The 5/2,3/2 Spin Admixture in the Chloroiron(III) Derivative of the Sterically Crowded 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetraphenylporphyrin[**]

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Dedicated to Professor Gottfried Huttner
on the occasion of his 62nd birthday

Interest in how nonplanar distortions affect the properties of tetrapyrrole macrocycles, in particular their biological function, has led to the syntheses of and structural studies on a large number of sterically crowded porphyrins.[1, 2] Important results of these studies are that porphyrins are considerably more flexible than originally suspected, and that conformational variations offer an attractive mechanism for the modulation of a wide range of physical and chemical properties of porphyrins in vitro and in vivo.[3]

Cheng et al.[4] recently showed that the chloroiron(III) derivative of the sterically crowded 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin [$\mathrm{Fe^{III}Cl(oetpp)}$] (**1**) displays a nonplanar saddled and slightly ruffled conformation. Owing to the ring distortion this species possesses magnetic properties corresponding to a quantum-mechanically spin-admixed $S = 5/2,3/2$ state with an effective magnetic moment of 5.2 μ_B in the solid state at 300 K and an EPR spectrum with a $g_\perp$ value of 5.2 at 77 K in frozen 2-methyltetrahydrofuran (2-MeTHF) solution. According to the Maltempo model, a $g_\perp$ value of 5.2 corresponds to an $S = 5/2$ spin state with approximately 40 % $S = 3/2$ spin admixture.[5, 6]

Several iron(III) complexes of nonsaddled porphyrins that can be regarded as having a spin-admixed 5/2,3/2 state are known.[7–9] A well-documented case is [$\mathrm{Fe^{III}(tpp)}$]$\mathrm{ClO_4}$ (tpp = 5,10,15,20-tetraphenylporphyrin dianion).[8] The fact that the spin states of iron(III) porphyrins (high-spin $S = 5/2$, low-spin $S = 1/2$, and mixed intermediate-spin $S = 5/2,3/2$) can vary in response to subtly changing conditions and can be nearly degenerate depending on the axial ligand(s) and the geometrical environment around the iron center has long been recognized.[10–12] Five-coordinate ferric complexes which exhibit a strong quantum-mechanically spin-admixed state ($S =$ 5/2,3/2) typically exhibit large Mössbauer quadrupole splittings that remain almost unchanged throughout the whole temperature range.[13–15] At 280 K, the zero-field Mössbauer spectrum of a powder sample of [$\mathrm{Fe^{III}Cl(oetpp)}$] (**1**) synthesized by us consisted of a well-defined quadrupole doublet, which, although asymmetric due to relaxation effects, displayed an isomer shift of $\delta = 0.35\ \mathrm{mm\,s^{-1}}$ and a quadrupole splitting ΔE_Q of only $0.95\ \mathrm{mm\,s^{-1}}$, inconsistent with a substantial spin admixture. Therefore, we investigated the X-ray structure and the ^{1}H NMR, Mössbauer, EPR, and magnetic properties of a sample of [$\mathrm{Fe^{III}Cl(oetpp)}$] (**1**). Here we report the results of these studies.

In spite of having a nonplanar saddled and slightly ruffled conformation similar to that reported by Cheng et al.,[4] the [$\mathrm{Fe^{III}Cl(oetpp)}$] (**1**) compound synthesized by us showed a quantum-mechanical spin admixture with a contribution from the $S = 3/2$ state of 10 % or less, as opposed to the 40 % found in the [$\mathrm{Fe^{III}Cl(oetpp)}$] studied by Cheng et al.

