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Magnetic and Infrared Properties of the Azide Complex of (2,7,12,17-Tetrapropylporphycenato)iron(III): A Novel Admixing Mechanism of the S = 5/2 and S = 3/2 States

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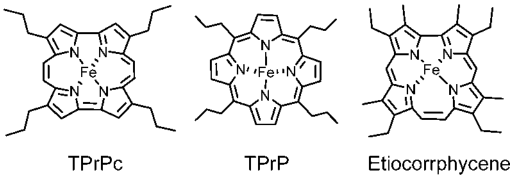
The five-coordinate ferric azide complex of 2,7,12,17-tetrapropylporphyrcene [Fe(TPrPc)N_3] was characterized with proton NMR, electron paramagnetic resonance (EPR), Mössbauer, and IR techniques. The paramagnetic NMR showed the pyrrole-H signal that exhibits anomalous *anti*-Curie type of 1/T-dependence over a 310–190 K range. The EPR of the solid sample resolved a signal with g = 5.42, 5.40, and 2.00 at 5 K. The quadrupole splitting parameter of the Mössbauer spectrum was 2.20 mm s^{-1} at 290 K, and the magnetic moment was 4.70 μ_B at 290 K for the microcrystalline sample. These results suggest that [Fe(TPrPc)N_3] is not pure high-spin (S = 5/2) but a spin mixture of the S = 5/2, 3/2 states. The azide in [Fe(TPrPc)N_3] exhibited split IR bands ascribed to the two spin isomers at 2066 and 2049 cm^{-1}. The 2049-cm^{-1} band, assigned to the S = 3/2 species, was reversibly intensified with decreasing temperature. The IR results demonstrate that the S = 3/2, 5/2 states are not quantum-mechanically admixed but in thermal equilibrium. The thermodynamic parameters associated with the spin equilibrium, ΔH = –3 990 cal mol^{-1} and ΔS = –16.5 cal mol^{-1} K^{-1}, were obtained from the NMR shift analysis, and the population of the S = 3/2 isomer was calculated to be 0.19 at 293 K. A minimum lifetime of the two spin isomers was estimated to be 0.3 ps with IR.

Introduction

Understanding of hemoprotein function is aided by the elucidation of the structure of the prosthetic group. There is a general consensus that heme is not always rigid but flexible and can deform easily. Nonplanar heme deformation in a crowded protein matrix is suggested to be functionally important.[1] Porphyrin molecular shape can be artificially changed with organic synthesis by rearranging the tetrapyrrole array.[2] A typical example is 2,7,12,17-tetrapropylporphycene (TPrPc; Scheme 1), discovered by Vogel et al. in 1987.[3] The macrocycle consists of a rectangular tetrapyrrole, in marked contrast with the square porphyrin. The modified tetrapyrrole extensively alters the physicochemical properties of parent porphyrin. TPrPc exhibits characteristic light absorption spectra[2,3] and redox properties.[4]



Scheme 1. Structure of the Fe^{III} complex of the porphyrinoids. The coordinating azide ion is omitted for clarity.

Among the exogenous heme ligands, azide ion (N_3^-) occupies a distinctive position to induce a thermal equilibrium between the high- (S = 5/2) and low-spin (S = 1/2) states in ferric hemoprotein.[5] The equilibrium was analyzed to monitor the heme–globin interactions.[6,7] The spin-state equilibrium of azide hemoprotein has been well reproduced with six-coordinate model hemes.[8–12] In contrast, the five-coordinate ferric heme [Fe(porphyrinato)N_3] is a typical high-spin complex.[10,11] The X-ray analysis for [Fe(TPP)-

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N_3] (TPP, *meso*-tetraphenylporphyrinato) provided structural rationale for the high-spin state in five-coordinate azide heme.[11]

The coordination core in porphycene is contracted.[2,3] Recent spectroscopic investigations suggest that the narrower metallo cavity in porphycene affects the magnetic properties of the central iron(III) atom. The five-coordinate ferric chloride complex of porphycene, for instance, exhibits some intermediate-spin (S = 3/2) character,[13,14] whereas the corresponding iron porphyrin is pure high-spin. In six-coordinate ferric porphycene with axial azide/imidazole, the high-spin population is lost, whereas the corresponding porphyrin is 15% high-spin.[6] The unique structure of the corrphycene molecule suggests that the azide complex of ferric iron porphycene [Fe(TPrPc)N_3] is likely to exhibit an unusual behavior. We found that [Fe(TPrPc)N_3] has magnetic properties, which are intermediate between the S = 5/2 and 3/2 states, in marked contrast with the pure S = 5/2 state of the corresponding iron porphyrins. Although the mixed-spin S = 5/2, 3/2 compounds have been extensively elucidated with various physical methods,[15,16] there has apparently been no IR spectroscopic report for this system. We demonstrate here that IR spectroscopy, when applied to [Fe(TPrPc)N_3], discloses a novel picture of the spin admixing.

