

charge transfer energy in hemin is at 15.3 kK, and in hematin at 15.5 kK. Thus, hemin is expected to show the larger conversion at a given pressure as indeed it does (see Fig. 10). In imidazole protohemichrome there is no evidence of a ligand to metal charge transfer peak at an energy lower than the *Q* bands. If the transition exists, it must be buried under the *B* band at higher energy than the charge transfer peaks in the high spin ferric compounds hemin and hematin. The net result is the lower conversion for this ferric compound.

It has been shown^{19,20,32} that for a wide variety of systems the conversion follows the relationship

$$K = C_{II}/C_{III} = AP^B,$$

where C_{II} and C_{III} are the fractions of ferrous and ferric sites, P is the pressure, and A and B are constants. The values of A and B for hemin, hematin, and imidazole protohemichrome appear in Table III.

Zerner's¹³ calculation for ferrous porphyrins indicated that if the metal were in the plane of the porphyrin, the ferrous ion would be in the intermediate spin state. By moving the iron out of the plane by 0.49 Å, the $d_{x^2-y^2}$ orbital lowered in energy because of decreased repulsion, and the high spin state became possible. The data presented above indicated that at high pressure the ferrous iron in hemin and hematin is probably intermediate spin. Koenig³³ found that the ferric iron in hemin lies out of the porphyrin plane towards the chlorine molecule by 0.475 Å. It is possible

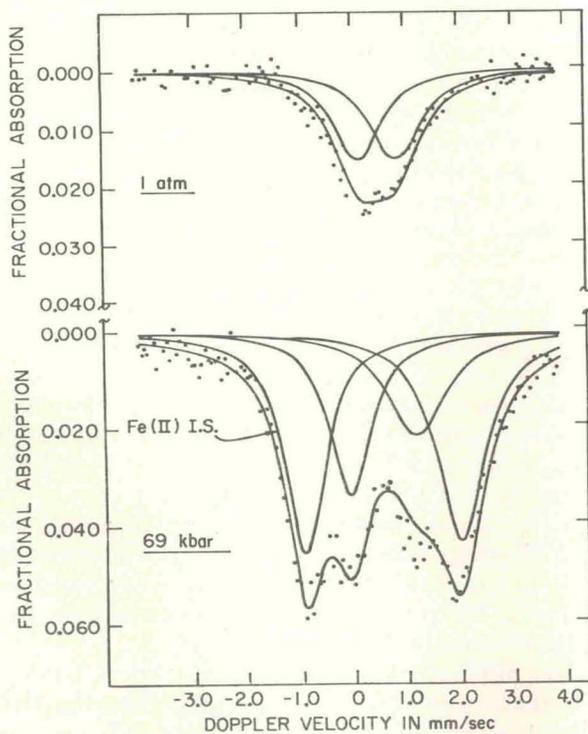


FIG. 13. Mössbauer spectra of $\text{Fe}(\text{DTC})_2\text{Cl}$.

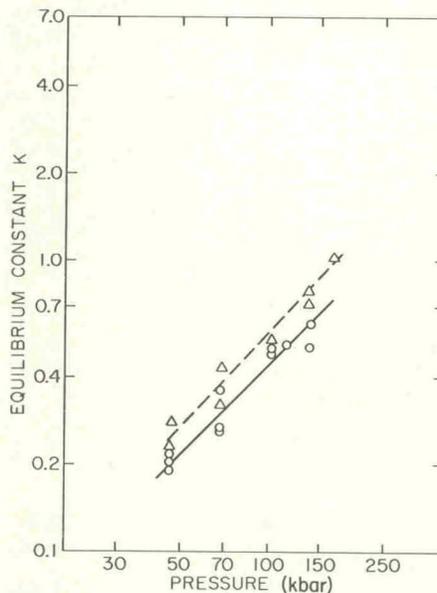


FIG. 14. $\ln K$ vs $\ln P$ — $\text{Fe}(\text{DTC})_2\text{Cl}$. O, 23°C; Δ, 106°C.

that with increasing pressure the iron could be forced back towards the porphyrin plane. This would have two noticeable effects on the observed parameters.

Moss⁷ presents a formula for the electric field gradient at the iron nucleus in ferric protohemes:

$$V_{zz} = (-q_r | r_r^2 - 2z_r^2 |) / (| r_r^2 + Z_r^2 |^{5/2}) + (2q_5/Z_5^3) + (2q_6/Z_6^3),$$

where r_r is the radius of an effective ring of total charge q on the porphyrin, Z_r is the distance of the iron out of the porphyrin ring, and Z_5 and Z_6 are the out of plane coordinates of the axial charges q_5 and q_6 . Referring back to this formula, as z_r decreases, the $\text{Fe}(\text{III})$ quadrupole splitting will increase. Second, as calculated by Zerner, as the iron moves closer in to the porphyrin plane, the intermediate spin state for ferrous iron will become more favorable. Both of these effects are observed. Figure 12 shows the large increase in $\text{Fe}(\text{III})$ quadrupole splitting with increasing pressure. In addition, the isomer shift and quadrupole splitting of the ferrous iron produced at high pressure is characteristic of the intermediate spin ferrous ion.

