pendicular to the molecular planes, one molecule is rotated about the normal to the NLS plane by approximately 45° with respect to the molecule below. This rotation in the stacking arrangement probably results in more space for the side chains; a similar but larger rotation (~90°) was found in the packing of TPP.[2] The stacking is efficient producing a short NB-CP51 intermolecular distance of 3.36 Å, which apparently causes the small tilt observed with pyrrole ring B. The intermolecular distance between NB and CA2 is also short (3.43 Å) and could effect contributions to the tilts of both pyrrole rings. The propyl side chains are in an extended configuration filling the space between the molecules related by the glide plane. One propyl group is rotated about the C_m–CP1 bond producing a short intramolecular contact (3.48 Å) to the adjacent β carbon atom of the pyrrole. This configuration probably arises from a close contact between the methyl carbon atoms, CP63–CP53, in the molecules as they are stacked along *b* (separation of 3.71 Å, which is short in comparison to the sum of the van der Waals radii for two methyl groups, which is about 4.0 Å). The methyl group on the twisted propyl side chain is also fairly close to the β pyrrole carbon of the adjacent molecule along *c* (3.87 Å).

The average distance for the C–H bonds is 1.05 ± 0.08 Å; the imino N–H bond length is significantly shorter (0.78 Å). Similar shorter distances for the N–H lengths were observed with TPP (0.96 Å) and porphine (0.86 Å). In contrast to the other structures, the imino hydrogen atom in the TPrP structure is within ±0.01 Å of the NLS plane and the two ∠CNH angles are essentially the same. However, the shorter N–H bond contributes to give the longest free base H–H distance across the center of the ring: 2.60 Å in TPrP, 2.41 Å in porphine, and 2.36 Å in TPP.

Finally, the relatively short average distance of the CN–CP1 bond (1.522 Å) is probably due to the influence of the sp^2 hybrid bridge carbon atom. However, the second and third atoms of the side chains also show distances shorter than expected. Since it is unlikely that the aromatic character of the macrocycle can affect atoms this remote, the shortening might or might not be real. These atoms have appreciable thermal motion, fairly small peak heights, and the largest expected errors.

Acknowledgment. We would like to take the opportunity here to gratefully acknowledge the support of this work by the National Science Foundation, Molecular Biology Section (Grants GB-5686, GB-7399, and GB-15402).

Mössbauer Studies on Hemin Derivatives of α,β,γ,δ-Tetraphenylporphine

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Received May 21, 1971

Abstract: The Mössbauer spectra of α,β,γ,δ-tetraphenylporphinatoiron(III) chloride, bromide, iodide, and thiocyanate have been measured at room temperature, 78 and 4.2–6°K. The spectra show a broad asymmetric peak at higher temperatures, which becomes a resolved doublet at 4.2°K. The quadrupole splitting increases in the order chloride < thiocyanate < bromide < iodide.

The hemins are a group of 5-coordinated iron(III) complexes containing a porphyrin dianion and a monodentate anion such as a halide. Hemin itself is (protoporphyrin IX)iron(III) chloride, protoporphyrin IX being the porphyrin occurring in hemoglobin. The hemins have been the subject of numerous Mössbauer studies.[2–9] Data on isomer shifts and quadrupole splittings obtained much above about 20°K are quite imprecise because of the unusual broadness and poor peak resolution on the spectra.

We have measured the Mössbauer spectra at 4.2–6°K of [TPPFeCl], [TPPFeBr], [TPPFeI], and [TPPFeSCN], where TPP indicates the α,β,γ,δ-tetraphenylporphine dianion. These derivatives were selected in order to determine the effect of the fifth ligand upon isomer shift and quadrupole splitting. In a following paper we will report Mössbauer studies on several α,β,γ,δ-tetrakis(substituted phenyl)porphinatoiron(III) complexes.[10]

Experimental Section

The complexes [TPPFeCl], [TPPFeBr], [TPPFeI], and [TPPFeNCS] were prepared as previously described[11] using 90% ^{57}Fe. Samples for the Mössbauer spectrometer were prepared by powder-

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Table I. Mössbauer Spectral Data[a] for [TPPFeX]