Results

^{1}H NMR and EPR

We recorded the ^{1}H NMR of [Fe(TPrPc)N_3] to elucidate the magnetic anomaly inferred from the unique structure. Figure 1 shows the NMR spectrum recorded in CD_2Cl_2. The α-CH_2, β-CH_2, and γ-CH_3 signals of the *n*-propyl substituents were observed at 37.2, 33.6, 6.1, 6.0, and 3.6 ppm, respectively. The ethene-bridge proton was located at –11.6 ppm, and pyrrole-H was at δ = 19.1 ppm. The assignment is based on the peak intensity and iron–proton distance. The methylene doublets come from the magnetic anisotropy brought about by iron displacement from the porphycene plane (diastereotropic effect), and indicate the five-coordinate state.[17] The five-coordinate structure is supported from the pyrrole-H shift at δ = 19 ppm because the six-coordinate high-spin heme iron exhibits the pyrrole-H shift at about 65 ppm.[17] The $1/T$ dependence of these signals is irregular. The protons in the propyl groups and ethene bridges do not follow the Curie law to exhibit curved plots. The Curie plots of the pyrrole-H are especially anomalous. The signal shifted to –30 ppm at 200 K beyond the diamagnetic region (Figure 1, part B). The behavior of the pyrrole-H closely resembles that of [Fe(TPP)ClO_4][18] and [Fe(TPrPc)X] (X = Cl, Br, I),[13] which are in the mixed-spin S = 5/2, 3/2 state. The nonlinear Curie behaviors suggest that [Fe(TPrPc)N_3] is not pure high spin.

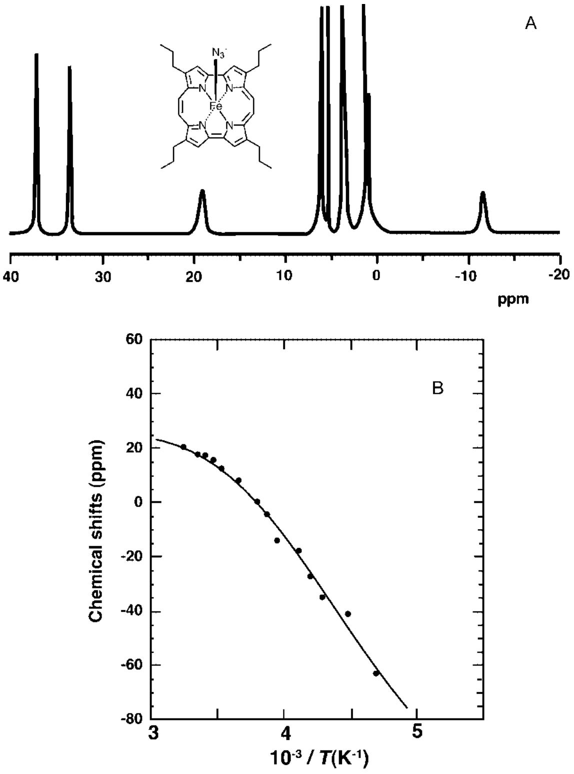

Figure 1. Proton NMR spectroscopy. (A) [Fe(TPrPc)N_3] in CD_2Cl_2 at 300 K. (B) The Curie plots for the pyrrole-H signal. The solid curve is theoretical fit calculated with the equation in the text.

