

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 ~ 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 π - π^* 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 π 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.¹⁻³ 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 CN^- . These have empty orbitals (π^* 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, Δ , 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^{4,5} (very crudely it varies as R^{-5} , where R is the metal-ligand distance), and to decrease the Racah parameters.^{4,5} 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 Jorgensen⁶). The ligand field may increase as much as 15%–20% in 200 kbar. For high-spin systems with reasonably strong ligand

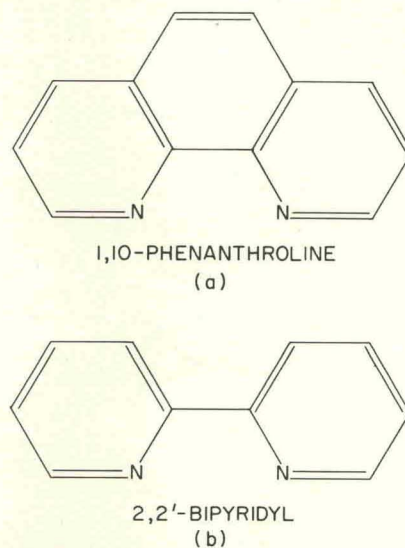


FIG. 1. Structure of 1,10-phenanthroline and 2,2'-bipyridyl.

fields a transition to low spin may be observed, e.g., for Fe(II) as a dilute substitutional impurity in MnS_2 .⁷

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 ⁵⁷Fe, using techniques from the literature.⁸⁻¹¹ Analyses for C, N, H, and Fe gave agreement generally

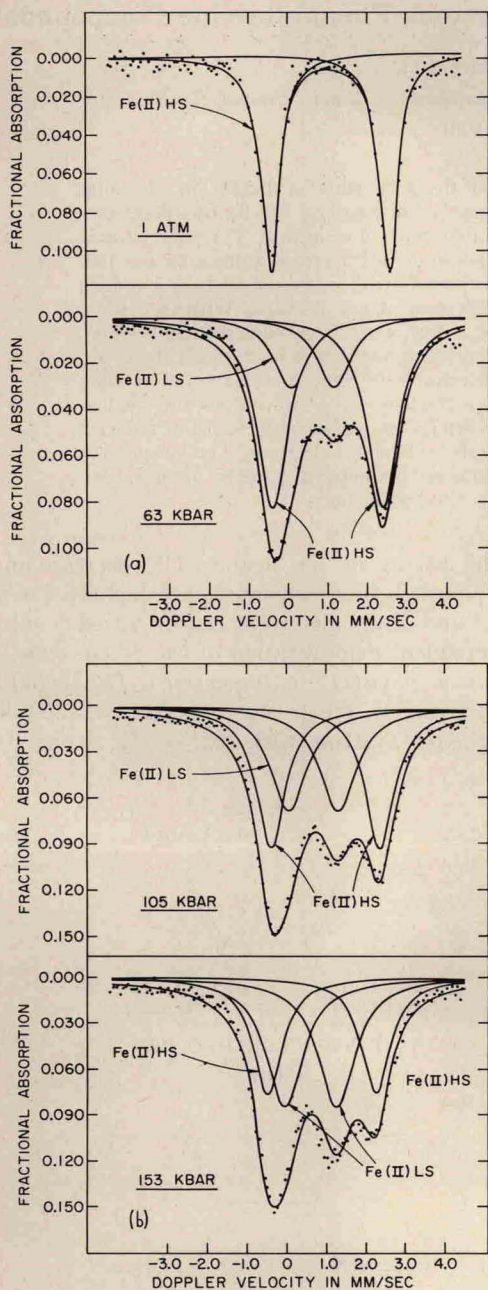


FIG. 2. Mössbauer spectra of $\text{Fe}(\text{phen})_2\text{Cl}_2$.

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.¹²⁻¹⁴

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 (~ 0.1 – 0.3 mm/sec), primarily because the *t_{2g}* electrons are delocalized into the ligand π^* 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_{2g}* orbitals to the ligand π^* orbital and the ultraviolet peaks involving excitation of an electron from the ligand π orbitals to the π^* 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

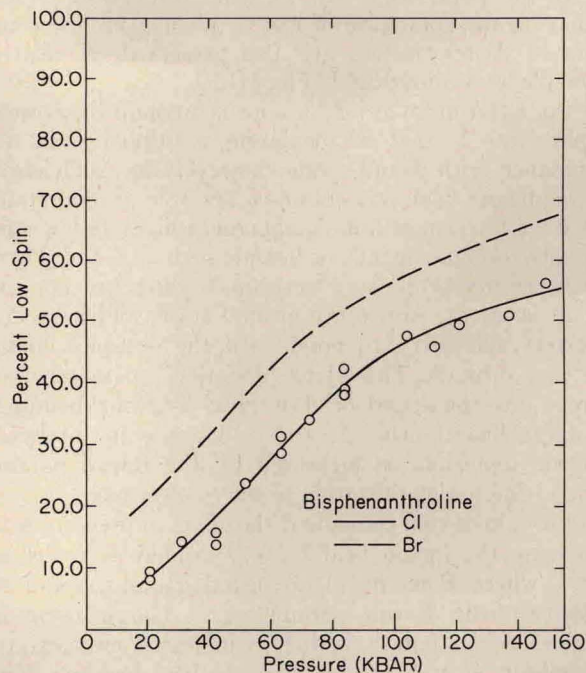


FIG. 3. Percent low spin vs pressure, $\text{Fe}(\text{phen})_2\text{Cl}_2$ and $\text{Fe}(\text{phen})_2\text{Br}_2$.

TABLE I. High-spin isomer shifts at 298°K (mm/sec) (relative to metallic iron).