Compound	Temp, °K	δ	Δ	Γ^b(left)	Γ^b(right)	R^c	% effect[d]
[TPPFeCl]	4.2	0.68	0.46	0.29	0.42		12
[TPPFeNCS]	6	0.66	0.49	0.32	0.32	0.51	11
[TPPFeBr]	6	0.72	0.72	0.23	0.23	0.86	13
[TPPFeI]	6	0.72	0.75	0.21	0.21	0.97	0.9
	78	0.69	0.70	0.54	0.70	1.33	0.8

[a] Values in mm/sec, relative to sodium nitroprusside. [b] Full width at half-maximum. [c] Intensity of left peak over intensity of right peak. [d] % effect = $(N_\infty - N_p)/N_\infty \times 100$, where N_∞ is the number of γ-ray counts at large velocities (nonresonant condition) and N_p is the number of counts at the velocity corresponding to the peak of absorption. No corrections were made for saturation, or for background counts.

ing about 15 mg of [TPPFeX] with 30–40 mg of boron nitride and sealing between milled plexiglass windows with epoxy cement.

A Superior Air Products Research dewar was used to maintain the samples at 6°K using liquid helium as the refrigerant. The spectrum of [TPPFeCl] was measured at 4.2°K using a Janis liquid helium dewar. A precalibrated carbon resistor was used as the temperature sensor. Spectra were also measured at 298 and 78°K.

All Mössbauer spectra were recorded using a 400 channel analyzer operating in the time mode with a constant acceleration drive. A sodium nitroprusside absorber was used to calibrate the velocity scale and provide the zero reference for the isomer shifts (nitroprusside splitting, 1.705 mm/sec). The data were fit with a least-squares approximation assuming Lorentzian line shapes and plotted with a Calcomp plotter. The computer program was originally written by P. A. Flinn of Carnegie-Mellon University and modified by G. Von Nieda of this laboratory.

Results

The Mössbauer spectra of [TPPFeCl], [TPPFeBr], [TPPFeI], and [TPPFeNCS] at 78 and 4.2–6°K are shown in Figures 1 and 2. The bold dots are experimental data and the smooth line represents the best computer fit assuming a doublet with equal peak widths. The spectral parameters for these compounds are given in Table I; the estimated uncertainty in the isomer shift and quadrupole splitting values is ±0.04 mm/sec.

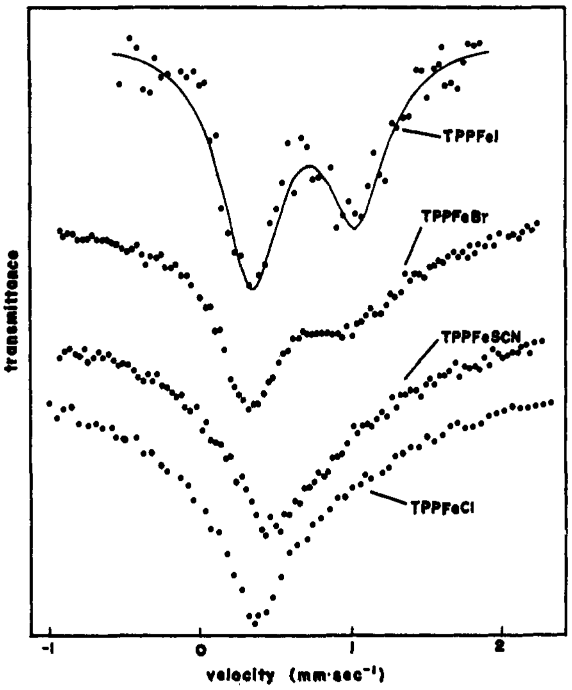

Figure 1. Mössbauer spectra of [TPPFeI], [TPPFeBr], [TPPFeNCS], and [TPPFeCl] at 78°K.

At 78°K the chloride and thiocyanate spectra show a broad asymmetric peak with an unresolved shoulder on the high energy side; the bromide spectrum shows somewhat better resolution and the iodide spectrum shows the best resolution, but with only a very small effect due to nonresonant absorption by the iodine. The broadness and asymmetry of the peaks preclude reasonable Lorentzian fitting and good values of the isomer shift and quadrupole splitting cannot be obtained, except perhaps for the iodide, at 78°K.

