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Mössbauer Spectra of Iron Tetraphenylporphins

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Mössbauer spectra were measured for a series of the central iron in Fe(II)- and Fe(III) complexes of tetraphenylporphin. The electronic structure of the central iron in the complex was modified by the axial ligand field. The Mössbauer spectra assigned the most probable electronic configurations to various iron states in the iron porphins.

Mössbauer spectroscopy provides valuable information on the electronic structure of iron complexes, complementary to those from the measurements of magnetic susceptibility and from paramagnetic resonance spectroscopy. Recently this technique has been applied to the study of some biologically important substances containing iron atom. Mössbauer effect has been observed with heme proteins such as hemoglobin, myoglobin, cytochromes, catalase, peroxidase and others.[1,2] However, a systematic investigation of the Mössbauer spectra has never been carried out with synthetic iron porphyrin complexes other than those obtained from the naturally occurring heme proteins.[3] Some studies have been performed on the adducts of nitrogeneous ligands and synthetic iron porphyrins.[4,5] Another study on the iron phthalocyanines has also been published.[6] Recently a series of the Fe(II)- and Fe(III) complexes of tetraphenylporphin (TPP) have been synthesized in our laboratory.[7] We present Mössbauer spectra observed for a series of the central iron in the tetraphenylporphin complexes.

Experimental

The Mössbauer spectra were obtained with a scanned velocity spectrometer operating in the time mode. The instrument consisting of an electromagnetic velocity transducer, a gamma-ray counting system and a Dewar has been described.[2] The radiation source was ^{57}Co diffused into metallic Pd. The absorber could be maintained at room temperature, dry ice acetone temperature (195°K) or liquid nitrogen temperature (77°K).

Since our radiation source was strong enough, it was not necessary to enrich ^{57}Fe for the measurements of Mössbauer spectra of our synthetic iron porphins. The measurements were carried out with the powder samples of TPPFe(III)Cl ($S=5/2$), TPPFe(III)OCH$_3$ ($S=1/2$), TPPFe(II) ($S=2$), TPPFe(II)·2THF ($S=1$) and TPPFe(II)·2Py ($S=0$), where THF denotes tetrahydrofuran and Py, pyridine. All samples had been synthesized in our laboratory and identified by elementary analysis. Their spin states determined by magnetic susceptibility measurements are given above in the brackets. The Fe(III) complexes were fairly stable even in the atmospheric circumstance, while the Fe(II) complexes were very sensitive to oxygen and moisture in the air. In a dried nitrogen atmosphere, the Fe(II) porphin was homogeneously packed and sealed in a planar capsule made of polyacrylic resin.

The velocity scale was calibrated absolutely from an independent Mössbauer run using a thin metallic iron absorber and the center of symmetry of the spectrum was taken as zero velocity. The velocity was determined to an accuracy of ±0.06 mm/sec for the Fe(III) complexes, and ±0.04 mm/sec for the Fe(II) complexes.

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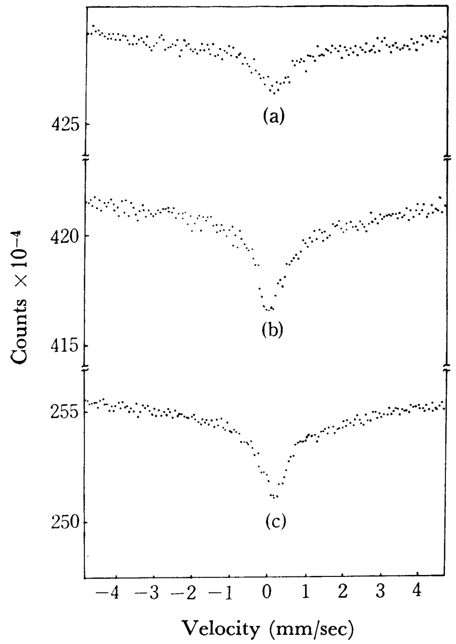

Fig. 1. Mössbauer spectrum of tetraphenylporphin iron(III) chloride.
(a) room temperature (b) 195°K and (c) 77°K