Figure 2 displays the EPR spectrum of solid [Fe(TPrPc)N_3] at 5 K. The spectrum shows nearly axial-symmetric signals with g = 5.42, 5.40, and 2.00. These g-values were determined from the theoretical simulation. The split $g_\perp$ signals are consistent with the lower symmetry of the porphycene. The $g_\perp$ = 5.42 is between $g_\perp$ = 6 and 4 for the typical S = 5/2 and 3/2 species, respectively.[19,20] A similar spectrum with g = 5.82, 5.78, and 2.00 was obtained in toluene at 5 K (result not shown). Another notable EPR observation is the considerable temperature dependence. The EPR

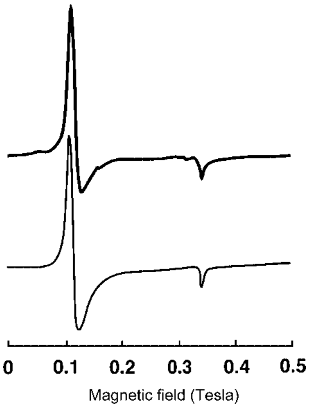

Figure 2. The EPR spectra of microcrystalline [Fe(TPrPc)N_3] at 5 K. The upper spectrum is the observed spectrum, and the lower is a simulation with g = 5.42, 5.40, and 2.00.

spectrum broadened out above 10 K and no signals were detected at 77 K. This is in contrast with ordinary ferric high-spin heme with well-defined EPR signals at liquid nitrogen temperature.[20]

Analysis of NMR Isotropic Shift

Unusual NMR behavior of the pyrrole-H signal (Figure 1) and the characteristic EPR (Figure 2) suggest a magnetic anomaly for [Fe(TPrPc)N_3]. The paramagnetic shift was analyzed on the basis of the two-spin model. The observed pyrrole-H shift δ consists of the diamagnetic and isotropic contributions.[17] A 9.6-ppm diamagnetic of the pyrrole-H shift was adopted from the metal-free TPrPc.[3] Then we obtain $\delta - 9.6 = a\delta_A + (1 - a)\delta_B$, where $\delta_A = A/T$ and $\delta_B = B/T$ are the isotropic shifts of the two paramagnetic components **A** and **B**. The constants A and B define, respectively, the slope of the straight lines in the Curie plots for **A** and **B**, and a and $(1 - a)$ represent fractions of the two components. It follows that the isotropic shift is $\delta - 9.6 = a(A/T) + (1 - a)(B/T)$ and that the equilibrium constant is $K = [\mathbf{A}]/[\mathbf{B}] = a/(1 - a) = [A - T(\delta - 9.6)]/[T(\delta - 9.6) - B]$. The van't Hoff equation, $\ln K = -\Delta H/RT + \Delta S/R$, is modified for the NMR analysis into the following form:

$$\ln\frac{A-T(\delta-9.6)}{T(\delta-9.6)-B}=-\frac{\Delta H}{R}\frac{1}{T}+\frac{\Delta S}{R}$$

The pyrrole-H shift δ was analyzed by fitting the temperature profiles for [Fe(TPrPc)N_3] (Figure 1, part B) to the van't Hoff formalism. For this end, the parameters A and B were varied at $\delta = 10$ ppm$\,K^{-1}$ intervals in a realistic (A, B) = (40000 to 5000, –1500 to –50000) region, and an (A, B) set that gives rise to the best linear plots was looked for. The computer program that was originally used for the analysis of the thermochromism[21] and isotropic shift[22] of azide hemoprotein was employed. The best linear plot, with a correlation coefficient 0.99579, was obtained at (A, B) = (7940, –22660), corresponding to $\Delta H = -3990$ cal mol^{-1} and $\Delta S = -16.5$ cal mol^{-1} K^{-1}. From these thermodynamic values, an equilibrium constant $K = [\mathbf{A}]/[\mathbf{B}] = 19{:}81$ at 295 K and the midpoint of transition $T_c = \Delta H/\Delta S = 242$ K were determined. The solid curve for the pyrrole-H shift in Figure 1 represents the theoretical fit calculated with these parameters.

Mössbauer

We examined the Mössbauer of [Fe(TPrPc)N_3] to ascertain further the anomalies inferred from the above NMR and EPR. The Mössbauer spectra of a powder sample are shown in Figure 3. The isomer shift δ_{Fe} is 0.19 mm s^{-1} and quadrupole splitting ΔE_q is 2.20 mm s^{-1} at 290 K. These values are temperature dependent, and gradually changed to $\delta_{Fe} = 0.26$ mm s^{-1} and $\Delta E_q = 2.68$ mm s^{-1} at 77 K.