Compound	Pressure (kilobars)						
	10	25	50	75	100	150	170
Fe(phen) ₂ X ₂							
Cl	1.00	0.97	0.92	0.89	0.85	0.77	0.74
Br	0.96	0.94	0.91	0.88	0.84	0.77	0.74
NCS	1.01	1.02	0.95	0.88	0.81	0.69	0.67
NCS _e	1.02	...	0.90(62) ^b	0.87	0.82	0.73	0.70
N ₃	0.97	0.98	0.92	0.85	0.80	0.69	0.65
NCO	1.00	0.98	0.97	0.94	0.89	0.81	0.79
CN(1H ₂ O) ^a	0.78(90)	0.72	0.60(123)	...
$\frac{1}{2}$ C ₂ O ₄ (5H ₂ O)	...	1.00	0.99	0.97	0.94	0.92	0.92
Fe(phen) ₃ X ₂							
Cl(7H ₂ O)	1.00	0.96	0.92	0.83	0.80
SCN(1H ₂ O)	0.96	0.91	0.86	0.76	0.73
N ₃ (6H ₂ O)	0.97	0.92	0.87	0.81	0.79
NCO(<i>n</i> H ₂ O)	1.01	0.97	0.93	0.88	0.85
Fe(bipy) ₂ X ₂							
CN(3H ₂ O)	1.16(60)	1.14	1.10	0.90	0.78
$\frac{1}{2}$ C ₂ O ₄ (3H ₂ O)	1.08	1.01	0.98	0.94	0.93
Fe(bipy) ₃ X ₂							
Cl(5H ₂ O)	0.94	0.92	0.90	0.85	0.83
N ₃ (5H ₂ O)	0.92(63)	0.90	0.87	0.80	0.77

^a Denotes the known number of molecules of water of hydration.^b Data point at pressure designated in parentheses.

TABLE II. Low-spin isomer shifts at 298°K (mm/sec) (relative to metallic iron).

Compound	Pressure (kilobars)						
	10	25	50	75	100	150	175
Fe(phen) ₂ X ₂							
Cl	...	0.11	0.38	0.50	0.50	0.47	0.46
Br	...	0.22	0.42	0.40	0.38	0.35	0.34
NCS	0.35	0.32	0.27	0.24	0.23	0.21	0.20
NCS _e	0.32	0.29	0.25	0.23	0.22	0.21	0.21
N ₃	0.29	0.34	0.31	0.29	0.27	0.24	0.23
NCO	0.20	0.27	0.31	0.29	0.29	0.28	0.28
CN(1H ₂ O) ^a	0.15	0.13	0.10	0.06	0.02	-0.01(125) ^b	...
Fe(phen) ₃ X ₂							
Cl(7H ₂ O)	0.29	0.27	0.25	0.24	0.24	0.23	0.23
SCN(1H ₂ O)	0.30	0.28	0.25	0.24	0.23	0.21	0.21
N ₃ (6H ₂ O)	0.29	0.27	0.25	0.24	0.23	0.22	0.22
NCO(<i>n</i> H ₂ O)	0.31	0.28	0.25	0.22	0.20	0.17	0.15
Fe(bipy) ₂ X ₂							
CN(3H ₂ O)	0.16	0.13	0.10	0.08	0.06	0.03	0.01
Fe(bipy) ₃ X ₂							
Cl(5H ₂ O)	0.28	0.25	0.23	0.22	0.21	0.20	0.20
N ₃ (5H ₂ O)	0.30	0.26	0.23	0.21	0.20	0.19	0.19

^a Designated number of waters of hydration in parentheses.^b Data point at pressure designated in parentheses.

TABLE III. Intermediate-spin isomer shifts at 298°K (mm/sec) (relative to metallic iron).

Compounds	Pressure (kilobars)						
	10	25	50	75	100	150	170
Fe(phen) ₂ (C ₂ O ₄)·5H ₂ O	0.35	0.37	0.41	0.45	0.49	0.54	0.54
Fe(bipy) ₂ (C ₂ O ₄)·3H ₂ O	0.29	0.28	0.28	0.28	0.30	0.32	0.33

bis- and trisphenanthroline complexes and the interpretation of the transitions between high and low spin states. The last sections discuss an intermediate-spin case, and finally, some bipyridyl-iron complexes.

BISPHENANTHROLINE COMPOUNDS

In the bisphenanthroline compounds the back bonding of the metal *3d* electrons to the phenanthroline π^* orbitals is probably about the same for all complexes. It is convenient to classify the complexes according to the degree of back bonding to the other two ligands. Complexes with halide ligands, i.e., chlorine or bromine [Fe(phen)₂Cl₂ and Fe(phen)₂Br₂], have the lowest

total amount of back bonding since the chlorine or bromine ions have no empty ligand levels of π symmetry to bond to the ferrous ion. These compounds are high spin. The bisphenanthroline compounds of the form Fe(phen)₂X₂ where X equals NCS, NCSe, NCO, and N₃ exhibit a moderate degree of back bonding since in this case back bonding can occur to empty π^* levels in these anionic ligands. The total amount of back donation is still low enough that these compounds are high spin at atmospheric pressure. Fe(phen)₂(CN)₂·H₂O exhibits a very high degree of back bonding to the empty cyanide ligand π^* levels and exists in a low-spin ground state at 1 atm.

TABLE IV. High-spin quadrupole splittings (mm/sec).^a

Compound	Pressure (kilobars)						
	10	25	50	75	100	150	170
Fe(phen) ₂ X ₂							
Cl	2.99	2.95	2.85	2.79	2.77	2.72	2.71
Br	2.92	2.95	2.81	2.73	2.68	2.60	2.58
NCS	2.61	2.48	2.48	2.51	2.53	2.56	2.58
NCSe	2.50	...	2.55(60) ^c	2.54	2.52	2.47	2.44
N ₃	2.73	2.62	2.53	2.52	2.53	2.58	2.60
N ₃	2.52	2.41	2.34	2.35	2.39	2.45(120)	... (383°K)
NCO	2.81	2.77	2.68	2.61	2.56	2.53	2.53
CN(1H ₂ O) ^b	1.61(90)	1.56	1.45(120)	...
CN(1H ₂ O)	1.76(60)	1.81	1.87	1.88	... (383°K)
$\frac{1}{2}$ C ₂ O ₄ (5H ₂ O)	...	2.51	2.65	2.71	2.74	2.75	2.75
$\frac{1}{2}$ C ₂ O ₄ (5H ₂ O)	...	2.36	2.42	2.46	2.48	2.50	2.51 (383°K)
Fe(phen) ₃ X ₂							
Cl(7H ₂ O)	2.62	2.64	2.66	2.69	2.71
SCN(1H ₂ O)	2.56	2.60	2.63	2.70	2.73
N ₃ (6H ₂ O)	2.57	2.57	2.60	2.68	2.72
NCO(<i>n</i> H ₂ O)	2.66	2.64	2.63	2.60	2.59
Fe(bipy) ₂ X ₂							
CN(3H ₂ O)	2.11(60)	2.10	2.07	1.95	...
CN(3H ₂ O)	2.03(60)	2.01	1.97	1.90	... (383°K)
$\frac{1}{2}$ C ₂ O ₄ (3H ₂ O)	2.51	2.57	2.61	2.68	...
$\frac{1}{2}$ C ₂ O ₄ (3H ₂ O)	2.38	2.46	2.50	2.55	... (383°K)
Fe(bipy) ₃ X ₂							
Cl(5H ₂ O)	2.52(60)	2.60	2.71	2.84	...
N ₃ (5H ₂ O)	2.61	2.63	2.65	2.69	...