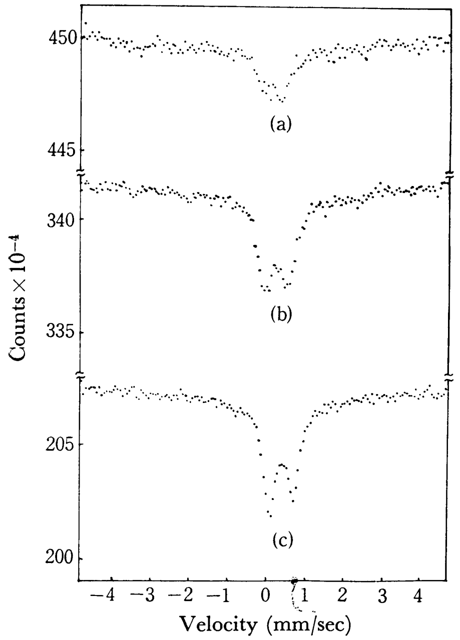

Fig. 2. Mössbauer spectrum of tetraphenylporphin iron(III) methoxide.
(a) room temperature (b) 195°K and (c) 77°K

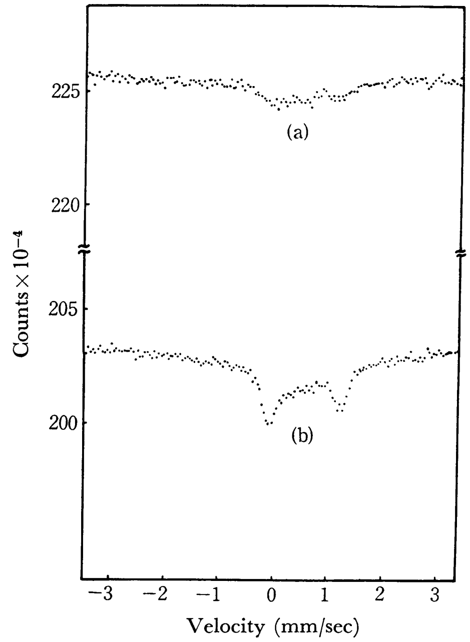

Fig. 3. Mössbauer spectrum of tetraphenylporphin iron(II).
(a) room temperature and (b) 77°K

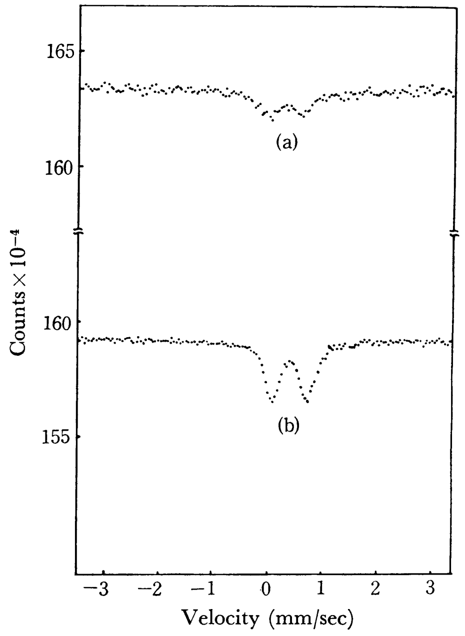

Fig. 4. Mössbauer spectrum of bis-tetrahydrofuran tetraphenylporphin iron(II).
(a) room temperature and (b) 77°K

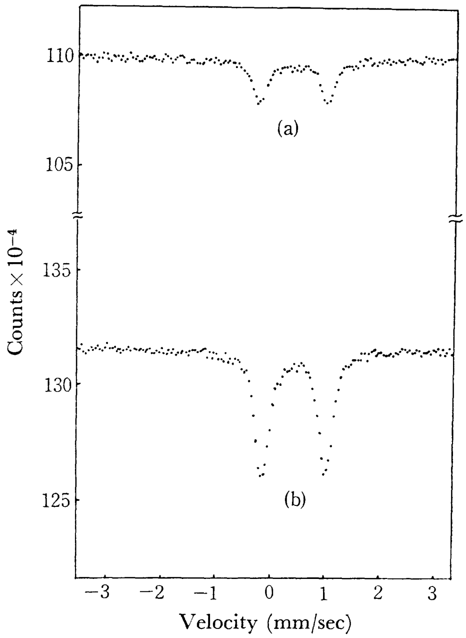

Fig. 5. Mössbauer spectrum of bis-pyridine tetraphenylporphin iron (II).
(a) room temperature and (b) 77°K.

Table 1. Experimental isomer shift and quadrupole splitting

Material	Temperature (°K)	Quadrupole splitting (mm/sec)	Isomer shift (mm/sec)
TPPFe(III)Cl	300	0	0.08
(S=5/2)	195	0	0.00
	77	0	0.14
TPPFe(III)OCH$_3$	300	0.44	0.14
(S=1/2)	195	0.54	0.25
	77	0.62	0.40
TPPFe(II)	300	—	—
(S=2)	77	1.32	0.52
TPPFe(II)·2THF	300	0.57	0.26
(S=1)	77	0.64	0.33
TPPFe(II)·2Py	300	1.22	0.36
(S=0)	77	1.15	0.41

Results and Discussion

The observed spectra are shown in Figs. 1—5. The isomer shift, δ, and the quadrupole splitting, ΔE_Q, obtained from the spectra are summarized in Table 1.