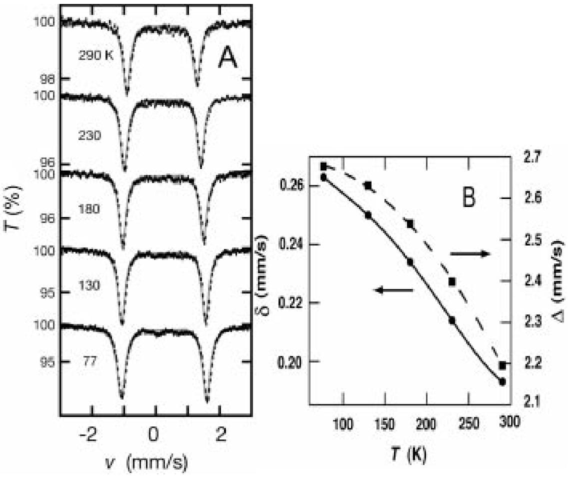

Figure 3. The solid-state Mössbauer spectra of [Fe(TPrPc)N_3]. (A) Observed spectra at the indicated temperatures. (B) Temperature dependence of quadrupole splitting ΔE_q and isomer shift δ_{Fe}.

Magnetic Susceptibility

The magnetic moment provides the direct and quantitative evaluation of the spin configuration of metal complexes. Figure 4 shows the magnetic susceptibility of microcrystalline [Fe(TPrPc)N_3] recorded over a 5–300 K range. The effective magnetic moment 4.80 μ_B at 290 K gradually fell down to 4.06 μ_B at 50 K. The values are intermediate between 5.92 and 3.87 μ_B, expected for the pure $S = 5/2$ and 3/2 states, respectively.[5]

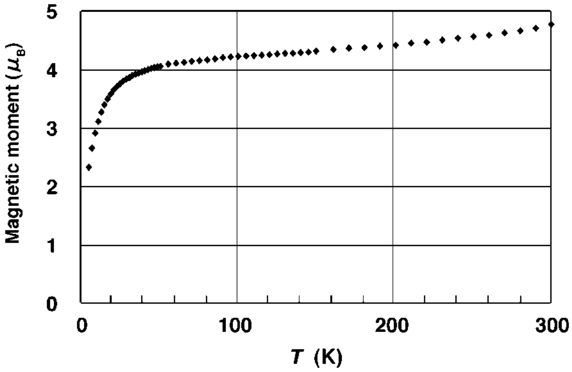

Figure 4. Temperature dependence of the effective magnetic moments of microcrystalline [Fe(TPrPc)N_3].

IR Spectra

Several iron-bound ligands of heme exhibit sufficiently intense vibrational bands. The antisymmetric IR stretching band of the azide is observed around 2030 cm^{-1}.[6–9] Figure 5 compares the IR spectra of the azide in [Fe(TPrP)N_3], [Fe(corrphycenato)N_3], and [Fe(TPrPc)N_3]. In the spectra of the former two compounds, single bands with a half-height width $\Delta\nu_{1/2} = 18$ cm^{-1} were observed at 2060 cm^{-1}. The spectral profile is in agreement with those observed for azide complexes of protohemin (2065 cm^{-1}, $\Delta\nu_{1/2}$ = 19 cm^{-1})[7,10] and another iron corrphycene (2058 cm^{-1},

$\Delta\nu_{1/2}$ = 16 cm^{-1}).[23] The single IR bands for [Fe(TPrP)N$_3$] and [Fe(corrphycenato)N$_3$] suggest their pure high-spin (S = 5/2) state. On the other hand, the azide band of porphycene [Fe(TPrPc)N$_3$] at 2062 cm^{-1} is not symmetric and somewhat broader, with a shoulder around 2040 cm^{-1} (Figure 5, part C). The curve analysis resolved two peaks at 2066 cm^{-1} ($\Delta\nu_{1/2}$ = 28 cm^{-1}) and 2049 cm^{-1} ($\Delta\nu_{1/2}$ = 18 cm^{-1}) with an integrated intensity ratio of I_{2049}/I_{2066} = 24/76. The IR spectrum was temperature-dependent, the 2049-cm^{-1} peak being notably intensified with an isosbestic point at 2055 cm^{-1} upon cooling (Figure 6). The transition was fully reversible. We recorded the IR spectrum in the solid state to examine the consistency with EPR and Mössbauer spectra. Figure 7 shows the IR spectrum of [Fe(TPrPc)N$_3$] in solid state. The bands were also identified at 2027 cm^{-1} ($\Delta\nu_{1/2}$ = 18 cm^{-1}) and 2012 cm^{-1} ($\Delta\nu_{1/2}$ = 15 cm^{-1}) with I_{2012}/I_{2027} = 26/74.