^a All values are for 298°K isotherms unless otherwise designated.

^b Waters of hydration designated in parentheses.

^c Data point at pressure designated in parentheses.

TABLE V. Low-spin quadrupole splittings (mm/sec).^a

Compound	Pressure (kilobars)						
	10	25	50	75	100	150	170
Fe(phen) ₂ X ₂							
Cl	...	0.38	0.89	1.18	1.24	1.29	1.31
Br	...	0.60	1.03	1.23	1.30	1.36	1.37
NCS	0.29	0.34	0.44	0.57	0.71	0.92	0.94
NCSe	0.29	0.36	0.46	0.59	0.68	0.78	0.80
N ₃	0.55	0.60	0.67	0.75	0.83	0.98	1.05
N ₃	0.56	0.61	0.67	0.73	0.80	0.85(120) ^c	... (393°K)
NCO	0.29	0.38	0.49	0.58	0.68	0.85	0.91
CN(1H ₂ O) ^b	0.51	0.56	0.64	0.73	0.81	0.89(125)	...
CN(1H ₂ O)	0.56	0.57	0.63	0.76	0.84	0.91	... (383°K)
Fe(phen) ₃ X ₂							
Cl(7H ₂ O)	0.32	0.36	0.42	0.49	0.56	0.69	0.75
SCN(1H ₂ O)	0.30	0.34	0.43	0.51	0.60	0.77	0.85
N ₃ (6H ₂ O)	0.27	0.33	0.43	0.51	0.59	0.73	0.78
NCO(<i>n</i> H ₂ O)	0.31	0.35	0.42	0.49	0.55	0.69	0.74
Fe(bipy) ₂ X ₂							
CN(3H ₂ O)	0.60	0.62	0.69	0.78	0.87	0.96	...
CN(3H ₂ O)	0.60	0.61	0.71	0.89	1.01	1.12	... (383°K)
Fe(bipy) ₃ X ₂							
Cl(5H ₂ O)	0.36	0.40	0.46	0.51	0.56	0.65	...
N ₃ (5H ₂ O)	0.34	0.38	0.46	0.57	0.67	0.87	...

^a All values are for 298°K isotherms unless otherwise designated.^c Data point at pressure designated in parentheses.^b Waters of hydration designated in parentheses.**Ferrous Bisphenanthroline Dichloride and Dibromide**

The chloride and bromide bisphenanthroline-iron compounds exhibit a high spin to low spin change of electronic ground state with pressure. Typical Mössbauer spectra for Fe(phen)₂Cl₂ as a function of pressure are presented in Figs. 2(a) and 2(b). Data for the percent of ferrous complex in the low-spin state versus pressure for Fe(phen)₂Cl₂ is given in Fig. 3. One observes a steady increase in the amount of low-spin ferrous species from 20 to 80 kbar and then a lower rate of increase of conversion with pressure at higher pressures.

The Mössbauer parameters (isomer shifts and quadrupole splittings) appear in Tables I-VI for all spin species studied. General discussions of the effect

of pressure on these quantities have been given elsewhere.^{15,16} Here we discuss only the behavior of the high-spin isomer shift as that is directly germane to understanding the spin transformations. The high-spin isomer shifts for ferrous phenanthroline compounds are typically in the range 0.95-1.05 mm/sec relative to iron metal. Data for the high-spin isomer shift versus pressure for the chloride are presented in Fig. 4. The bromide behaved similarly. The isomer shift of the high-spin ferrous species is unchanged over the first few kilobars, then shows a steady decrease from about 1.00 to 0.77 mm/sec over 150 kbar. The steady decrease of isomer shift (increasing *s*-electron density at iron nucleus) is primarily due to the delocalization of the 3*d* orbitals with pressure, because of increased covalency.

TABLE VI. Intermediate-spin quadrupole splitting (mm/sec).

Compound	Pressure (kilobars)						
	10	25	50	75	100	150	170
Fe(phen) ₂ (C ₂ O ₄)·5H ₂ O	0.50	0.54	0.63	0.67	0.68	0.70	0.70 (298°K)
	0.52	0.53	0.55	0.55	0.55	0.54	0.53 (383°K)
Fe(bipy) ₂ (C ₂ O ₄)·3H ₂ O	0.43	0.46	0.57	0.64	0.69	0.73	... (298°K)
	0.44	0.48	0.52	0.54	0.55	0.56	... (383°K)

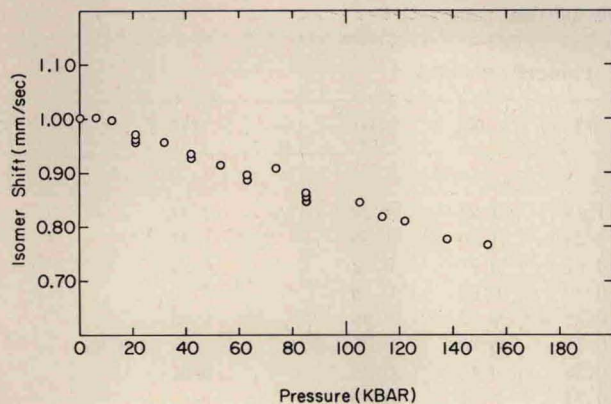


FIG. 4. High-spin isomer shift vs pressure, $\text{Fe}(\text{phen})_2\text{Cl}_2$.

A comparison of percent low-spin conversion for $\text{Fe}(\text{phen})_2\text{Cl}_2$ and $\text{Fe}(\text{phen})_2\text{Br}_2$ is presented in Fig. 3. Although the amount of conversion to low-spin ferrous species is somewhat greater for $\text{Fe}(\text{phen})_2\text{Br}_2$, the behavior with pressure is similar for both. The high-spin isomer shift versus pressure is nearly identical for the chloride and bromide.

