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Effect of Pressure on the Electronic Structure of Protoporphyrin IX, Hemiporphyrins, and Related Compounds*

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Studies have been made on the effect of pressure to 170 kbar on the electronic structure of protoporphyrin IX, several hemiporphyrins, and related compounds using optical absorption and Mössbauer resonance. The optical absorption peaks which correspond to $\pi-\pi^*$ transitions shifted to lower energy and decreased in intensity with increasing pressure. This could be explained in terms of changes in the configuration interaction involving a shift of the electrons to the outer portions of the porphyrin ring. Imidazole protohemichrome is a low spin ferric compound. At room temperature and pressures above about 45–50 kbar it reduced apparently to an intermediate spin (or mixed spin) ferrous state. At 110° it reduced at moderate pressure to a low spin ferrous state, but with increasing pressure the Fe(II) transformed to intermediate spin. Hemin and hematin are high spin ferric compounds. With increasing pressure they reduced apparently to intermediate spin (or mixed spin) ferrous compounds. The amount of reduction with pressure was consistent with the location and shift of the observable metal to ligand-charge transfer bonds. Two ferric compounds with square pyramidal symmetry like hemin and hematin but with planar neighbors of oxygen or sulfur instead of nitrogen were studied. Both reduced with increasing pressure, in one case with a probable change of spin state. All reductions observed were reversible.

The biological pigments responsible for the red coloration of blood and the green coloration of most plants are the porphyrins. In plants chlorophylls are magnesium porphyrin compounds, and in blood proteins, the active iron site is coordinated to a porphyrin compound. For example, in hemoglobin there are four protoporphyrin IX iron compounds coordinated to the globin protein. Because of their central importance in biochemistry, the literature on porphyrins and metalloporphyrins is extensive. Reviews occur in many places including two books.^{1,2}

The basic structure of porphyrin consists of four pyrrole rings linked together by methine carbon bridges. Differences are in the nature of the substituents on the outer pyrrole carbons. The porphyrins readily coordinate to iron, forming the biologically important hemes. The ferrous compound protoporphyrin iron(II) is not stable and is autoxidized to the ferriprotoporphyrin.

The residual positive charge on the iron is taken up by coordination to an anion such as Cl^- or OH^- . The protoporphyrin iron(III) chloride compound is known as hemin, and the hydroxide compound is known as hematin. These ferric compounds are pentacoordinated, and the iron is pulled out of the plane towards the anion. In addition to anions, organic bases such as pyridine can coordinate to both ferric and ferrous hemes. The resulting hexacoordinated compounds are known as hemichromes for ferric compounds and hemochromes for the ferrous compounds. In imidazole protohemichrome the iron is very slightly out of the plane, towards the more distant imidazole molecule. Because of their sixfold coordination, the hemochromes and hemichromes serve as useful model compounds for the heme proteins.

In this paper we present studies of the effect of pressure to 170 kbar on the electronic structure of a num-

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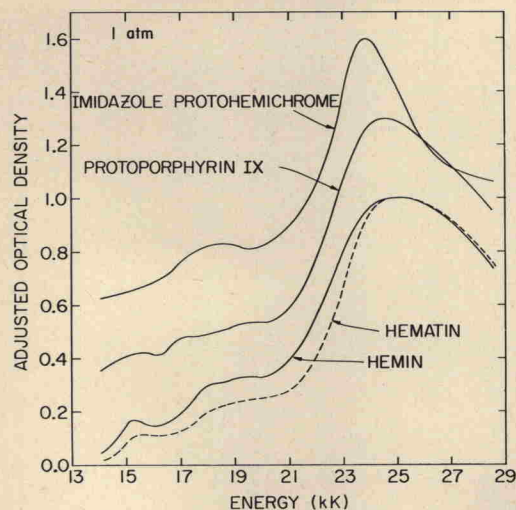


FIG. 1. One atm optical spectra of protoporphyrin IX and protohemes.