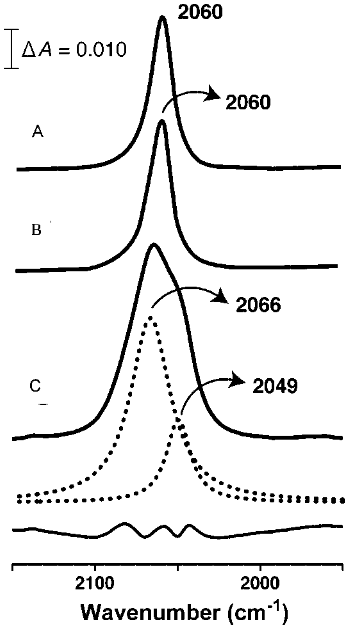

Figure 5. The IR absorption of iron-bound azide at 295 K. The iron concentration is about 2 mM in chloroform. (A) [Fe(TPrP)N$_3$], (B) [Fe(etiocorrphycenato)N$_3$], and (C) [Fe(TPrPc)N$_3$]. The broken curves in (C) are from Gaussian fitting. The half-height widths of the 2066- and 2049-cm^{-1} bands are 29 and 18 cm^{-1}, respectively. The lowest curve in (C) is the residual.

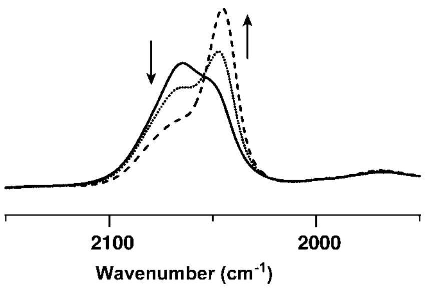

Figure 6. The IR absorption spectra of [Fe(TPrPc)N$_3$] in chloroform. Temperature decreases (295, 254, and 216 K) as indicated by the arrows.

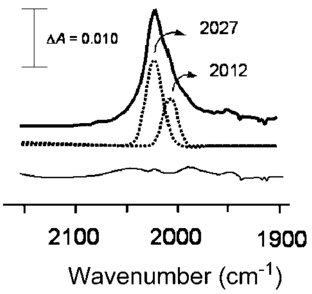

Figure 7. The IR absorption spectra of solid [Fe(TPrPc)N$_3$] at 295 K.

Discussion

Magnetic Anomalies in [Fe(TPrPc)N$_3$]

[Fe(TPrPc)N$_3$] exhibits several magnetic anomalies. The pyrrole-H shift does not follow the Curie law (Figure 1). The NMR behavior parallels that reported for [Fe(TPP)-ClO$_4$][18] and [Fe(TPrPc)X] (X = Br, Cl, I).[13] The NMR similarity suggests that [Fe(TPrPc)N$_3$] is predominantly high-spin, with an appreciable intermediate-spin (S = 3/2) character. The pyrrole-H shift of 19 ppm (Figure 1) supports the mixing of the S = 3/2 state because the signal resonates at 48 and –30 ppm for the five-coordinate ferric porphyrin in the S = 5/2 and S = 3/2 states, respectively.[17,18] The strong upfield bias of this signal at lower temperature indicates the S = 3/2 ground state. Mixing of the S = 3/2 state in [Fe(TPrPc)N$_3$] is supported from the EPR spectrum with $g_\perp$ = 5.42 (Figure 2). The quadrupole splitting ΔE_q = 2.20 mm s^{-1} at 290 K (Figure 3) is also intermediate between those of the typical S = 5/2 (ΔE_q = 0.8 ± 0.2) and S = 3/2 complexes (ΔE_q = 3.2 ± 0.3).[24] Quantitative support for the S = 5/2, 3/2 assignment comes from the magnetic moment of 4.8–4.1 μ_B over a 300–20 K range. On the basis of these physical results, we assign a mixed S = 5/2, 3/2 state to [Fe(TPrPc)N$_3$].