Ferrous Bisphenanthroline Diisothiocyanate, Diisoselenocyanate, Diisocyanate, and Diazide

Ferrous bisphenanthroline compounds with NCS, NCSe, NCO, and N_3 as anionic ligands all exhibit a high-spin to low-spin state change as a function of pressure. The isothiocyanate and isoselenocyanate compounds have been shown to undergo a relatively sharp transition to a low-spin ground state at 174°K and 232°K, respectively, at 1 atm pressure.¹⁷ These compounds have anionic ligands possessing empty ligand π^* orbitals that can participate in back bonding with the metal $3d(\pi)$ or t_{2g} orbitals.

Typical Mössbauer spectra following the conversion from high to low spin with pressure of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ are presented in Figs. 5(a) and 5(b). The atmospheric pressure spectrum is completely high spin. By 15 kbar, there is 60%–70% conversion to low spin. At higher pressure a decrease in the amount of low spin is observed. One can follow the percent low-spin ferrous species versus pressure more readily in Fig. 6 for $\text{Fe}(\text{phen})_2(\text{NCS})_2$. There is a steady conversion to the low-spin state up to about 20 kbar, then there is a maximum and a decrease in the amount of low-spin species above 40 kbar. This is surprising and not in accord with the simple concepts presented above which would indicate increasing low spin with increasing pressure. The behavior of the isomer shift for the high-spin species is presented for the isothiocyanate in Fig. 7. From 1 atm to 20 kbar there is a slight increase in high-spin isomer shift. Above 20 kbar there is a

steady, almost linear, decrease of 0.30 mm/sec to 150 kbar. This is discussed below.

A comparison of the conversion to low spin with pressure for these moderately back bonding compounds is given in Fig. 8. A complete transition to a low-spin ground state is observed for the isoselenocyanate, while the isothiocyanate, azide, and isocyanate showed decreasing maximum conversion to a low-spin state

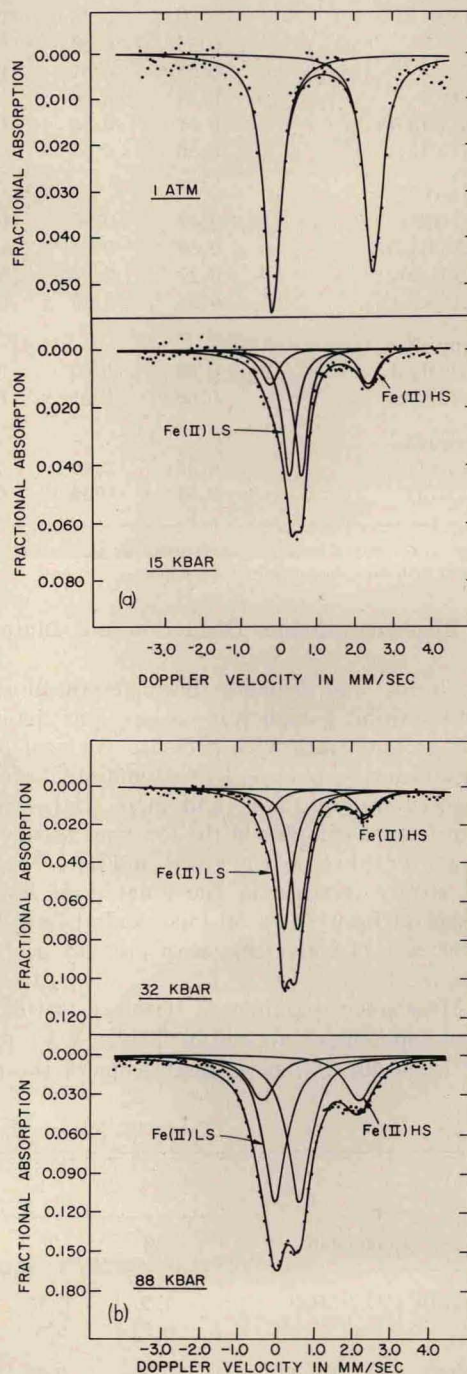


FIG. 5. Mössbauer spectra of $\text{Fe}(\text{phen})_2(\text{NCS})_2$.

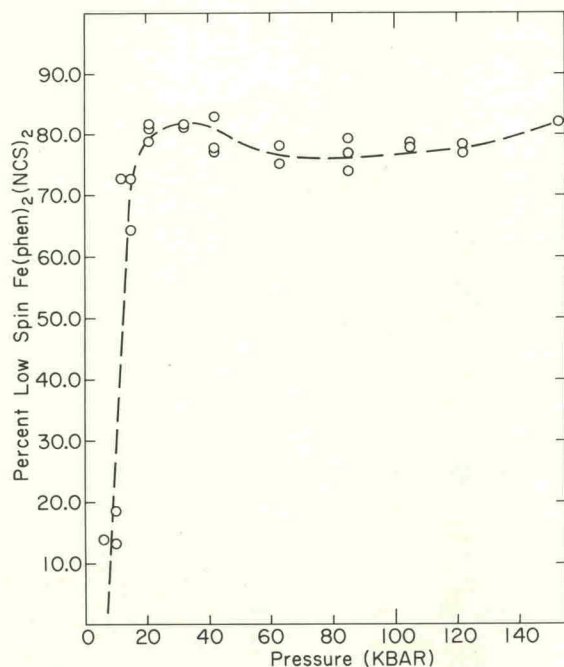


FIG. 6. Percent to low spin vs pressure, $\text{Fe}(\text{phen})_2(\text{NCS})_2$.

with pressure. All these compounds exhibit a sharp increase in conversion with pressure at first, and then an actual decrease in low-spin conversion or a leveling off as in the case of the isocyanate. The high-spin isomer shifts for all four compounds are compared in Table I. They all exhibit the same behavior as the isothiocyanate.

An isobar at 95 kbar on the azide compound revealed a modest decrease in the amount of low-spin ferrous species with increasing temperature. The percentages of low-spin species were 66.6% at 298°K, 61.5% at 335°K, 58.0% at 383°K, and 55.6% at 420°K.