ber of hemiporphyrins and related compounds, using optical absorption and Mössbauer resonance. The high pressure optical and Mössbauer techniques have been described elsewhere.³⁻⁵ The compounds studied include imidazole protohemichrome, hemin, and hematin. In the last section we discuss monochlorobis (*N,N*-diethyldithiocarbamate) Fe(III) [Fe(DTC)₂Cl], and monohydroxybis(salicyl) Fe(III) [Fe(SAL)₂OH]. These compounds have local symmetries like hemin and hematin but with sulfur and oxygen replacing the nitrogen. All materials were synthesized from iron enriched to 90% in ⁵⁷Fe. For the porphyrin derivatives the starting material, unenriched hemin (equine, crystalline, Type III), was obtained from the Sigma Chemical Company. Protoporphyrin was prepared by the method of Ramsey.⁶ Enriched hemin was made by the technique described by Moss⁷ and was purified by multiple recrystallization. Hematin was made from enriched hemin by the technique of Fischer.⁸ The imidazole protohemichrome was synthesized by the method of Corwin *et al.*⁹ The Fe(DTC)₂Cl was synthesized by the method of Wickman *et al.*¹⁰ and the Fe(SAL)₂OH by the technique of Hantsch *et al.*¹¹

OPTICAL DATA

The intense absorption of porphyrins and metalloporphyrins in the visible region is due to the $\pi-\pi^*$ transitions. In porphyrins the low energy absorption is split into four bands because of a modest departure from d_{4h} symmetry. The four bands range from about 15 to 20 kK and are of moderate intensity. At about 25 kK there is an intense absorption (10-20 times as strong as the low energy bands) called the Soret peak. Various peripheral substituents have marked effects on the absorption spectra of porphyrins, particularly the low energy absorption. Falk² discusses these spectral

differences. Protoporphyrin IX has an aetio-type spectrum, which is characterized by increasing intensity of the four visible bands with increasing energy. The absorption spectrum of protoporphyrin IX at 1 atm in the solid state, is shown in Fig. 1. There are bands at approximately 15, 17.2, 18.5, and 19.5 kK. The spectra in Fig. 1 were obtained by mixing the sample and NaCl in a mortar and fusing the mixture at 20 kbar into a clear pellet.

The Soret peak in protoporphyrin IX is at about 24.6 kK. The effect of pressure on the absorption of protoporphyrin IX is shown in Fig. 2. At each pressure the spectrum was normalized at the maximum absorption of the Soret peak. The maximum absorption of the Soret peak shifts to lower energy by about 0.9 kK in the pressure range 20-140 kbar. Over the same pressure range, at 80% of the maximum absorption, the shift is about 1.5 kK. The low energy peaks appear to shift to lower energy and fade relative to the Soret peak. Because of the large intensity difference between the Soret peak and the visible bands, and the close proximity of the two sets of peaks, the relative decrease in intensity and shift to lower energy of the low energy bands were impossible to measure. The Soret peak essentially swamped the visible peaks at high pressure. With the optical pressure apparatus used, it is usually very difficult to obtain changes in the absolute intensity of peaks. However, because of the position and intensity of the Soret peak, an estimate of the intensity change with pressure was possible. Thus, in the pressure range 20-140 kbar, the intensity of the Soret peak in protoporphyrin IX decreased by about a factor of 15.

The iron compounds studied were the low spin imidazole protohemichrome, and the high spin ferric compounds, hemin and hematin. The atmospheric spectrum of imidazole protohemichrome is shown in Fig. 1. The sharp Soret peak is at 23.8 kK, and the low energy bands are at 17.6 and 18.5 kK. In the metalloporphyrins the visible absorption is split into two vibrational bands, labeled with increasing energy the α

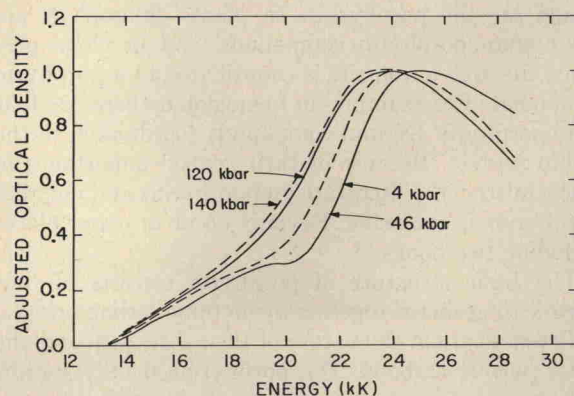


FIG. 2. Optical absorption spectra of protoporphyrin IX vs pressure.