TABLE II. Mössbauer parameters for hemin and hematin.

Pressure (kbar)	5	10	20	30	60	90	120	150	
	Isomer shift (mm/sec)[a]								
Hemin									
Fe(III)[H.S.]	0.290	0.30	0.31	0.33	0.41	0.50	0.50	0.50	(23°C)
Fe(II)[I.S.]	···	···	0.26	0.25	0.23	0.22	0.22	0.22	
Hematin									
Fe(III)[H.S.]	0.29	0.31	0.33	0.35	0.43	0.47	0.48	0.48	(23°C)
Fe(II)[I.S.]	···	0.23	0.23	0.23	0.23	0.22	0.22	0.22	
	Quadrupole splitting (mm/sec)								
Hemin									
Fe(III)[H.S.]	(0.75)	1.02	1.18	1.40	1.83	2.15	2.23	2.30	(23°C)
Fe(II)[I.S.]	···	···	3.10	3.08	3.05	3.00	2.97	2.97	
Fe(III)[H.S.]	···	···	1.10	1.30	1.75	2.10	2.15	2.20	(90°C)
Fe(II)[I.S.]	···	···	···	2.75	2.85	2.92	2.90	2.90	
Hematin									
Fe(III)[H.S.]	(0.75)	1.08	1.30	1.50	1.95	2.10	2.20	2.30	(23°C)
Fe(II)[I.S.]	···	···	···	3.00	2.95	2.90	2.90	2.90	
Fe(III)[H.S.]	···	···	···	1.45	1.90	2.10	2.20	2.25	(90°C)
Fe(II)[I.S.]	···	···	···	2.76	2.80	2.79	2.78	2.76	

[a] Relative to iron metal.

ular crystals there is always a large increase of f number with pressure. In these circumstances the relative areas under the peaks may depend somewhat on the amount of material in the path of the gamma rays. These data were obtained at a number of dilutions of sample with boron, and all data reported were for dilutions where further change of concentration did not affect the measured conversions.

The Mössbauer spectra of hematin are similar to those of hemin, and therefore are not shown. The conversions to ferrous iron are shown in Figs. 9 and 10. It is seen that the hematin converts less than hemin. Mössbauer parameters appear in Table II. The isomer shift for ferric ion in hemin is shown in Fig. 11. Extrapolating the pressure data back to one atmosphere gives a value for the isomer shift of 0.28 mm/sec. Figure 12 shows the quadrupole splitting of the ferric iron in hemin as a function of pressure. The atmospheric value for the quadrupole splitting is about 0.75 mm/sec at 23°C. The latest values reported by Moss *et al.*[18] for hemin are 0.23 mm/sec isomer shift and 0.7 mm/sec quadrupole splitting. The isomer shifts and quadrupole splittings of the various states in hemin are given in Table II.

At 23°C and 20 kbar, the isomer shift and quadrupole splitting of the state labeled intermediate spin ferrous iron are 0.26 and 3.10 mm/sec, respectively. At 150 kbar the isomer shift is 0.22 mm/sec, and the quadrupole splitting is 2.97 mm/sec. The isomer shift is much too low for typical high spin ferrous iron (0.9–1.3 mm/sec), and the large quaerupole splitting eliminates low spin as the likely state for the ferrous iron. At 20 kbar, ferrous phthalocyanine, which is a true intermediate spin ferrous compound, has an isomer shift of 0.375 mm/sec and a quadrupole splitting of 2.71 mm/sec, and at 150 kbar the isomer shift is 0.28 mm/sec, and the quadrupole splitting is 3.21 mm/sec. The two sets of values for these compounds are sufficiently close to justify the designation of the high pressure ferrous iron as intermediate spin, although the possibility of a mixed spin state cannot be eliminated. It is also possible that the differences in the parameters of the intermediate spin states of hemin on the one hand, and the imidazole protohemichrome on the other, involve difference in the degree of spin mixing as well as differences in the type of bonding.

It must be remembered that the assignment of spin state on the basis of the isomer shift and quadrupole splitting is not unequivocal. In the absence of magnetic susceptibility measurements at high pressure and over a large range of temperature these assignments must be regarded as reasonable but tentative. Even were the requisite susceptibility measurements possible, their interpretation, in a system where iron exists in two

oxidation states as well as two or more spin states, would be very difficult.

As can be seen from Figs. 9 and 10, the conversion to ferrous iron is slightly less at high temperature. This contrasts with the reduction observed in a wide variety of other compounds.[19,20] It may in part be associated with temperature effects on the shape of the potential well; however, it may be associated with the fact that the ferrous state produced is of lower spin than the ferric state. At higher temperature there should be a greater tendency to produce a high spin ferrous state, which is probably less stable in hemoporphyrins than lower spin configurations. This may inhibit the reduction process. In the imidazole compound, where one is dealing only with low and intermediate spin states, this factor is not important, and the reduction increases with temperature (see Fig. 6). For hemin and hematin the reduction was reversible with very slight hysteresis. There were some irreversible effects in the imidazole compound which will be discussed at another time.