Ferrous Bisphenanthroline Dicyanide

The ferrous phenanthroline compound with the cyanide ligand, $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{H}_2\text{O}$, is a low-spin

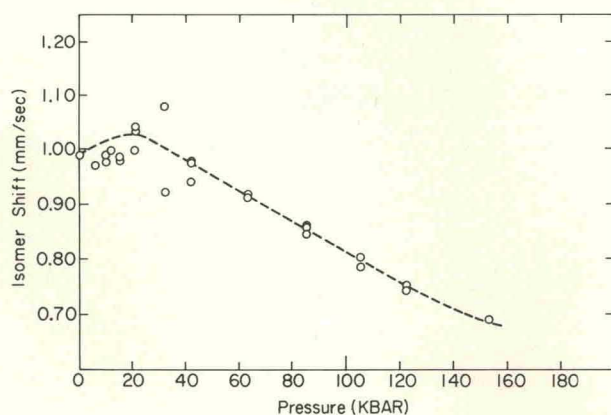


FIG. 7. High-spin isomer shift vs pressure, $\text{Fe}(\text{phen})_2(\text{NCS})_2$.

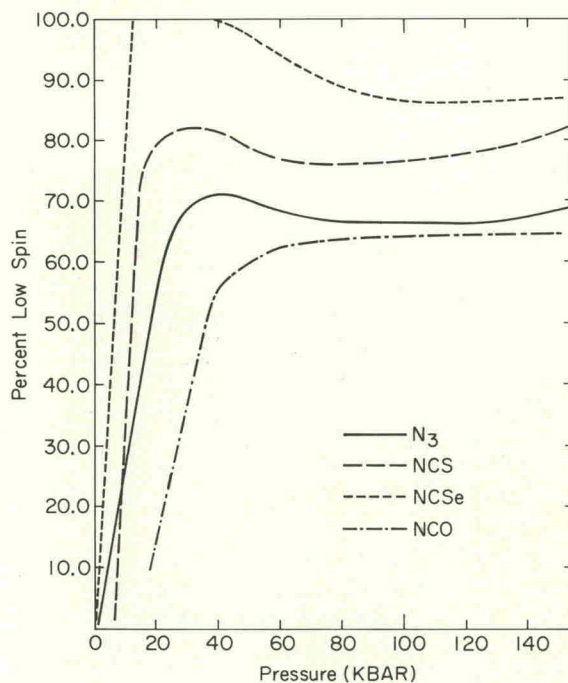


FIG. 8. Percent low spin vs pressure, moderately band bonding bisphenanthroline compounds.

compound. This is due to the high degree of back bonding between metal $t_{2g}(\pi)$ orbitals and empty π^* orbitals of the cyanide ligand. The cyanide exhibited a low-spin to high-spin ground state change with pressure. Only a small amount of conversion from the low-spin state was observed at 95 kbar (83.7% low spin) and 122 kbar (77.0% low spin) at 298°K. Below 95 kbar the compound was completely in a low-spin ground state. Isotherms at 383°K exhibit a pronounced increase in conversion from a low-spin to a high-spin ground state. The percent low-spin ferrous species versus pressure at 383°K is presented in Fig. 9. Clearly, for the cyanide, a substantial reduction in the back π bonding must occur to allow the partial stabilization of the high-spin state under pressure.

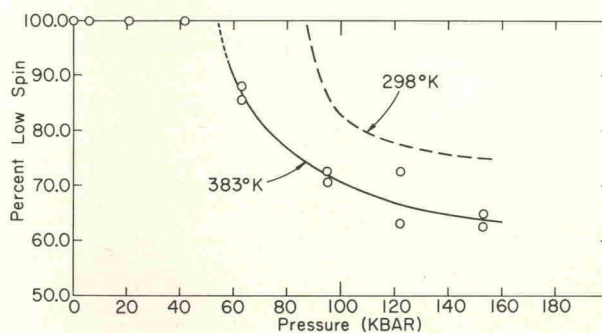


FIG. 9. Percent low spin vs pressure $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{H}_2\text{O}$.

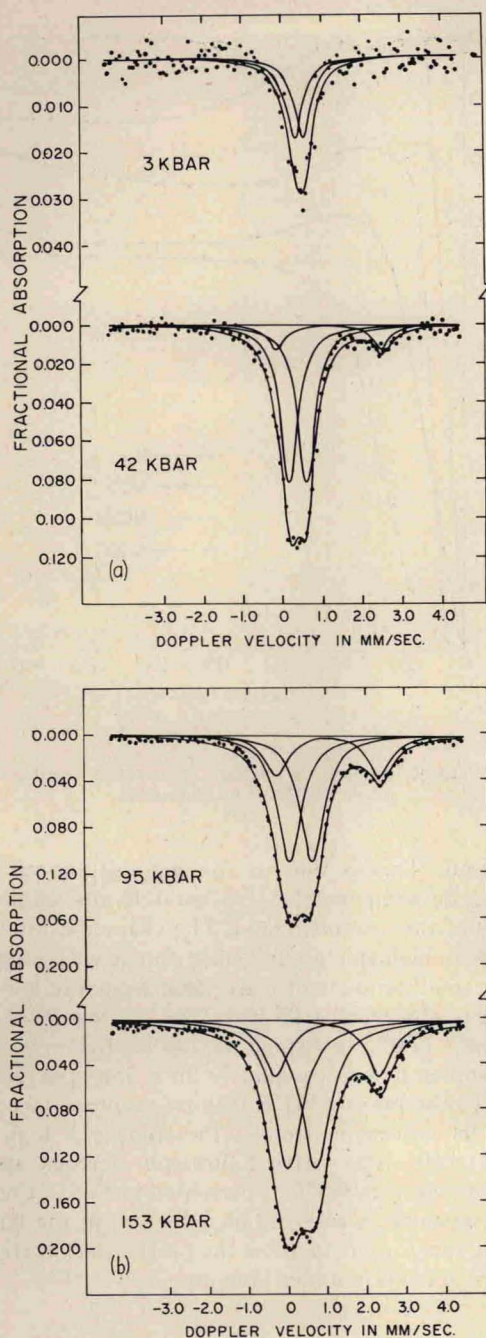
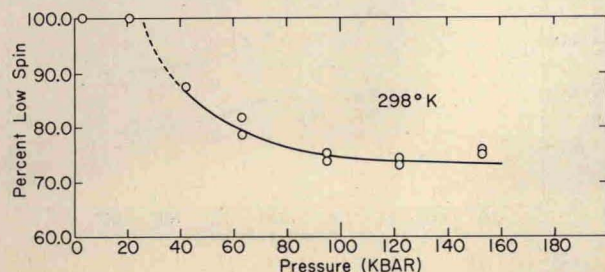
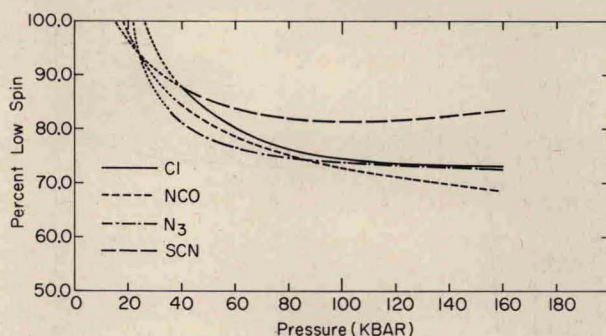
FIG. 10. Mössbauer spectra, $\text{Fe}(\text{phen})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$.FIG. 11. Percent low spin vs pressure, $\text{Fe}(\text{phen})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$.