As the ranking of azide in the spectrochemical[25] and magnetochemical[19] series is comparable with halides, a pure S = 5/2 state, which is ordinarily found in [Fe(porphyrinato)X] (X = halides), may be expected for [Fe(TPrPc)N$_3$] as well. Contrary to the expectation, [Fe(TPrPc)N$_3$] is not pure high-spin. We note similar deviation from the pure high-spin state in [Fe(TPrPc)X] (X = Cl, Br, I)[13] and the all-alkyl porphycene derivatives.[14] The X-ray analyses of free base TPrPc[3] and relevant iron(III) porphyrins[26–28] provide the structural account for the mixing of the S = 3/2 state. Porphycene has a narrower coordination core.[3] The narrower metallo cavity in TPrPc results in a shorter Fe–N(pyrrole) bond and strengthens the equatorial ligand field of the iron. Under the circumstances, the $d_{x^2-y^2}$ orbital of high-spin iron is destabilized to induce the S = 3/2 state. Thus, the mixed S = 3/2 state in [Fe(TPrPc)N$_3$] is achieved with the synchronization of the core contraction[3,26–28] and a moderately small ligand-field splitting parameter of azide.[19,25]

IR Spectra

The most characteristic observation for [Fe(TPrPc)N_3] is the split IR bands of the coordinating azide (Figure 5, part C). This is in contrast with the single azide band in [Fe(TPrP)N_3] (2060 cm^{-1}; Figure 5, part A) or [Fe(protoporphyrinato)N_3] (2064 cm^{-1}).[7,10] It may be possible, however, that the 2049-cm^{-1} band in [Fe(TPrPc)N_3] is from a plausible contaminant, a di-azide species. Contamination with di-azide species is set aside because a bis-azide hemin displays the two IR bands at about 2035 and 2015 cm^{-1}.[12] In addition, the proton NMR spectrum of [Fe(TPrPc)N_3] (Figure 1) shows a single pyrrole-H peak at δ = 19 ppm to rule out the sample contamination. It is possible that the 2049-cm^{-1} peak is from a trace amount of the sodium azide, which is NMR invisible, suspended in the chloroform. This possibility is eliminated because the IR band of sodium azide in chloroform is at 2170 cm^{-1}.[7] It might also be possible that the split IR bands in [Fe(TPrPc)N_3] come from an equilibrium between five-coordinate [Fe(TPrPc)N_3] and six-coordinate [Fe(TPrPc)N_3(H_2O)], where the iron-bound water molecule comes from a trace amount of residual water in chloroform. This possibility is unlikely because a reference porphyrin [Fe(TPrP)N_3] (Figure 5, part A), measured in the same lot of chloroform, exhibits a single band. As porphycene has a rectangular molecule with a C_2 symmetry, one may claim that the two IR bands in [Fe(TPrPc)N_3] arise from the rotational isomers of azide about the azide–iron bond. The possibility is also eliminated because [Fe(etiocorrphycenato)N_3] (Figure 5, part B) and [Fe{bis(ethoxycarbonyl)corrphycenato}N_3][23] exhibit single azide bands despite their trapezoidal molecular shape. The prospect of Fermi resonance[29] for the split azide bands may be neglected because no sharp signal occurred at 1024 cm^{-1}, and because the 2049-cm^{-1} band is markedly intensified at lower temperature. Thus the two IR bands in [Fe(TPrPc)N_3] reflect a real magnetic anomaly of the iron.

Another notable observation is that the IR peak width is different between the 2049- ($\Delta\nu_{1/2}$ = 18 cm^{-1}) and 2066-cm^{-1} ($\Delta\nu_{1/2}$ = 28 cm^{-1}) bands (Figure 5). The notably larger line width of the latter may reflect increased orientation variability of the azide about the iron–azide bond because the IR band width of iron-bound azide has been demonstrated to increase with increasing ligand fluctuation.[30] Consistent with this proposal, the IR bands of the solid [Fe(TPrPc)N_3] in Figure 7, that is, $\Delta\nu_{1/2}$ = 18 cm^{-1} (2027 cm^{-1}) and 15 cm^{-1} (2012 cm^{-1}), are narrower owing to a decreased ligand motion in the solid.

