

TABLE III. Measured properties of FePc and FePc (treated).

| Reflection number | X-ray reflections | | | | | | | | | |
|-------------------|------------------------|-------|----------------|-------|-------------------------|-------|--------------------------|-------|--------------------------|-------|
| | FePc | | FePc (sheared) | | FePc (air) ^a | | FePc(2-Pic) ^b | | FePc(4-Pic) ₂ | |
| | Intensity ^c | 2θ | Intensity | 2θ | Intensity | 2θ | Intensity | 2θ | Intensity | 2θ |
| 1 | 5 | 7.15 | 2 | 6.70 | 2 | 6.75 | 4 | 6.85 | 5 | 8.05 |
| 2 | 5 | 9.25 | 2 | 9.10 | 3 | 7.20 | 3 | 8.05 | 5 | 9.60 |
| 3 | 2 | 10.50 | 1 | 23.75 | 3 | 9.15 | 1 | 9.20 | 5 | 11.50 |
| 4 | 1 | 11.55 | 1 | 26.35 | 1 | 10.40 | 2 | 10.25 | 1 | 14.60 |
| 5 | 2 | 12.55 | 1 | 30.55 | 1 | 12.40 | 3 | 11.00 | 2 | 16.85 |
| 6 | 1 | 13.95 | | | 2 | 18.40 | 1 | 12.90 | 3 | 17.90 |
| 7 | 1 | 15.45 | | | 1 | 19.70 | 2 | 13.80 | 2 | 18.80 |
| 8 | 3 | 18.50 | | | 2 | 21.40 | 2 | 15.25 | 4 | 20.95 |
| 9 | 1 | 19.85 | | | 3 | 23.85 | 1 | 16.30 | 1 | 22.20 |
| 10 | 2 | 21.50 | | | 2 | 26.30 | 1 | 17.10 | 1 | 22.70 |
| 11 | 1 | 22.30 | | | 1 | 26.95 | 1 | 18.80 | 4 | 24.70 |
| 12 | 1 | 23.15 | | | 2 | 28.10 | 2 | 19.65 | 1 | 25.65 |
| 13 | 4 | 23.85 | | | 1 | 29.55 | 1 | 21.25 | 2 | 26.90 |
| 14 | 4 | 26.35 | | | 2 | 30.55 | 2 | 22.00 | 3 | 28.70 |
| 15 | 3 | 28.15 | | | | | 2 | 23.60 | | |
| 16 | 2 | 29.60 | | | | | 2 | 25.20 | | |
| 17 | 4 | 30.55 | | | | | 4 | 26.15 | | |
| 18 | 1 | 32.45 | | | | | 1 | 27.65 | | |
| 19 | 1 | 33.15 | | | | | 1 | 29.40 | | |
| 20 | | | | | | | 1 | 31.70 | | |

^a FePc(air) = FePc (heated in air).^b FePc(2-Pic) = FePc (heated in 2-picoline).^c Intensity is arbitrary. 1 is very weak, 6 is very intense.

tives. Apparently the Fe-N distances for the axial ligands, and especially the electronic orbitals on those nitrogens, are sufficiently different from those of the phthalocyanine nitrogens that the field at the iron very significantly deviates from octahedral symmetry. Since the *low spin* quadrupole splitting is ~ 2.0 mm/sec, this is an entirely reasonable assumption. It is also possible that the new spin state is "mixed spin" rather than true intermediate spin.

OTHER FORMS OF FePc

Ferrous phthalocyanine is a well characterized substance. It has a known crystal structure²⁴ and a measured magnetic susceptibility ranging from 3.71 to 3.96 μ_B .¹²⁻¹⁵ At 1 atm it has a measured quadrupole of approximately 2.6 mm/sec and an isomer shift of 0.40 mm/sec. FePc, however, is sensitive to the manner in which it is handled. In the course of working with FePc, three materials different from ordinary FePc were observed. One was obtained by shearing FePc in a mortar, another was obtained by heating FePc in 2-picoline, and the third material was obtained by heating FePc in air at 150°C. A brief discussion of the properties of the three materials will be given, and the effect of pressure upon them will be discussed. For convenience some of measured properties are presented in Tables III and IV.

FePc (sheared) are appeared to be amorphous, as an x-ray powder diagram showed only a few weak diffuse

lines (Table III). It appears that grinding the material destroys the crystalline nature of FePc obtained by sublimation. In a somewhat similar manner, H₂Pc has been shown to undergo a transformation from its β form

TABLE IV. Measured properties of FePc and FePc(treated).

| Percent: | C | H | N | Fe |
|-------------------------------------|-------------------|-------------------|-------------------|-------------------|
| Chemical analysis | | | | |
| FePc(calc) | 67.60 | 2.84 | 19.70 | 9.80 |
| FePc(found) | 67.27 | 2.86 | 19.39 | 9.97 |
| FePc(sheared) | 65.09 | 2.81 | 19.03 | 9.67 |
| FePc(heated in 2-picoline) | 66.84 | 2.81 | 19.49 | 9.55 |
| FePc(heated in air) | 61.01 | 2.87 | 17.19 | 10.17 |
| Magnetic susceptibility (μ_B) | | | | |
| FePc(literature) | 3.71 ^a | 3.85 ^b | 3.89 ^c | 3.96 ^d |
| FePc(found) | 3.75 | | | |
| FePc(sheared) | 3.22 | | | |
| FePc(heated in 2-picoline) | 1.83 | | | |
| FePc(heated in air) | 3.00 | | | |

^a Reference 14.^b Reference 15.^c Reference 13.^d Reference 16.

to its α form by grinding in KBr.⁸ Lever³ points out in his review that many metallic phthalocyanines have similar polymorphic forms. The Mössbauer spectrum of FePc (sheared) is shown in Fig. 13. At 1 atm the quadrupole splitting is 0.71 mm/sec, and its isomer shift is 0.35 mm/sec. The magnetic susceptibility was measured on a Faraday balance and found to be $3.22 \mu_B$. On the same apparatus the susceptibility for FePc was found to be $3.75 \mu_B$. The chemical analysis of FePc (sheared) was very close to FePc (Table IV).