FIG. 12. Percent low spin vs pressure, various trisphenanthroline compounds.

FERROUS TRISPHENANTHROLINE COMPOUNDS

The ferrous trisphenanthroline compounds studied in this work are all low spin at 1 atm and room temperature. They all exhibited low-spin to high-spin ground state changes under pressure. Typical Mössbauer spectra of ferrous trisphenanthroline chloride, $\text{Fe}(\text{phen})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$, are presented in Figs. 10(a) and 10(b). The percent of low-spin ferrous species as a function of pressure presented in Fig. 11 exhibits a gradual decrease from 87.5% at 42 kbar to a nearly constant 73%–74% at 140–160 kbar. This low-spin to high-spin ground state change can also be understood in terms of a significant reduction in the amount of back bonding to the phenanthroline π^* orbitals with pressure.

The trisphenanthroline compounds with chlorine, cyanate, azide, and thiocyanate ligands all show low-spin to high-spin conversions in the range 88%–73% low-spin species from 40 to 160 kbar (Fig. 12). An isobar of the trisphenanthroline thiocyanate at 85 kbar showed a decrease in the low-spin species with increasing temperature. The percentages of low-spin species present were 86.7% at 298°K, 85.0% at 335°K, 72.8% at 383°K, and 69.3% at 420°K.

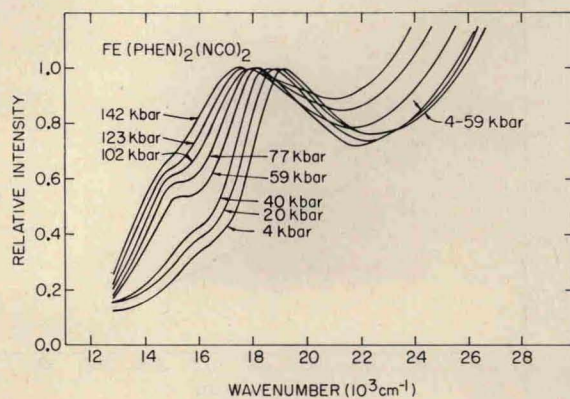
FIG. 13. Visible absorption spectra vs pressure, $\text{Fe}(\text{phen})_2(\text{NCO})_2$.

TABLE VII. Shift of $\pi-\pi^*$ band ($\Delta\nu$, cm^{-1}).

Compound	Pressure (kilobars)					
	20 (position)	50	75	100	120	140
Fe(phen)₂X₂						
Cl	(35 900)	-780	-1430	-1990	-2300	-2420
NCS _e	(35 470)	-1000	-1440	-1650	-1730	-1770
N ₃	(36 630)	-610	-1250	-1940	-2500	-3040
NCO	(36 800)	-1130	-1940	-2640	-3050	-3320
CN(1H ₂ O) ^a	(36 000)	-900	-1380	-1780	-2160	-2380
Fe(phen)₃X₂						
N ₂ (6H ₂ O)	(37 110)	-730	-1340	-1750	-2000	-2150
SCN(1H ₂ O)	(35 870)	-1050	-1800	-2350	-2600	-2670
1,10-phenanthroline	(35 820)	-970	-1520	-2000	-2350	-2710

^a Waters of hydration are indicated in parentheses.

OPTICAL ABSORPTION RESULTS

Studies of optical spectra as a function of pressure are of assistance in understanding these effects. In Fig. 13 we show spectra at various pressures for the visible region of the spectrum for a typical bisphenanthroline complex, Fe(phen)₂(NCO)₂. Because of the *cis* configuration for bisphenanthroline complexes there is sufficient distortion on the approximately octahedral ligand field to cause splitting of the $t_{2g}(\pi)$ levels into a higher energy nondegenerate and a lower energy doubly degenerate level. Therefore, two metal-ligand charge transfer bands are expected and are indeed observed in the optical spectrum (at 4 kbar located about 19 200 cm^{-1} and 16 200 cm^{-1} , respectively). First, consider the lower pressure to about 40 kbar where rapid high- to low-spin state change occurs (Fig. 8). This region is characterized by a small red shift of both charge transfer peaks and a smaller shift of the low energy tail of the phenanthroline $\pi-\pi^*$ band. This behavior is also reflected in the ultraviolet spectrum of Fe(phen)₂(NCO)₂ as a function of pressure which affords one an observation of the phenanthroline $\pi-\pi^*$ transitions (Fig. 14). One observes a steady red

shift of the $\pi-\pi^*$ band with pressure above 20 kbar. In the higher pressure region (above 40 kbar for the NCO compounds) where the low-spin state reverses toward high spin with increasing pressure (or as in the halides, low-spin state increases at a much slower rate) several changes occur in the visible spectrum. One observes a sudden relative intensity increase and accompanying red shift of the lower energy metal-ligand charge transfer peak. The higher energy charge transfer peak shows a steady shift to lower energy with pressure. Especially, there is a rapid shift of the low energy tail of the ligand $\pi-\pi^*$ band (Fig. 13) and a large red shift of the peak (Fig. 14). As is shown in Figs. 15 and 16, the charge transfer and ligand $\pi\rightarrow\pi^*$ transitions for the tris complexes also exhibited a large shift to lower energy with increasing pressure.

