because the transition is, in some degree, a cooperative phenomenon. When a ferrous ion changes spin state there is a change in local geometry or configuration introducing a local strain which inhibits the transformation of neighboring sites. The situation is similar in principle to the reduction of iron under pressure described previously¹⁸ where ferric and ferrous sites coexist over a large range of pressure.

It should be pointed out that a low-spin to high-spin transition with increasing pressure has been observed in ferrocyanides and nitroprussides.¹⁹ Where the conversion was large an increase in isomer shift with pressure was observed. In this case also, the cause of the spin change is increased occupation of the ligand π^* orbitals by noniron electrons. For these compounds both ligand π electrons and electrons from the cation contribute. The order of the conversion to high spin for a series of ferrocyanides is $\text{Cu} > \text{Ni} > \text{Sn} > \text{Na} > \text{K}$. The copper, which shows the greatest tendency for covalent bonding and which will thus donate the most electrons to the ligand π^* orbitals, showed the most spin conversion, while the alkali metals showed virtually none.

AN INTERMEDIATE-SPIN CASE: FERROUS BISPHENANTHROLINE OXALATE

Ferrous bisphenanthroline oxalate, $\text{Fe}(\text{phen})_2(\text{C}_2\text{O}_4) \cdot 5\text{H}_2\text{O}$, is an intermediate-spin compound at room temperature and atmospheric pressure. König and Madeja⁹ found the effective magnetic moment to be $3.98 \mu_B$ at 293°K. A change from a ground state of intermediate spin to one of high spin is observed with pressure. Since less potential energy must be overcome to attain the high-spin state than for a low-spin to high-spin change, one expects it should be easier to produce an intermediate to high spin change. This behavior is verified by Fig. 19 where a large decrease in intermediate-spin species at elevated temperature is

also indicated. The decrease of intermediate spin with increasing temperature at constant pressure is consistent with the thermal electron transfer process which has an important effect upon the back π bonding and destabilization of lower-spin ground states. The greater ability to convert to a higher-spin state for an intermediate-spin compound as compared to a low-spin compound is shown by a typical conversion curve (percent low spin) for a low-spin trisphenanthroline compound at 298°K (Fig. 19).

SOME ANALOGOUS FERROUS 2,2'-BIPYRIDYL COMPOUNDS

Iron(II) forms several compounds with 2,2'-bipyridyl which are analogous to some of the ferrous phenanthroline compounds discussed above. 2,2'-bipyridyl is also a bidentate ligand with two nitrogen atoms per molecule bonding to the central metal ion. It is similar to 1,10-phenanthroline but lacks the cyclic ring which connects the two nitrogen-containing rings. [See Fig. 1(b).] The ligand field produced by the bipyridyl ligands about the ferrous ion is very similar to that produced by phenanthroline. As a result, analogous compounds with bipyridyl exhibit similar spin state changes with applied pressure.

Ferrous Bisbipyridyl Dicyanide

The ferrous bisbipyridyl cyanide, $\text{Fe}(\text{bipy})_2(\text{CN})_2 \cdot 3\text{H}_2\text{O}$ (bipy = 2,2'-bipyridyl) is a low-spin compound at room temperature and 1 atm. Mössbauer resonance as a function of pressure at 298°K and 383°K reveals a low spin to high-spin transition with pressure (Fig. 20). There is a large observed decrease in low-spin species at 383°K relative to the 298°K isotherm. Clearly, reduction in the back π bonding caused by an increasing occupation of bipyridyl π^* orbitals with pressure is the mechanism by which this low spin to high spin change occurs. The bipyridyl cyanide exhibits a greater conversion to high spin than the phenanthroline cyanide for the 383°K isotherm.

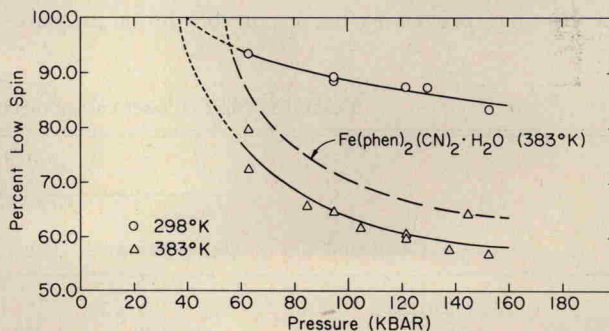


FIG. 20. Percent low-spin Fe(II) vs pressure, bisbipyridyl cyanide.