In an attempt to make the 2-picoline adduct of FePc, FePc was heated in 2-picoline. The adduct was not made, but the resulting solid showed markedly different properties from FePc. FePc (heated in 2-picoline) has a crystal structure different from both FePc and FePc-(4-picoline)₂, as shown in Table III. The chemical analysis was the same as that for FePc (Table IV). The Mössbauer spectrum of this material is shown in Fig. 14. At 1 atm it has a quadrupole splitting of 0.36 mm/sec and an isomer shift of 0.29 mm/sec. The low isomer shift is representative of a low spin complex, and its measured magnetic susceptibility of $1.83 \mu_B$ is likewise indicative of a lower moment material.

The third substance was obtained by heating FePc in air at 150°C. The resulting solid was weakly crystal-

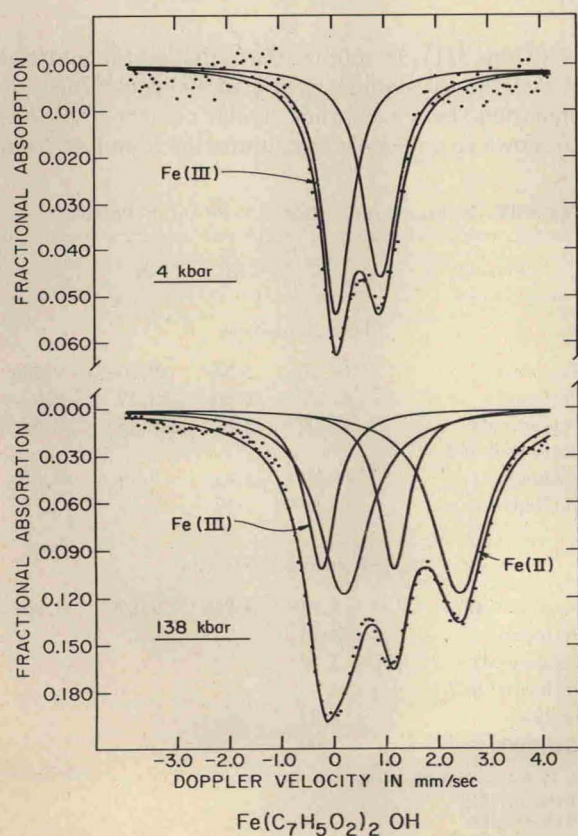


FIG. 14. Mössbauer spectra of FePc heated in air.

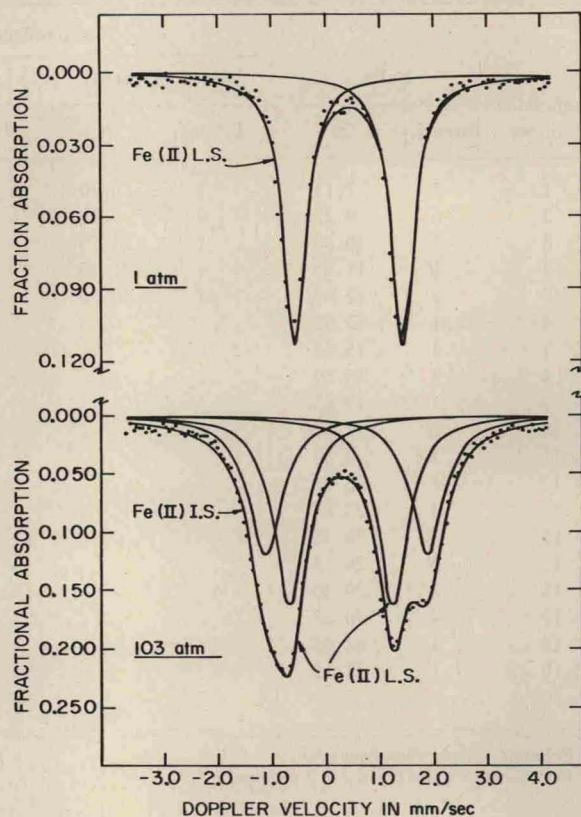


FIG. 15. Mössbauer spectra of FePc heated in 2-picoline.

line, with the observed lines of its powder diagram closely similar to the intense lines in FePc, as shown in Table III. The chemical analysis indicated that oxygen has reacted in some manner with FePc (Table IV). Oxygen was shown to be necessary since heating in vacuum produced no change in the properties of FePc. The measured susceptibility of this material was $3.00 \mu_B$. The Mössbauer spectra of this material is shown in Fig. 15. At 1 atm it has a quadrupole splitting of 1.13 mm/sec and an isomer shift of 0.35 mm/sec.

The effects of pressure on these materials are similar, as can be seen from their respective Mössbauer spectra at high pressure (Figs. 13-15). The resemblance is that at high pressure two new peaks are present which have similar Mössbauer parameters in each material. These are compared in Table V. It is seen that the high pressure material has parameters similar to FePc. It thus appears that pressure favors the "normal" form of FePc, which is the intermediate spin form with wide quadrupole splitting. In the case of FePc (sheared) it appears that pressure reorders the crystal, thereby restoring the normal FePc spectrum. Upon release of pressure the initial spectrum reappears. This is possible because of additional shear associated with the release of pressure. For FePc (heated in air), pressure again