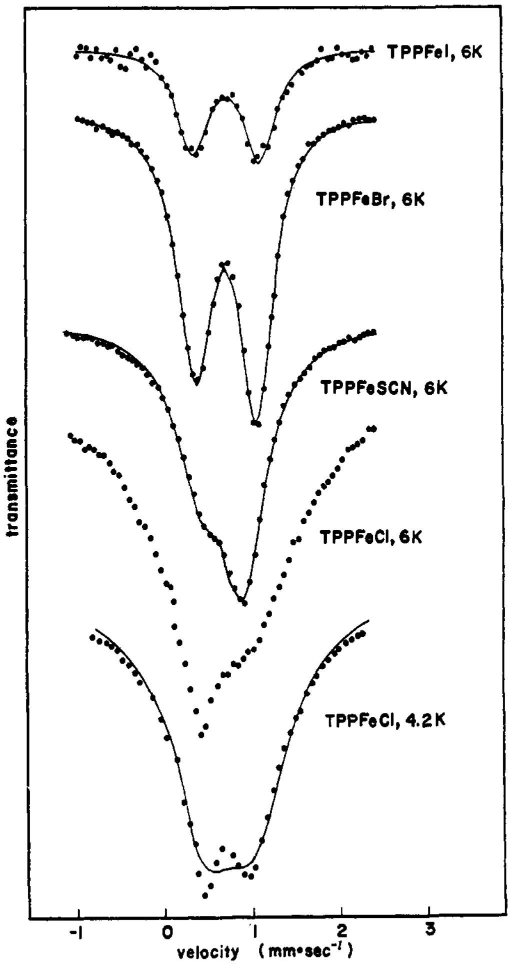

Figure 2. Mössbauer spectra of [TPPFeI], [TPPFeBr], [TPPFeNCS], and [TPPFeCl] at 6 and 4.2°K.

At 6°K the spectra of the bromide, thiocyanate, and iodide show good resolution, judging from the widths of the lines and the quality of the fit. The spectrum of the chloride at 6°K is, however, still not resolved and is only poorly resolved at 4.2°K. The values given in Table I for [TPPFeCl] were obtained by inspection and not from a computer fit spectrum.

Discussion

A thermomagnetic investigation has shown that hemin, [TPPFeCl], [TPPFeBr], [TPPFeI], and [TPPFeNCS] contain the ferric ion in a ${}^6S_{5/2}$ ground state.[11] In an axial field the sixfold spin degeneracy is partially lifted: the Kramer's doublets $M_s = \pm {}^1/_2, \pm {}^3/_2, \pm {}^5/_2$ occur at 0, $2D$, and $6D$, respectively, where D is the zero field splitting parameter. Richards, *et al.*,[12] using infrared radiation have shown D to be 7 cm^{-1} for hemin. Rhombic distortion is small.[13]

Harris has carried out extensive crystal field calculations on the iron porphyrins.[14–17] Some of her conclusions are (1) the splitting of the ${}^6A_1$ ground state is due to differences in the spin–orbit interaction of the three sextet components with the ${}^4E$ and ${}^4A_2$ components arising from the ${}^4T_1$ state in a tetragonal field; (2) the splitting increases with Dq because such an increase brings the quartet state components closer to the sextet; (3) for a given value of Dq, the splitting depends primarily on the separation of the ${}^4E$ and ${}^4A_2$ states; (4) for the ${}^4E$ state lower in energy than the ${}^4A_2$ (negative tetragonal splitting, indicating a stronger axial than in-plane crystal field interaction) the order of the sextet components is $\pm {}^3/_2, < \pm {}^1/_2 < \pm {}^5/_2$; for the ${}^4A_2$ state lower, the order is $\pm {}^1/_2 < \pm {}^3/_2 < \pm {}^5/_2$; (5) in the series [porphyrin–FeX] with X = CH_3O^-, F^-, N_3^-, Cl^-, Br^-, I^-, the coefficients of the ${}^6A_1 \pm {}^1/_2$ component of the ground state decrease from 0.996 to 0.9606, indicating some increase in spin mixing, which, however is still very small; (6) in this same series D and Dq increase, and the tetragonal splitting decreases, in going from CH_3O^- to I^-; and, finally, (7) the lattice contribution completely dominates the valence contribution to the electric field gradient, as is expected for an S-state ion.