Novel View Emerged from IR

It has been proposed for the ferric porphyrin with a mixed-spin S = 5/2, 3/2 system that the two states are quantum-mechanically admixed through the spin-orbit coupling and that the admixed state has a new discrete ground state.[15,16] The spin mixing has been proposed to occur in hemoproteins like cytochrome c' and horseradish peroxidase.[16] NMR, EPR, and Mössbauer results for the model compounds of cytochrome c' are apparently consistent with the quantum mechanical model.[19,26–28] In the proton NMR of [Fe(TPP)ClO_4][18,19] and [Fe(TPrPc)X] (X = Cl, Br, I),[13] the single pyrrole-H peaks shift far-upfield at lower temperature. The EPR and Mössbauer do not exhibit the two signals from the spin isomers. Present NMR, EPR, and Mössbauer results for [Fe(TPrPc)N_3] parallel those reported for [Fe(TPP)ClO_4] and [Fe(TPcPc)X].[13,18,19]

IR, on the other hand, resolves two azide peaks for [Fe(TPrPc)N_3] (Figure 5, part C). This observation demonstrates that the S = 5/2 and 3/2 states are not quantum-mechanically admixed but that they coexist separately. Based on the NMR, EPR, and Mössbauer results indicating dominance of the S = 3/2 species at lower temperature, we assign the 2049-cm^{-1} IR peak, which prevails at 216 K, to the S = 3/2 isomer and the 2066-cm^{-1} band to the S = 5/2 isomer. Population of the S = 3/2 species is estimated to be 0.21 at 20 °C on the assumption that the two magnetic isomers have closely similar extinction coefficients in the IR spectrum. The equilibrium is more quantitatively evaluated from the pyrrole-H shift in Figure 1. We now assign the **A** and **B** states assumed in the NMR analysis to the S = 3/2 and S = 5/2 states, respectively. Fractions of the S = 3/2 isomer, calculated with the ΔH and ΔS for the NMR analysis, are 0.20 (293 K), 0.43 (254 K), and 0.72 (216 K). These values are in good agreement with 0.24 (293 K), 0.43 (254 K), and 0.61 (216 K) estimated from the solution IR (Figure 6). The IR spectrum of the solid in Figure 7 resolves two IR bands. Existence of the two spin isomers in the IR spectrum is consistent with the implication from EPR, Mössbauer, and magnetic susceptibility, which were measured for the solid sample (Figures 2–4).

We emphasize that IR resolves the two spin isomers of [Fe(TPrPc)N_3] while EPR, NMR, and Mössbauer do not. Why does IR alone discriminate the spin isomers? The conflict is explained by realizing the timescale of the applied spectroscopic methods. The approximate timescales of IR, EPR, NMR, and Mössbauer are 10^{-13}, 10^{-4}–10^{-8}, 10^{-1}–10^{-9}, and 10^{-7} s^{-1}, respectively.[31] IR has excellent temporal resolution over EPR, NMR, and Mössbauer, which observe the time-averaged structures. Consequently, we can discern with IR the thermal spin-state equilibrium and the quantum mechanical mixing in the mixed S = 5/2, 3/2 system. Increase of the 2049-cm^{-1} peak and concomitant decrease of the 2066-cm^{-1} band with decreasing temperature, accompanied with the 2054-cm^{-1} isosbestic point (Figure 6), demonstrate that the S = 5/2 and S = 3/2 isomers are in a thermal equilibrium. This is in marked contrast with the claim that a homogeneous S = 5/2, 3/2 state in the ferric heme iron is solely created by quantum mechanical spin-orbit coupling.[16]

A closely related coexistence of two spin isomers has been reported for ferric azide heme in a mixed S = 5/2, 1/2 system where the two states are in a thermal equilibrium. IR distinguishes the S = 5/2, 1/2 spin isomers of the azide hemes[9,10,21] and hemoproteins,[7,8] while NMR and EPR do not. Unfortunately, IR has been scarcely applied to the mixed S = 5/2, 3/2 heme. Strong IR absorption of the iron-bound azide in [Fe(TPrPc)N_3] provides a unique opportunity to make use of the vibration spectroscopy to the mixed $S = 5/2$, 3/2 heme. IR resolves the $S = 5/2$, 3/2 isomers, demonstrating that the $S = 3/2$ and 5/2 states of [Fe(TPrPc)-N_3] are not uniformly admixed but slowly interchanging on the IR timescale. From the peak separation of 17 cm^{-1} and the relationship $\tau = 1/(2\pi\Delta\nu)$, where $\Delta\nu$ = (light velocity) × (peak separation),[31] we can estimate a minimum lifetime $\tau = 0.3$ ps for the two magnetic isomers.

