

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 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

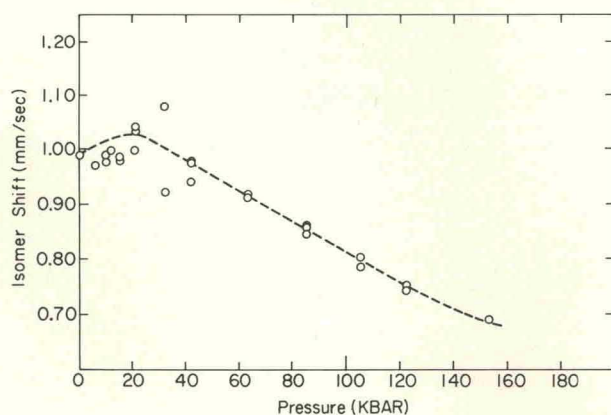


FIG. 7. High-spin isomer shift vs pressure, $\text{Fe}(\text{phen})_2(\text{NCS})_2$.

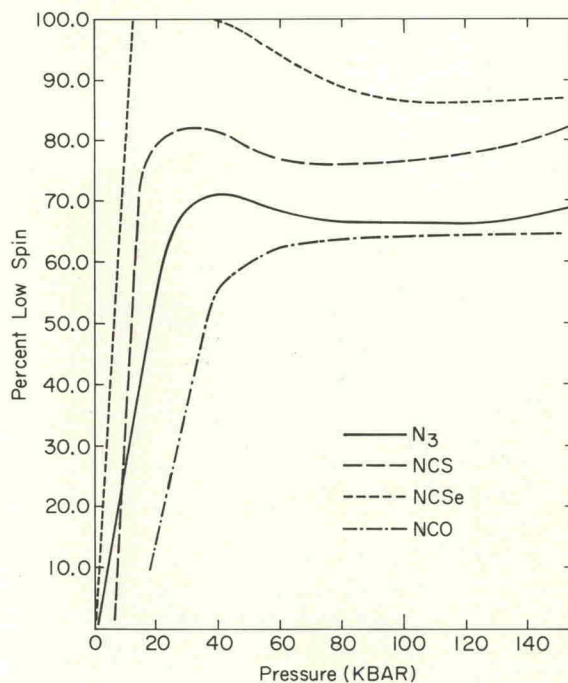


FIG. 8. Percent low spin vs pressure, moderately band bonding bisphenanthroline compounds.

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.

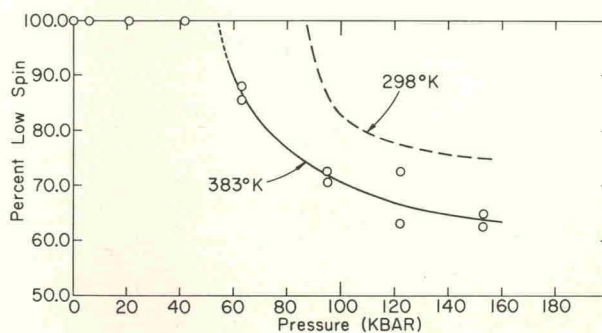


FIG. 9. Percent low spin vs pressure $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{H}_2\text{O}$.

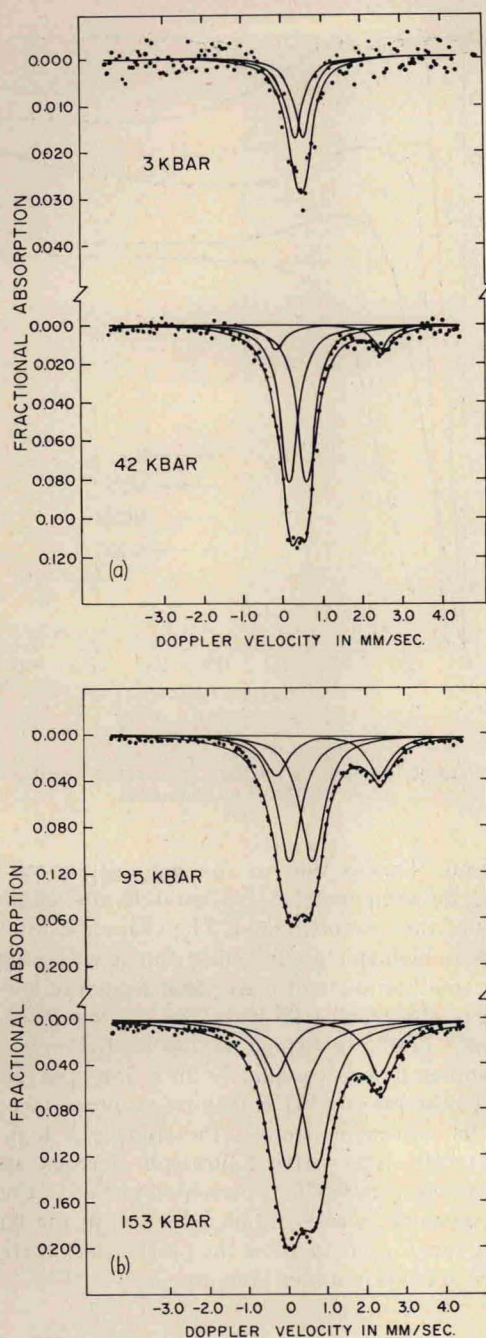
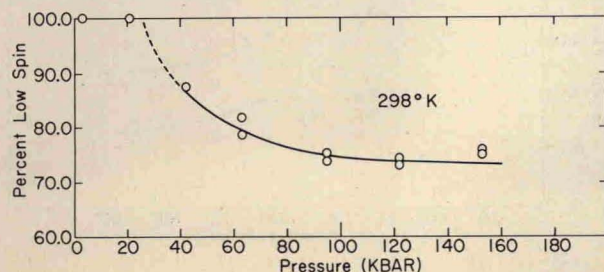
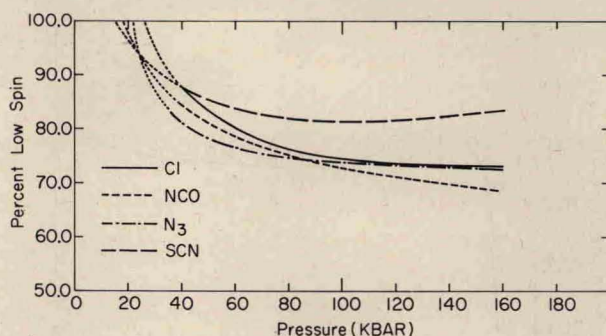
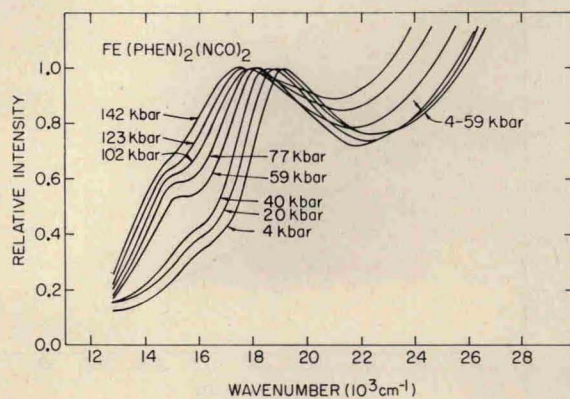
FIG. 10. Mössbauer spectra, $\text{Fe}(\text{phen})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$.FIG. 11. Percent low spin vs pressure, $\text{Fe}(\text{phen})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$.

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, $\text{Fe}(\text{phen})_2(\text{NCO})_2$.