

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)

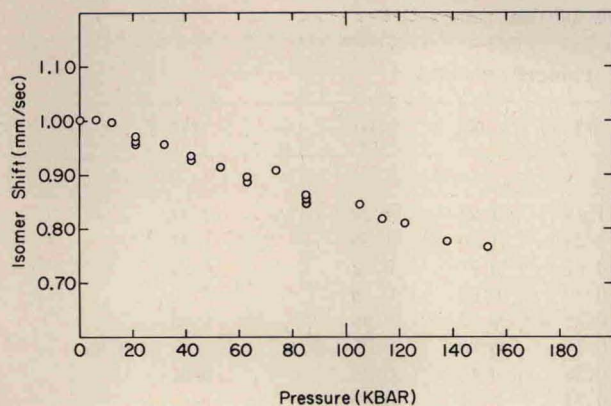


FIG. 4. High-spin isomer shift vs pressure, $\text{Fe}(\text{phen})_2\text{Cl}_2$.

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

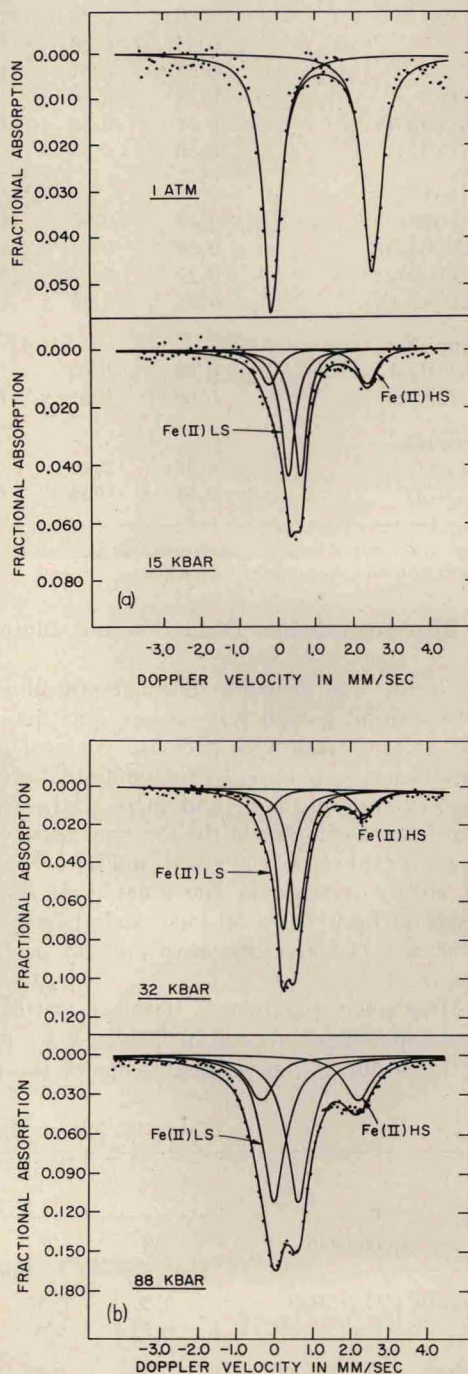


FIG. 5. Mössbauer spectra of $\text{Fe}(\text{phen})_2(\text{NCS})_2$.