Unified View of the Spin Mixing in Iron(III)

The ferric heme iron adopts either $S = 5/2$, 3/2, or 1/2 state depending on the axial ligand and/or macrocycle conformation. Mixing of the three spin states is frequently observed. The thermal mixing of the $S = 5/2$, 1/2 states or spin crossover of ferric hemes and hemoproteins has been established.[5–10] Recently, Nakamura et al. have found a novel type of spin crossover between the $S = 3/2$ and 1/2 states for the saddle-shaped ferric porphyrins.[32–34] The deformed iron porphyrin is magnetically inhomogeneous with independent $S = 3/2$ and 1/2 components in the mixed $S = 3/2$, 1/2 system. An analogous thermal mixing of the $S = 3/2$, 1/2 isomers has been reported for a non-heme complex of bis(*o*-iminobenzoquinonato)iron(III) by Chun et al.[35] Thus, the spin mixing in the $S = 5/2$, 1/2 and $S = 3/2$, 1/2 systems occurs through thermal spin crossover. Present IR analysis for [Fe(TPrPc)N_3] demonstrates that the $S = 5/2$ and 3/2 states are not quantum-mechanically admixed but in a thermal equilibrium. This situation parallels those found in the $S = 5/2$, 1/2[5–10] and $S = 3/2$, 1/2[32–34] systems. The temperature-dependent changes of the EPR, NMR, and Mössbauer for [Fe(TPrPc)N_3] are thus interpreted to reflect the spin crossover. In view of the IR elucidation for [Fe(TPrPc)N_3], the quantum chemical admixing of the two ground states is unlikely for this complex. We therefore point out the possibility that the three types of magnetic mixing among the $S = 5/2$, 3/2, and 1/2 states in ferric heme could be commonly described in terms of thermal spin crossover between the two magnetic isomers. The general distinction of the quantum-mechanical or thermal mixing of the spin states, however, is still to be established by further case-by-case analyses.

Experimental Section

TPrPc, [Fe(TPrPc)N_3], and Related Macrocycles: 2,7,12,17-Tetrapropylporphycene (TPrPc) was prepared by the method of Vogel et al.[3] The ferric chloride complex [Fe(TPrPc)Cl][36] was purified with silica-gel column chromatography with chloroform/methanol (97:3, v/v) mixture. The [Fe(TPrPc)Cl] in benzene was vigorously mixed overnight with aqueous sodium azide (5 M)[7] overnight to furnish [Fe(TPrPc)N_3]. The sample was recrystallized from hexane/dichloromethane. $C_{32}H_{36}FeN_7$: calcd. C 66.90, H 6.31, N 16.89; found C 67.15, H 6.12, N 17.02. Formation of [Fe(TPrPc)N_3] was also confirmed with the ^{1}H NMR spectrum where the hyperfine-shifted pyrrole-H signal (δ = 28.2 ppm in $CDCl_3$) of [Fe(TPrPc)Cl] was replaced with the new signal (δ = 24.3 ppm) from [Fe(TPrPc)-N_3].

meso-Tetrapropylporphyrin (TPrP, Scheme 1) and the iron chloride [Fe(TPrP)Cl] were obtained according to the literature methods.[37,38] The azide complex [Fe(TPrP)N_3] was derived from the chloride compound after the ligand exchange as carried out for [Fe(TPrPc)N_3]; the sample was recrystallized from hexane/dichloromethane. Synthesis of [Fe(etiocorrphycenato)N_3] (Scheme 1) has been reported.[6]

Spectroscopic Measurements: ^{1}H NMR spectra at 300 MHz were recorded with a JEOL LA300 with a temperature variation unit, and chemical shifts were referenced to tetramethylsilane. The X-band electron paramagnetic resonance (EPR) spectra were recorded with a Bruker E500 spectrometer equipped with an Oxford helium cryostat. IR spectra were obtained on a Nicolet Avatar spectrometer at a 2-cm^{-1} resolution with a 50-µm cell, and apodized with a Happe–Genzel function. IR spectra at low temperature were obtained on a Digilab FTS-7000 spectrometer equipped with an Oxford cooling unit.[38] The IR spectrum of the solid material was recorded after evaporation of concentrated sample in dichloromethane over the CaF_2 disk. ^{57}Fe Mössbauer spectra were measured on a Wissel–Mössbauer spectrometer system. The sample was kept in a gas-flow cryostat and ^{57}Co(Rh) source was kept at room temperature. Isomer shifts δ_{Fe} were referenced to α-iron at room temperature. The solid-state magnetic susceptibilities were measured over a 5–300 K range at 1 T with a Quantum Design MPMS-7 SQUID magnetometer. The data were corrected for both the diamagnetism of the basket and molecule Pascal's constants.

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