(1) Isomer Shift. The isomer shift arises from the electrostatic shift of nuclear levels by an interaction between the charge distribution at the nucleus of definite dimension and the electronic charge distribution surrounding the nucleus.[8,9] The isomer shift is decreased when the s electron density at the nucleus is increased or the s orbitals are contracted, which depends upon the number of non-bonding d electrons and the charge distributions of σ-and π coordination bonds.

For ionic complexes, ferrous ion $(3d)^6$ usually shows a larger shift than ferric ion $(3d)^5$. For covalent complexes, strong σ donation by the ligands gives rise to two competitive effects to the isomer shift. The σ donation enhances the charge density in $4s$ orbital and also in $3d$ orbitals and $4p$ orbitals. An increase in the charge density in $4s$ orbital decreases the isomer shift, whereas an increase in the charge densities in $3d$ and $4p$ orbitals gives rise to an expansion of inner s orbitals and therefore an increase in the isomer shift. Another factor to be considered is an effect due to the π electron delocalization between $d\pi$ orbitals and the π molecular orbitals of the ligand.

TPPFe(III)Cl (S=5/2) shows the lowest isomer shift. In the ferric porphins, the central iron behaves like a σ and π acceptor. Since the low spin iron in TPPFe(III)OCH$_3$ (S=1/2) is a much stronger electron acceptor than the iron in TPPFe(III)Cl, the increase of isomer shift observed for TPPFe(III)OCH$_3$ can be explained by a predominant contribution from the expansion of the inner s orbitals due to an enhancement of shielding by the donated electrons. For an adduct of TPPFe(III)Cl and imidazole, of which an effective moment of S=1/2 has been observed, the value of isomer shift is still very close to that of the high spin iron in TPPFe(III)Cl.[4] Similar phenomena have been observed for the Fe(III) hemoglobins in the low spin state and in the highest spin state.[1e] In these cases, both the two competitive effects seem to be of equivalent importance.

In the case of ferrous porphin, the central iron behaves like a σ acceptor but a π donor. The iron with intermediate spin shows the lowest isomer shift. The iron has relatively higher π donating power. If there exists a significant migration of $d\pi$ electron to the ligands, a decrease in the isomer is expected. However, the iron is coordinated by relatively weak axial ligands with no electron acceptable π molecular orbital. Some migration of the $d\pi$ electron into the porphin ring is possible. The low value of isomer shift may arise from a higher population in $4s$ orbital due to the σ donations by the axial ligands and by the porphin. The iron in the highest spin state (S=2) shows the highest value of isomer shift. The iron has no axial ligand. Since it is less σ-acceptable and less π-donating, its high value of

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[8] See for example, A. Abragam, "L'Effet Mössbauer," Gordon and Breach Science Publishers, New York (1964).

[9] G. K. Wertheim, "Mössbauer Effect," Academic Press, New York (1964).

isomer shift may readily be expected.

The diamagnetic iron(II) porphin shows an intermediate value of isomer shift. The iron is a strong σ acceptor and π-donor. Although the strong σ donation by the axial ligands and the porphin should appreciably affect the isomer shift, the migration of $d\pi$ electron seems to take an important part in this particular case. The isomer shift, however, shows almost the same values for an adduct of TPPFe(II) and pyridine and that of piperidine.[4] Pyridine has electron acceptable π molecular orbitals, whereas piperidine lacks such orbitals. Therefore the $d\pi$ electron migration to the axial ligands does not seem to be of crucial importance for the isomer shift.