An explanation of the asymmetry and temperature dependence of the Mössbauer spectra of hemin has been given by Blume.[18] Equal populations of the spin substates at room temperature, each giving a different Mössbauer spectrum, together with magnetic broadening due to the slowly relaxing $\pm {}^3/_2$ and $\pm {}^5/_2$ substates can cause the observed spectra. However, at liquid helium temperature only the $\pm {}^1/_2$ ground state is appreciably populated. Relaxation between the $+{}^1/_2$ and $-{}^1/_2$ levels (there is slight splitting due to small magnetic dipoles in the crystal lattice) is so rapid compared to the Mössbauer lifetime ($\sim 10^{-7}$ sec) of ${}^{57}Fe^*$ that there is no magnetic broadening and a symmetric, sharp Mössbauer doublet results.

The Mössbauer data for the [TPPFeX] complexes allows them to be arranged according to increasing values of D (although absolute values of D are not easily obtained from such data) because the temperature range during which the asymmetric peaks are narrowing and becoming symmetric depends upon D, being higher for larger D. This range also is higher for larger quadrupole splitting because D in theory increases with increase in quadrupole splitting in these compounds. At 6°K the peaks of [TPPFeCl] and [TPPFeNCS] are not well separated; the chloride shows magnetic broadening while the thiocyanate does not. This indicates that the chloride has the lowest value of D. The quadrupole splitting of [TPPFeBr] is less than that of [TPPFeI]. Thus, D for [TPPFeBr] is less than D for [TPPFeI]. The probable ordering of D values is [TPPFeCl] < [TPPFeNCS] < [TPPFeBr] < [TPPFeI]. This is the same relative ordering obtained for (deuteroporphyrin IX dimethyl ester)iron(III) chloride (D = 8.9 cm^{-1}) and bromide (D = 11.8 cm^{-1}) from far infrared data.[12]

In all the spectra taken at 298 and 78°K, the less intense, broadened peak lies on the higher energy side and corresponds to the $\pm {}^1/_2 \rightarrow \pm {}^3/_2$ nuclear transition if the magnetic axis is parallel to the crystal field axis. The electric field gradient (V_{zz}) is thus positive. V_{zz} has been shown to be positive in several hemins[8] and myoglobin fluoride.[19] At 6°K, a remarkable reversal of the asymmetry takes place in the thiocyanate derivative: now it is the lower energy (left) peak which is the less intense. The shortening of the left peak in the bromide derivative is also evident, but there is no magnetic broadening apparent. Whether this behavior is unique for the bromide and thiocyanate is not known: it may be that at lower temperatures (*i.e.*, than 4.2 or 6°K) the chloride and iodide will also give similar results.[20]

A change in sign of the electric field gradient (V_{zz}) from positive to negative at 4.2°K could explain the asymmetry reversal; now the $\pm {}^1/_2 \rightarrow \pm {}^3/_2$ transition is the lower energy one. A negative gradient for a hemin at any temperature is extremely unlikely from Harris' theoretical studies. Also a negative gradient places the $\pm {}^3/_2$ level lowest (negative D), which is incorrect according to far infrared studies. A more reasonable possibility is that the magnetic field axis and the field gradient axis are now perpendicular to one another. Under this condition, and with positive V_{zz}, the $\pm {}^1/_2 \rightarrow \pm {}^3/_2$ transition is of lower energy.

The isomer shifts are in the range expected for high spin iron(III) compounds. The bromide and iodide have slightly higher values than the thiocyanate, indicating greater halide to iron π bonding. The thiocyanate is probably coordinated through the nitrogen; if it were coordinated through the sulfur, a larger isomer shift would be expected.

Acknowledgments. We wish to thank Professor F. deS. Barros and Dr. J. Viccaro, Department of Physics, Carnegie-Mellon University, for use of equipment and helpful discussions. This work was supported by the Division of Biology and Medicine, Atomic Energy Commission, through contract AT(30-1) 3859.

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(20) Subsequent work[10] has turned up many more examples and suggests that the phenomenon is general.