

TABLE II. Mössbauer parameters for FePc(L)<sub>2</sub>.

Pressure (kbar)	0	25	50	75	100	125	150	175
	Isomer shift (mm/sec) <sup>a</sup>							
Low spin								
FePc(Py) <sub>2</sub>	0.270	0.245	0.200	0.175	0.167	0.165	0.162	0.160
FePc(3-Pic) <sub>2</sub>	0.260	0.240	0.200	0.175	0.167	0.165	0.162	0.160
FePc(4-Pic) <sub>2</sub>	0.270	0.265	0.215	0.180	0.167	0.165	0.162	0.160
FePc(Pip) <sub>2</sub>	0.265	0.255	0.210	0.166	0.140	0.132	0.128	0.125
Intermediate spin								
FePc	0.385	0.373	0.350	0.324	0.302	0.290	0.280	0.274
FePc(Py) <sub>2</sub>	...	...	0.335	0.295	0.280	0.270	0.260	0.255
FePc(3-Pic) <sub>2</sub>	...	...	0.330	0.295	0.273	0.266	0.260	0.255
FePc(4-Pic) <sub>2</sub>	...	...	0.322	0.300	0.285	0.275	0.275	0.270
FePc(Pip) <sub>2</sub>	...	...	...	0.245	0.255	0.252	0.245	0.240
	Quadrupole splitting (mm/sec)							
Low spin								
FePc(Py) <sub>2</sub>	2.01	1.97	1.93	1.92	1.93	1.92	1.91	1.89
FePc(3-Pic) <sub>2</sub>	1.93	1.92	1.89	1.89	1.91	1.93	1.93	1.92
FePc(4-Pic) <sub>2</sub>	2.03	2.03	1.97	1.95	1.93	1.92	1.91	1.89
FePc(Pip) <sub>2</sub>	2.22	2.26	2.23	2.16	2.10	2.08	2.07	2.07
Intermediate spin								
FePc	2.58	2.74	2.90	3.06	3.14	3.18	3.21	3.23
FePc(Py) <sub>2</sub>	...	...	2.78	2.95	3.02	3.05	3.07	3.08
FePc(3-Pic) <sub>2</sub>	...	...	2.76	2.95	3.04	3.09	3.12	3.15
FePc(4-Pic) <sub>2</sub>	...	...	2.78	2.96	3.04	3.08	3.10	3.12
FePc(Pip) <sub>2</sub>	...	...	...	2.72	2.83	2.93	3.01	3.04

<sup>a</sup> Relative to iron metal.

it is possible to measure only order of magnitude changes in absolute intensity, so it is impossible to determine if the absolute intensity of the  $N$  transition is changing with pressure.

It has been established that the ground state of FePc is  $3B_{2g}$ .<sup>12</sup> The order of the  $d$  orbitals and their symmetries in  $D_{4h}$  are:  $d_{xz}$ ,  $d_{yz}(e_g)$ ;  $d_{xy}(b_{2g})$ ;  $d_z^2(a_{1g})$ ;  $d_{x^2-y^2}(b_{1g})$ . This order is slightly different from the order that Zerner *et al.*<sup>19</sup> calculated for the ferrous porphyrin complex. Their energy scheme had the  $d_{xy}$  orbital lower than the  $d_{xz}$ ,  $yz(d_\pi)$  orbitals. Their calculations indicated that the metal  $d_\pi$  orbitals were approximately 90% pure, indicating that there is some backbonding of the metal  $d_\pi$  orbitals to the porphyrin antibonding orbitals. Since the lowest-lying ligand antibonding orbital for both the porphyrins and the phthalocyanines is an  $e_g(\pi)$  orbital, backbonding of metal  $d_\pi$  electrons to this level is the most likely case. The additional resonance structure of FePc should allow for even more backbonding and thus a greater stabilization of the metal  $d_\pi$  orbitals. Therefore, in FePc the metal  $e_g$  orbital lies lower in energy than the metal  $b_{1g}$  orbital.

When additional ligands are coordinated perpendicular to the phthalocyanine plane, two additional per-

turbations of the energies of the metal  $d$  orbitals take place. The first is that the  $d_z^2$  orbital is raised in energy due to bonding of the axial ligands. This increase in energy is greater than the spin pairing energy, so that the electron formerly in the  $d_z^2$  orbital is paired with the electron in the  $d_{xy}$  orbital, forming the low spin complex. Also, if the axial ligands have empty  $\pi^*$  orbitals, the  $d_\pi$  electrons can backbond to those orbitals, causing a further decrease in the energy of the  $d_\pi$  orbital. The effect of this additional backbonding can be shown by the energy of the charge transfer transition in these low spin complexes. The more backbonded the metal  $\pi$  orbitals are, the higher in energy the charge transfer transition will be. According to Dale,<sup>9</sup> the order of increasing charge transfer energy is:  $n$ -butylamine,  $\text{NH}_3 < \text{piperidine} < \text{imidazole} < \text{pyridine}$ . This is also the order of increasing  $\pi$  acceptor character of these ligands, with the first three having comparable ability. It was found that the picoline adducts studied have lower charge transfer energies than the pyridine adduct.

In the piperidine adduct the axial ligands have no empty  $\pi^*$  orbitals available for backbonding. The fact that it is low spin is due to the very strong  $\sigma$  bonding which raises the energy of the  $d_z^2$  orbital. This is ex-



emphified by the fact that the acid dissociation constant  $pK_a$  for the piperidine derivative is 11.2 compared with 5.25, 5.60, and 6.0 for the pyridine, 3-picoline, and 4-picoline adducts.<sup>20</sup>

In the previous section it was shown that the low spin pyridine, picoline, and piperidine adducts of FePc convert to a different spin state with increasing pressure.