It is of interest to compare the shifts of the various charge transfer peaks and the ligand $\pi-\pi^*$ band as a function of pressure for bis- and trisphenanthroline ferrous compounds. The shift of the $\pi-\pi^*$ band with pressure for many of the compounds is presented in Table VII, where the shifts are given relative to the location at 20 kbar. The bis compounds shift 1800-

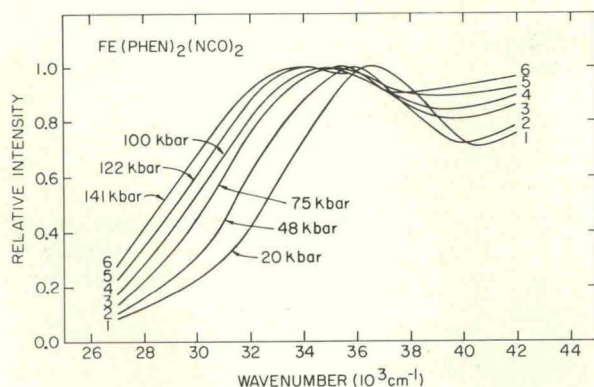


FIG. 14. Ultraviolet absorption spectra vs pressure, Fe(phen)₂(NCO)₂.

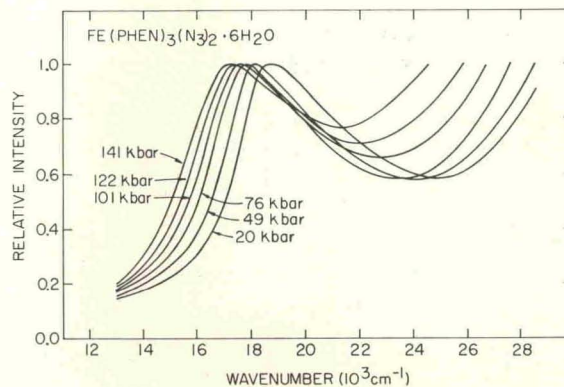


FIG. 15. Visible absorption spectra vs pressure, Fe(phen)₃(N₃)₂·6H₂O.

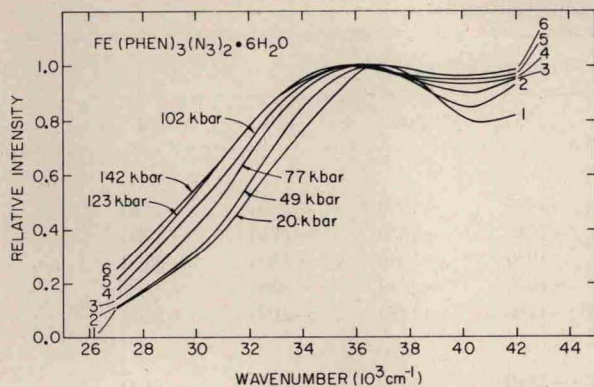


FIG. 16. Ultraviolet absorption spectrum vs pressure, $\text{Fe}(\text{phen})_3(\text{N}_3)_2 \cdot \text{H}_2\text{O}$.

3300 cm^{-1} and the tris compounds shift $2100\text{--}2700 \text{ cm}^{-1}$ to lower energy from 20 to 140 kbar. It is noted that the $\pi\text{--}\pi^*$ band in pure phenanthroline shifts by 2700 cm^{-1} to lower energy from 20 to 140 kbar. The shifts of the higher and lower energy metal-to-ligand charge transfer peaks with pressure are tabulated in Tables VIII and IX relative to the location at 20 kbar. Both charge transfer bands shift to lower energy with pressure, and the shift is of the same order. (Two charge transfer bands are resolved for some bispheanthroline compounds only.) The shifts of the single charge transfer band for the tris compounds are also comparable ($1400\text{--}1850 \text{ cm}^{-1}$ to lower energy). The shifts of the metal-ligand charge transfer bands and the ligand $\pi\text{--}\pi^*$ bands correlate with each other. That is, a smaller shift of the $\pi\text{--}\pi^*$ band corresponds to a smaller shift of the charge transfer band for the same compound as compared to others. It is important to note that the $\pi\text{--}\pi^*$ band is shifting red faster than the charge transfer bands. This means that the ligand π^* level is shifting to lower energy more rapidly than the metal $3d(\pi)$ levels are with pressure. The red shift of the $\pi\text{--}\pi^*$ transition has been observed in a variety of aromatic systems⁴ and is associated with a dipole

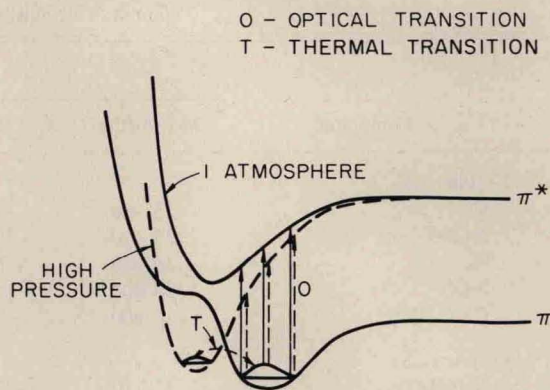


FIG. 18. Schematic configuration coordinate diagram illustrating thermal mixing of $\pi\text{--}\pi^*$ levels at high pressure.

moment in the excited state larger than that for the ground state. While there are observed differences in the shifts and the locations of the peaks at 20 kbar, these differences do not correlate particularly with the relative amount of conversion from one spin state to another. However, all systems show similar behavior and are consistent with the explanation of the spin state behavior as a function of pressure.

In the low pressure region the behavior of the complexes is characterized by conversion of the ferrous ion to low spin for the high-spin bis compounds, no change in spin state of the low-spin compounds, and modest red shifts of the peaks representing the charge transfer and $\pi\text{--}\pi^*$ transitions. These conditions are represented by the schematic molecular orbital diagram of Fig. 17(a). The dominant effect is the increase in ligand field due to the increased back bonding which results from increased overlap of the metal π orbitals with the empty ligand π^* orbitals. The increase in the ligand field overcomes the spin pairing energy and thus brings about the high spin to low spin transition.