(2) Quadrupole Splitting. The second nonzero term of the electrostatic interaction of a nucleus with its surrounding electrons is the electric quadrupole interaction. For the nucleus ^{57}Fe, the nuclear spins of the ground state and the excited state are 1/2 and 3/2, respectively, and the Mössbauer spectrum shows two resonance peaks. The separation between these peaks, ΔE_Q, is given by

$$\Delta E_Q = (e^2Q/2)q(1 + \tfrac{1}{3}\eta^2)^{1/2} = (e^2Q/2)X \qquad (1)$$

where Q is the quadrupole moment of the nucleus; $eq = V_{zz}$, $\eta = (V_{xx} - V_{yy})/V_{zz}$ and V_{xx}, V_{yy} and V_{zz} are the principal components of an electric-field gradient due to the electronic distribution.[8,9] For metalloporphyrin, as has been done by Weissbluth and Maling,[10] q and $(q\eta)$ are given by

$$\begin{aligned} q &= (1-R)_d q_d + (1-R)_p q_p + (1-\gamma_\infty) q_l, \\ (q\eta) &= (1-R)_d (q\eta)_d + (1-R)_p (q\eta)_p + (1-\gamma_\infty)(q\eta)_l, \end{aligned} \qquad (2)$$

in which q_d and q_p are contributions to q from the electrons occupying $3d$ and $4p$ orbitals, respectively; $(q\eta)_p$ and $(q\eta)_p$ have analogous definitions; q_l and $(q\eta)_l$ are contributions from the ligands and $(1-R)$ and $(1-\gamma_\infty)$ are Sternheimer factors.

Weissbluth and Maling have estimated the contributions to q and $(q\eta)$ from $3d$ and $4p$ orbitals and also from the ligand orbitals based on the molecular orbital calculations by Zerner, Gouterman and Kobayashi.[11] According to their estimation, the quadurpole splitting in hemoglobins predominantly arises from a charge distribution of the electrons occupying $3d$ orbitals. Therefore q and $(q\eta)$ are approximately given in terms of the contributions from the electrons occupying the molecular orbitals with equal symmetry of $3d$ orbitals.

$$\begin{aligned} q &= \sum\langle V_{zz}/e\rangle = \langle 1/r^3\rangle \sum_i A_i f_i \\ (q\eta) &= \sum\langle (V_{xx} - V_{yy})/e\rangle = \langle 1/r^3\rangle \sum_i B_i f_i \\ A_i &= -\langle 3\cos^2\theta - 1\rangle_i \\ B_i &= -\langle 3\sin^2\theta \cos 2\varphi\rangle_i \end{aligned} \qquad (3)$$

where f_i is orbital occupation number; A_i and B_i are readily calculated from the angular part of d orbital[12] and $\langle 1/r^3\rangle$ is also calculated from the radial part of d orbital, however, it can be regarded as a parameter for the intercomparison. As has been shown for the spin-orbit coupling constant in the complexes, the value of the integral $\langle 1/r^3\rangle$ should be adjusted for the molecular orbital formation.[13]

For the ferrous low spin state $(xy)^2(yz)^2(zx)^2$ and the ferric high spin state $(xy)(yz)(zx)(z^2)(x^2-y^2)$, the electronic charge distributions are approximately of spherical symmetry and therefore there are no electric field gradients. However, other electronic configurations should show electric field gradients. The values of X in (1) which actually determine the magnitude of quadrupole splittings

Table 2. The calculation of d electron contribution to ΔE_Q

			Fe(III)d^5			Fe(II)d^6					
			TPPFeCl $S=5/2$	TPPFeOCH$_3$ $S=1/2$		TPPFe $S=2$	TPPFe·2THF $S=1$		TPPFe·2Py $S=0$		
Isomer shift at 77°K			0.14	0.40		0.52	0.33		0.41		
Quadrupole splitting at 77°K			0	0.62		1.32	0.64		1.15		
	A	B									
x^2-y^2	4/7	0	1	0	0	1	0	0	0	0	0
z^2	−4/7	0	1	0	0	1	1	1	0	0	0
yz	−2/7	6/7	1	3/2	1	1	3/2	1	2	1	1
zx	−2/7	−6/7	1	3/2	2	1	3/2	2	2	1	2
xy	4/7	0	1	2	2	2	2	2	2	2	2
$\sum_i f_i A_i$			0	2/7	2/7	4/7	−2/7	−2/7	0	4/7	2/7
$\sum_i f_i B_i$			0	0	−6/7	0	0	−6/7	0	0	−6/7
$X=[(\sum_i f_i A_i)^2+1/3(\sum_i f_i B_i)^2]^{1/2}$			$\underline{0}$	$\underline{2/7}$	4/7	$\underline{4/7}$	$\underline{2/7}$	4/7	0	$\underline{4/7}$	$\underline{4/7}$

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[10] M. Weissbluth and J. E. Maling, *J. Chem. Phys.*, **47**, 4166 (1967).

[11] M. Zerner, M. Gouterman and H. Kobayashi, *Theoret. Chim. Acta*, **6**, 363 (1966).