The major cause for this conversion would seem to be a reduction in the backbonding of metal electrons to the empty  $\pi^*$  orbitals of the ligand. As indicated earlier, the  $\pi-\pi^*$  transitions all shift to lower energy with increasing pressure. The effect of this is to move charge into the  $e_g^*$  ligand antibonding orbitals. The shift of the lowest  $\pi-\pi^*$  peak is approximately 10% of the total energy of the peak maximum. However, the electron transfer is a thermal process. Figure 12 shows a schematic configuration coordinate diagram for the  $\pi-\pi^*$  system. A modest decrease in energy of the optical transition can be sufficient to cause a thermal population of the excited state as shown since the thermal transition is not restricted by the Franck-Condon principle. The  $e_g^*$  orbitals are the same ones that are available to the  $d_\pi$  electrons for backbonding. The effect of this additional ligand  $\pi$  electron character will be to decrease the backbonding of the metal  $d_\pi$  electrons to them. This in turn will raise the energy of the  $d_\pi$  orbitals and decrease the energy difference between the  $d_{z^2}$  and the  $d_\pi$  orbitals sufficiently to cause a change in the spin state of the ferrous iron with pressure. A transition to higher spin state has been observed in some ferrocyanides<sup>21</sup> and iron phenanthroline compounds,<sup>22</sup> where it has also been attributed to decreasing backbonding.

At high pressure the conversion to the new spin state stops. This appears to represent a balance between the reduced backbonding which tends to produce a higher spin state and then the delocalization of the  $3d$  electrons at high pressure which favors a lower spin state. The delocalization is facilitated by the thermal transfer of the ligand electron to the  $\pi^*$  orbitals which are nearer the perimeter of the molecule leaving room for greater expansion of the  $3d$  orbitals.

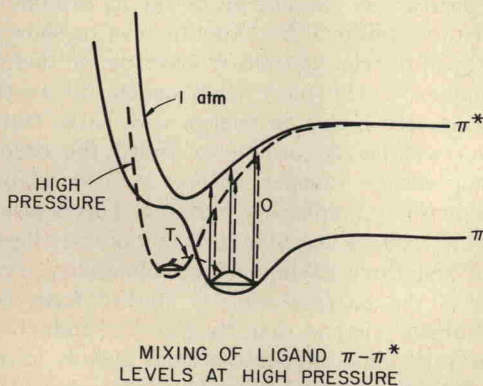


FIG. 12. Schematic configuration coordinate diagram. O, optical transition; T, thermal transition

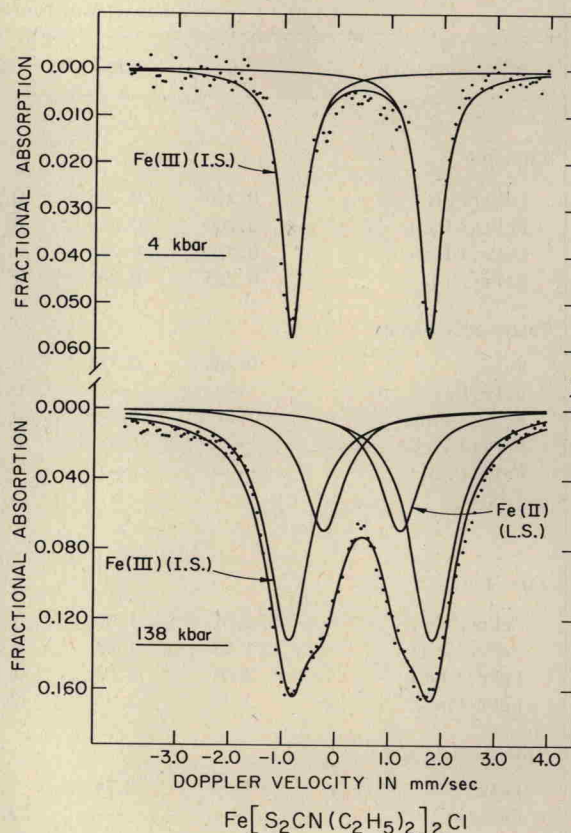


FIG. 13. Mössbauer spectra of sheared FePc.

The picoline adducts converted more to intermediate spin than did the pyridine adduct. The methyl substitution on the pyridine decreases the ability to accept metal  $d_\pi$  electrons. This is reflected by the lower energy of the charge transfer band. Since the energy difference between the  $d_\pi$  and  $d_{z^2}$  orbitals is then less in the picoline adducts, their increased conversion to intermediate spin is expected. The piperidine derivative showed the least conversion to intermediate spin. In this compound the only backbonding is to the phthalocyanine, so that the decrease in backbonding is less than for the other adducts, and the conversion to intermediate spin is less. The conversion actually decreases at the higher pressures where the spreading of the  $3d$  orbitals more than compensates for the decrease in backbonding.<sup>23</sup>

It is possible that changes in  $\pi$  bonding and  $\sigma$  bonding also contribute to the spin change, but we believe these effects are secondary.

The new spin state has been labeled intermediate spin because its isomer shift and quadrupole splitting are very nearly those of FePc. To obtain an intermediate spin state it is necessary to remove the degeneracy of the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals by a significant amount. It is perhaps surprising that this occurs in the pseudo-octahedral symmetry of the phthalocyanine deriva-