DISCUSSION

The optical spectra of porphyrins and metalloporphyrins have been extensively studied. The many papers of Williams[21,22] and Falk[2,23,24] yield detailed interpretations of the optical spectra. Gouterman and his co-workers[13,25–28] have undertaken extensive molecular orbital studies of porphyrin-type compounds, and Harris[12,29,30] has done crystal field calculations on hemin and related compounds.

The optical absorption of porphyrins and hemes are similar to phthalocyanine and the iron phthalocyanines discussed in the previous paper. The main absorption bands are due to π–π^* transitions. The lowest occupied π orbitals have a_{1u} and a_{2u} symmetry. In porphyrins these levels are accidentally degenerate, and their transitions to the lowest antibonding orbital $e_g(\pi)$ undergo extensive configuration interaction, which drives the bands apart. The resulting transitions are the $a_{2u}\rightarrow e_g$ transition (labeled Q following Weiss *et al.*[25]) at low energy and modest intensity, and the $a_{1u}\rightarrow e_g$ transition (labeled B) at higher energy and strong intensity. The effect of configuration interaction is much the same as that discussed for the phthalocyanine compounds. Any increase in configuration interaction will increase the intensity of the B band and decrease the intensity of the Q band. In both protoporphyrin and the ferric hemes, these π–π^* transitions shifted to lower energy. The B bands shifted by about 1 kK in 140 kbar. In addition, the Q bands lost intensity relative to the B band. The shift to lower energy of the B band is consistent with an increase of configuration interaction and the observed loss of intensity of the Q bands.

The a_{2u} wavefunction has its maximum electron density on the pyrrole nitrogens, while the a_{1u} wavefunction has its maximum density on the pyrrole carbons. The lowest lying antibonding orbital, $e_g(\pi)$, has its maximum electron density on the methine bridge atoms and the outer pyrrole carbons. Thus, the Q transition, and to a lesser extent the B transition, involve transfer of charge to the periphery of the molecule. Falk[2] has discussed in some detail how electrophyllic substitutions on the periphery of the molecule can cause the Q and B bands to shift to lower energy. The reasoning is that the more electrophyllic the periphery of the porphyrin is, the easier it will be to transfer electrons to the antibonding orbital having its electron density on the periphery. Caughey,[31] however, points out that some electrophyllic groups do not cause this shift to lower energy. It appears, however that groups that do not interact sterically with the porphyrin ring follow Falk's arguments. The salient point is that increased electron density at the periphery of the molecule is related to the shift of the visible transitions to lower energy. The shift to lower energy of the B and Q transitions is also consistent with a thermal occupation of the $e_g\pi^*$ orbital, as discussed in the previous paper[16] for the phthalocyanine compounds. This thermal occupation will in turn decrease any metal to ligand backbonding in the heme compounds with increasing pressure. As discussed before, this decrease in backbonding of the metal d_π orbitals will make the low spin complexes less stable. This is particularly true for low spin ferrous compounds, which are strong π donors. Thus, with increasing pressure the intermediate spin state for ferrous iron becomes more favorable than the low spin state, which explains why the ferrous iron produced by reduction of ferric iron in imidazole protohemichrome is intermediate spin at high pressure, and not low spin.

The theory for the reduction of ferric iron to ferrous iron has been discussed in detail.[19,20,32] It was shown that the reduction is a thermal process involving the transfer of an electron from the ligands to the metal. Not surprisingly, there is a strong correlation between the initial energy of the charge transfer peak and the amount of reduction observed.[32] Thus, for a similar set of compounds such as hemin and hematin, the compound having the lower charge transfer energy should show the larger conversion. It was stated above that the

TABLE III. Parameters A and B for $K=Ap^B$.

Compound	T (°C)	A	B	Pressure range (kbar)
Hemin	23	0.0273	0.85	20–140
Hematin	23	0.012	0.98	25–90
ImPH[a]	23	9.34×10^{-3}	1.03	45–175
	110	1.89×10^{-2}	1.03	20–120
$Fe(DTC)_2Cl$	23	3.95×10^{-3}	1.02	45–175
$Fe(DTC)_2Cl$	106	4.14×10^{-3}	1.07	45–175
$Fe(SAL)_2OH$	23	1.09×10^{-4}	2.01	45–175
$Fe(SAL)_2OH$	106	4.44×10^{-7}	3.46	45–135

[a] ImPH, Imidazole protohemichrome.