At higher pressures there is a tendency for low-spin to high-spin transformation in both the bis and tris

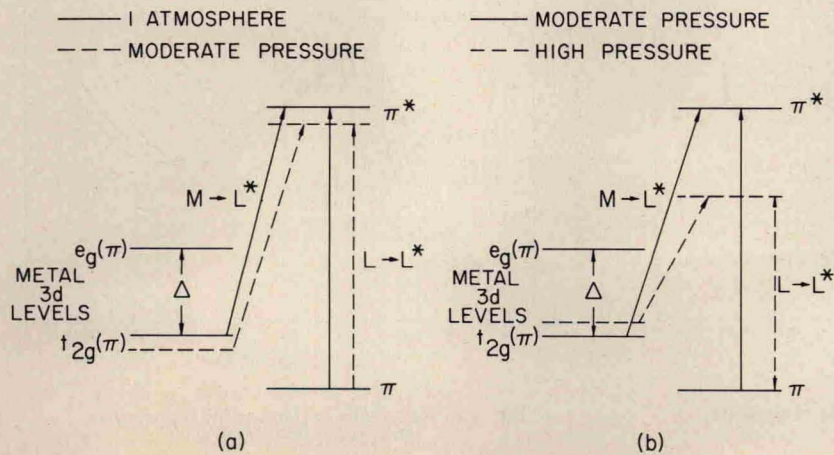


FIG. 17. Simplified MO diagram illustrating effects of pressure.

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

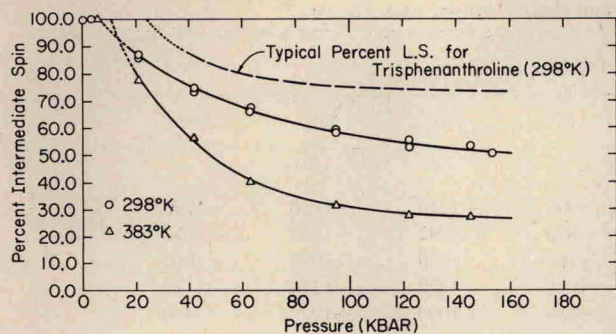


FIG. 19. Percent intermediate-spin Fe(II) vs pressure, $\text{Fe}(\text{phen})_2(\text{C}_2\text{O}_4) \cdot 5\text{H}_2\text{O}$.

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.

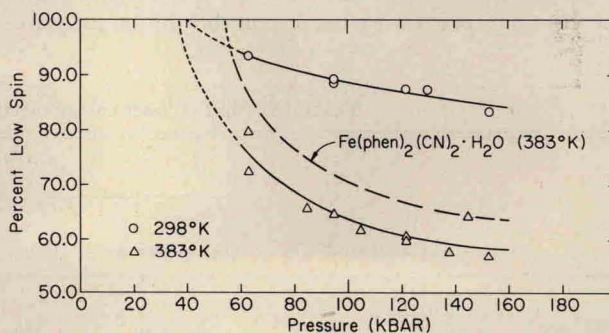


FIG. 20. Percent low-spin Fe(II) vs pressure, bisbipyridyl cyanide.

Ferrous Trisbipyridyl Chloride and Azide

$\text{Fe}(\text{bipy})_3\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{bipy})_3(\text{N}_3)_2 \cdot 5\text{H}_2\text{O}$ are low-spin compounds at room temperature and 1 atm. Under pressure one observes a low- to high-spin ground state change in both compounds. A comparison of the conversion from the low-spin state with pressure at 298°K for these trisbipyridyl compounds and conversion of a typical low-spin trisphenanthroline compound is presented in Fig. 21. The low-spin ferrous species in the trisbipyridyl chloride decreases from 88% at 40 kbar to about 79% at 150 kbar. The trisbipyridyl azide exhibits a nearly constant amount of low-spin species (86%–87%) over the range of 60–150 kbar. In general, the trisbipyridyl compounds exhibit less low-spin to high-spin conversion (Fig. 21) than the trisphenanthroline compounds.

Ferrous Bisbipyridyl Oxalate

Ferrous bisbipyridyl oxalate, $\text{Fe}(\text{bipy})_2(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$, is an intermediate-spin compound according to magnetic measurements made by König and Madeja.⁹ It is analogous to the bisphenanthroline oxalate discussed previously. A change from an intermediate-spin ground state to one of high spin is reflected in Fig. 22 which presents 298°K and 383°K isotherms for the bisbipyridyl oxalate. The higher conversion with pressure to the high-spin state expected for an intermediate-spin compound is observed. Also the thermal enhancement of the high-spin state at elevated temperature is again observed. The amount of conversion from the intermediate-spin ground state

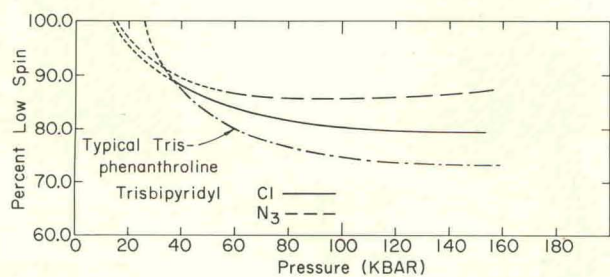


FIG. 21. Percent low-spin Fe(II) vs pressure, trisbipyridyl chloride and azide.

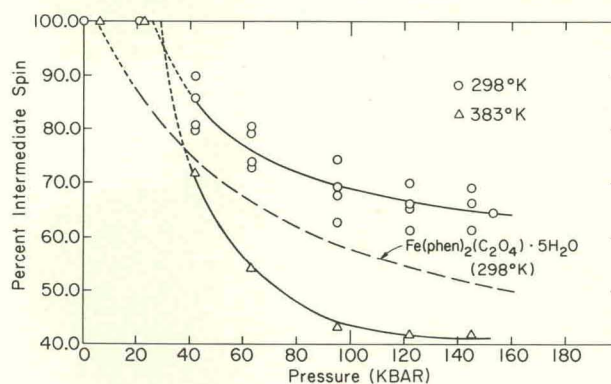


FIG. 22. Percent intermediate-spin Fe(II) vs pressure, $\text{Fe}(\text{bipy})_2(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$.

to a high-spin ground state is less for the bipyridyl oxalate than for the phenanthroline oxalate for corresponding isotherms, as is shown in Fig. 22.

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