

presence of spin-spin relaxation. Blume¹⁷ has discussed spin-spin relaxation in the similar compound, hemin. The ratio of peak widths at 4 kbar is only 1.18, indicating that the effects are small at low pressures, and at higher pressures the relaxation effects disappear. From Fig. 15 it is seen that there is substantial reduction of Fe(III) to Fe(II). By 170 kbar there is about 75% conversion at 23°C, and at 106°C there is about 90% conversion at 170 kbar. The equilibrium constant K

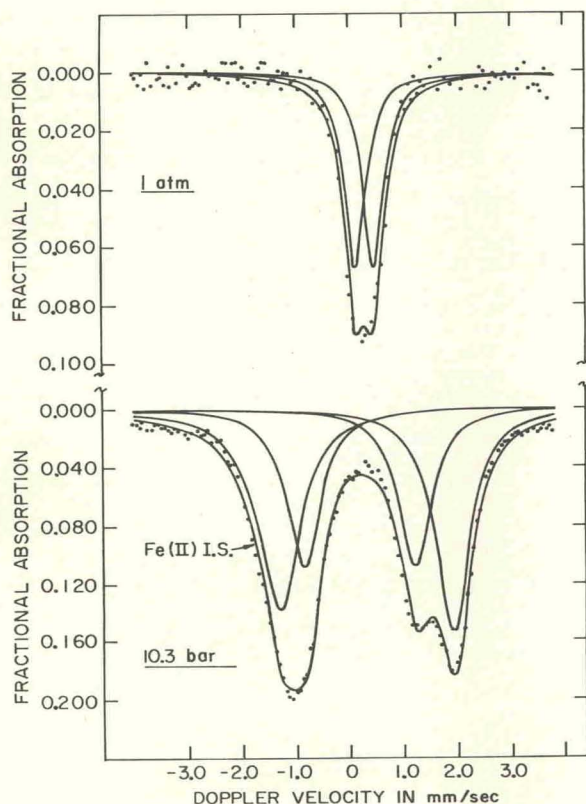


FIG. 15. Mössbauer spectra of $\text{Fe}(\text{SAL})_2\text{OH}$.

as a function of pressure is shown in Fig. 16. The steep slope (large B) indicates that there is little coupling between adjacent iron states.^{19,20} The constants A and B for both $\text{Fe}(\text{DTC})_2\text{Cl}$ and $\text{Fe}(\text{SAL})_2\text{OH}$ are given in Table III. The conversion in both compounds is reversible. The isomer shift and quadrupole splitting of both Fe(III) and Fe(II) are given in Table IV for $\text{Fe}(\text{SAL})_2\text{OH}$. The high values of the Fe(II) isomer shift, ranging from 1.34 to 1.22 mm/sec in the pressure range 50–175 kbar indicate that the Fe(II) produced is high spin.

It is of interest to compare the conversions of the four different square pyramidal compounds studied: hemin, hematin, $\text{Fe}(\text{DTC})_2\text{Cl}$, and $\text{Fe}(\text{SAL})_2\text{OH}$. Hemin and

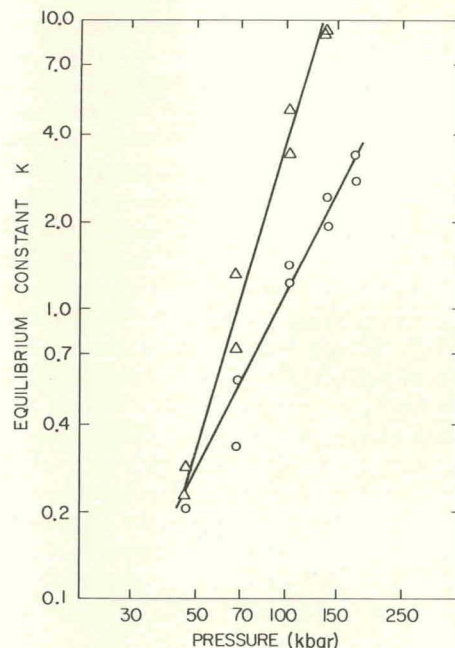


FIG. 16. $\ln K$ vs $\ln P$ — $\text{Fe}(\text{SAL})_2\text{OH}$. \circ , 23°C; \triangle , 106°C.

hemin are square planar nitrogen compounds with the axial ligand being Cl^- and OH^- , respectively. $\text{Fe}(\text{DTC})_2\text{Cl}$ is square planar sulfur with the axial ligand being Cl^- , and $\text{Fe}(\text{SAL})_2\text{OH}$ is believed to be square planar oxygen with the axial ligand being OH^- . The conversions are compared in Fig. 17. It is seen that

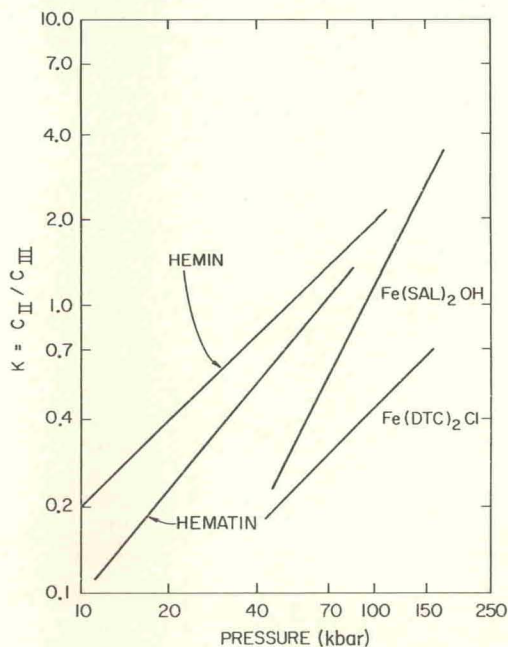


FIG. 17. $\ln K$ vs $\ln P$ for square pyramidal complexes at 23°C.

the nitrogen compounds convert more than the oxygen or sulfur compounds, and the oxygen compound more than the sulfur compound. In addition, in the planar nitrogen compounds, hemin and hematin, the compound with the Cl^- ligand converts more than that with the OH^- ligand. It is also interesting to compare the effect of temperature on the conversion. In hemin and hematin the conversion decreases slightly with increasing temperature, as shown in Figs. 9 and 10. In $\text{Fe}(\text{DTC})_2\text{Cl}$ there is a small increase in conversion with increasing temperature, as seen in Fig. 14, and for $\text{Fe}(\text{SAL})_2\text{OH}$ there is a somewhat greater increase in conversion, as seen in Fig. 16. It must be remembered that in the case of hemin and hematin there is a change of spin state—high spin to intermediate spin—as well as a change of oxidation state which may affect the temperature coefficient. The possible intermediate spin to low spin transition in $\text{Fe}(\text{DTC})_2\text{Cl}$ upon reduction may also affect in part the temperature coefficient for reduction. In general, for a detailed comparison of these compounds, one must consider the electronic energy levels of the complete ligand system.

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