[12] M. Weissbluth, "Structure and Bonding," Vol. 2, Springer-Verlag, Berlin (1967), p. 1.

[13] A. A. Misetich and R. E. Watson, *Phys. Rev.*, **143**, 335 (1966).

are obtained for the most probable configurations in the iron porphyrins with various spin states. The results are summarized in Table 2. For the ferric low spin state and also the ferrous intermediate spin state, two alternative configurations are possible. If an anisotropy is introduced in the porphin plane by a Jahn-Teller distortion of bi-axial ligand fields, the anisotropic contribution of B term is expected. However, as Table 2 shows, the ratios between the observed quadrupole splittings and the values of X obtained from the isotropic contributions (underlined in Table 2) are fairly constant except for the diamagnetic ferrous porphin.

In TPPFe(II)·2THF, the iron is in the intermediate spin state. As was shown by electronic absorption spectroscopy,[7] the observed intermediate spin value is not ascribed to a mixture of the state $S=2$ and the state $S=0$ but a single state $S=1$. Mössbauer spectrum also shows a spectrum characteristic of the intermediate spin iron(II) complex, which is quite different from a spectrum expected for a mixture of the high spin porphin $S=2$ and the diamagnetic one $S=0$.

The diamagnetic ferrous complex, TPPFe(II)·2Py shows a relatively higher quadrupole splitting despite its closed shell structure. Similar values have been found for carboxyhemoglobin, oxyhemoglobin[1e] and nitrogeneous base adducts of iron-porphyrins and[3e,4,5] phthalocyanine, all of which are diamagnetic. The delocalization of $d\pi$ electron to the porphin ring and also to the axial ligands produces some vacancy in the $d\pi$ orbital of the central iron. If a hole is produced in each of the degenerate yz and zx orbitals or a hole is produced in either split yz or zx orbital, the value of X (underlined in Table 2) can explain the observed quadrupole splitting. There might be anisotropy due to the coplanarity of the axial two pyridines. If this is the case, the production of an effective hole in the $d\pi$ orbital is sufficient.

A linear relationship was found between the quadrupole splitting and the isomer shift in these particular iron porphins except for the low spin ferric and also diamagnetic ferrous porphin (Fig. 6). Because of higher $d\pi$ electron affinity of the former, some of π electron charge of porphin ring can migrate into the iron and annihilates the hole existing in yz and/or zx orbital, while in the diamagnetic ferrous one, the charge migration of $d\pi$ electron over whole complex becomes significant and produces some vacancy in the $d\pi$ orbital.

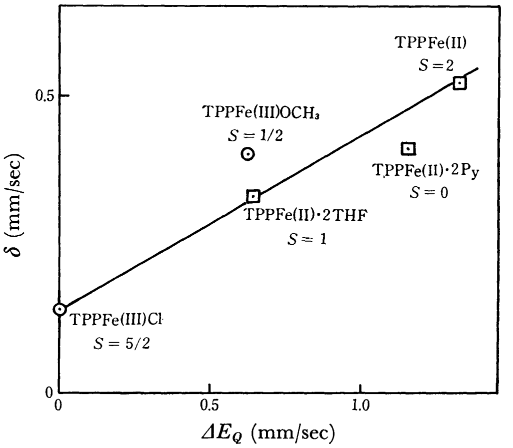

Fig. 6. The isomer shifts plotted *vs.* the quadrupole splittings.
The values were obtained at 77°K.

(3) Temperature Dependence. The existence of low-lying excited states is theoretically and experimentally identified. Temperature dependence of Mössbauer spectrum arises from a population of higher sublevels. Remarkable temperature dependence of the spectrum had been observed for the high spin ferric porphins,[1,3] while relatively small temperature dependence was observed for the isomer shift of TPPFe(III)Cl. Asymmetric spectrum observed for TPPFe(III)OCH$_3$ showed a temperature dependence, which was however, less remarkable than that observed for other iron porphins of naturally occurring source. In the case of TPPFe(II), no remarkable quadrupole splitting was observed at room temperature, the splitting being observed at 77°K. Between two intense bands, there seems to exist some bands which might be assigned to the lower sublevels, although a possible contamination of the impurity formed by partial oxidation can not be eliminated.

Generally speaking, an increase in the isomer shift seems to be parallel to an increase in the quadrupole splitting observed at low temperature. An increase in the isomer shift of TPPFe(II)·2Py is observed at low temperature, while the quadrupole splitting is decreased. Similar phenomena have been observed for the diamagnetic hemoglobins[1e] and bis(pyridine)phthalocyanine iron(II).[5]

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