COMPOUNDS WITH OXYGEN AND SULFUR BONDING

Two ferric compounds, monochlorobis(*N,N*-diethylthiocarbamato-iron(III) and monohydroxybis(salicyl)-iron(III) were prepared and studied as a function of pressure. For simplicity, the compounds will be referred to as $\text{Fe}(\text{DTC})_2\text{Cl}$ and $\text{Fe}(\text{SAL})_2\text{OH}$, respectively. These compounds were studied because of their square pyramidal structure, and also because of the novel spin state of $\text{Fe}(\text{DTC})_2\text{Cl}$. The crystal structure of

TABLE IV. Mössbauer parameters for Fe(DTC)₂Cl and Fe(SAL)₂OH.

Pressure (kbar)	Isomer shift (mm/sec) ^a								
	4	25	50	75	100	125	150	175	
Fe(DTC) ₂ Cl									
Fe(III)	0.410	0.392	0.388	0.391	0.400	0.400	0.400	...	(23°C)
Fe(II)	0.360	0.389	0.400	0.405	0.410	...	
Fe(SAL) ₂ OH									
Fe(III)	0.426	0.432	0.423	0.405	0.385	0.370	0.358	0.350	(23°C)
Fe(II)	1.34	1.30	1.26	1.24	1.23	1.22	
Quadrupole splitting (mm/sec)									
Fe(DTC) ₂ Cl									
Fe(III)	2.61	2.70	2.71	2.71	2.71	2.71	2.71	...	(23°C)
Fe(II)	0.98	1.14	1.26	1.36	1.42	...	
Fe(III)	...	2.68	2.68	2.69	2.69	2.69	2.69	2.70	(106°C)
Fe(II)	0.93	1.10	1.17	1.21	1.25	1.26	
Fe(SAL) ₂ OH									
Fe(III)	0.86	1.01	1.15	1.28	1.36	1.41	1.44	1.46	(23°C)
Fe(II)	2.14	2.16	2.18	2.20	2.22	2.24	
Fe(III)	...	1.08	1.21	1.29	1.36	1.41	1.44	...	(106°C)
Fe(II)	2.06	2.10	2.14	2.17	2.21	...	

^a Relative to iron metal.

Fe(DTC)₂Cl has been determined²⁴ and the iron is found to be in the center of a rectangle formed by four sulfur atoms. The chlorine atom is coordinated to the iron perpendicular to the plane of the four sulfurs. The iron atom actually is pulled out of the plane towards the chlorine atom. An analogous structure is assumed for Fe(SAL)₂OH with the four sulfurs replaced by oxygens, and the Cl⁻ ion replaced by an OH⁻ ion. The iron of Fe(DTC)₂Cl is intermediate spin with $S = \frac{3}{2}$.²⁵ It appears from the Mössbauer data that Fe(SAL)₂OH is high spin with $S = \frac{5}{2}$.

Mössbauer spectra of Fe(DTC)₂Cl are shown in Fig. 13 at 4 and 138 kbar. At low pressure the ferric iron exhibits a large quadrupole splitting indicative of both the low symmetry of the molecule and the unsymmetric distribution of electrons in the *d* levels. At 4 kbar its quadrupole splitting is 2.61 mm/sec, and its isomer shift is 0.41 mm/sec. At high pressure the ferric iron reduces to ferrous iron as shown in Fig. 13. The effect of pressure on the equilibrium constant *K* is shown in Fig. 14 at 23 and 106°C. At 23°C and 150 kbar there is about 33% Fe(II) present, and at 106°C and 150 kbar the conversion has increased to about 50%.

The isomer shift and quadrupole splitting of both Fe(III) and Fe(II) at various pressures are given in

Table IV. The quadrupole splitting and isomer shift of the Fe(III) ion show only modest pressure effects. The Fe(II) isomer shift increases from a value of about 0.35 mm/sec at 45 kbar to about 0.41 mm/sec at 150 kbar. Over the same pressure range, the quadrupole splitting increases from about 0.93 to 1.45 mm/sec. The quadrupole splitting, even at high pressure, is low for typical values of intermediate spin ferrous compounds. In ferrous phthalocyanine the quadrupole splitting is about 2.58 mm/sec at 1 atm, and it increases to about 3.17 mm/sec at 150 kbar. Even in imidazole protohemicrhone, the mixed spin or intermediate spin Fe(II) produced at high pressure has a quadrupole splitting greater than 2.0 mm/sec. Frank *et al.*²⁶ have studied some low spin nitrosyl bis(dithiocarbamate)-iron(II) compounds, and at 1 atm the quadrupole splitting and isomer shift are about 0.7 and 0.35 mm/sec, respectively. These values are reasonably close to the observed Fe(II) values in reduced Fe(DTC)₂Cl, and it is therefore believed that the Fe(II) produced by reduction of the intermediate spin Fe(III) is low spin, although the possibility that it is intermediate spin cannot be ruled out.

The Mössbauer spectra of Fe(SAL)₂OH at 4 and at 138 kbar are shown in Fig. 15. At low pressure the ferric iron shows an asymmetric pair of peaks, indicating the