Compound **1** was prepared by procedures described in the literature.[16] It was characterized by UV/Vis spectroscopy and mass spectrometry: UV/Vis ($\mathrm{CH_2Cl_2}$): λ_{max} ($\varepsilon \times 10^{-3}$) = 397.5 (40.5), 444.5 (37.3), 574 (6.1); MS (EI): m/z (%): 927 (100) [M^+], 892 (8) [$M^+ - \mathrm{Cl}$]. Single crystals suitable for X-ray studies were obtained by slow diffusion of dodecane into a solution of **1** in dichloromethane.[17a] A projection of the molecular structure of **1** onto the mean plane of the porphyrin core is displayed in Figure 1. Figure 1 also gives the perpendicular displacements of the porphyrin-core atoms relative to the mean plane of the porphyrin core. The molecule **1** is located on a twofold axis of the space group $C2/c$; therefore, the crystallographically required symmetry of **1** is C_2. The oetpp dianion adopts, as in the crystalline form studied by Cheng et al.[4] (**1'**), a saddled[18] and slightly ruffled nonplanar conformation. The mean values of the displacements of the geminal β-carbon atoms above and below the mean plane of the porphyrin core are not significantly different in the two

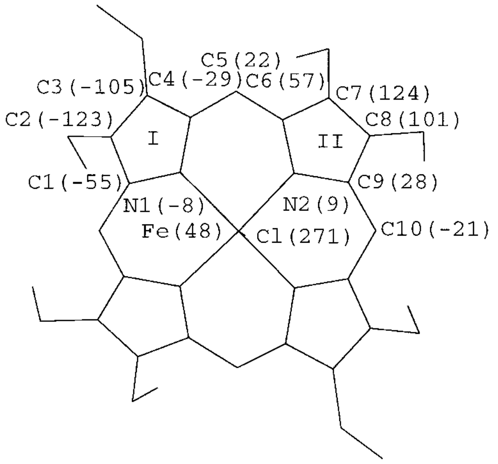

Figure 1. Projection of the structure of **1** (hydrogen atoms are omitted for clarity) on the mean plane of the porphyrin core. The perpendicular displacements (in 10^{-2} Å) of the atoms relative to the mean plane of the porphyrin core are given. Selected bond lengths [Å]: Fe–N1 2.053(6), Fe–N2 2.027(6), Fe–Cl 2.234(4).

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structures (av 1.133(8) Å in **1**, av 1.153(6) Å in **1'**). Both **1** and **1'** are also slightly ruffled. The ruffling is characterized by the mean value of the displacements of the *meso*-carbon atoms above and below the mean plane of the porphyrin core.[18] The mean values of 0.216(8) and 0.190(6) Å for **1** and **1'**, respectively, are not significantly different. The difference in the distances of the iron atom from the porphyrin core and from the mean planes of the four pyrrole nitrogen atoms N_p ($\Delta = 0.480(2) - 0.477(2) = 0.003(2)$ Å) is not significant and indicates that these two mean planes are superimposed in **1**. In contrast, in **1'** this difference ($\Delta = 0.434(1) - 0.467(1) = -0.032(1)$ Å) is significant and indicates a slight doming in this structure that is absent from the structure of **1**. Accordingly, the out-of-plane displacements of the iron atoms of 0.480(2) and 0.434(1) Å relative to the corresponding porphyrin mean planes of **1** and **1'**, respectively, are significantly different. However, the distances of 0.477(2) and 0.466(1) Å of the iron atom from the $4N_p$ mean planes of **1** and **1'**, respectively, are again very similar. The mean Fe–N_p bond lengths are 2.040(6) and 2.031(5) Å, and the Fe–Cl bond lengths are 2.233(1) and 2.242(2) Å in **1** and **1'**, respectively.[17b] All these data indicate that the molecular structures of **1** and **1'** are quite similar, despite their packing in two different space groups ($C2/c$ for **1** and $P2_1/c$ for **1'**).

Four signals ($\delta = 61.8$, 57.0, 29.6, 22.5) are present in the ^1H NMR spectrum of **1** (200 MHz, CD_2Cl_2, 200 K, TMS), corresponding to the eight methylene protons of the β-pyrrole ethyl substituents. The appearance of these four signals indicates that no inversion of the saddle/ruffle distortion occurs in solution at 200 K. Moreover, the variable-temperature ^1H NMR spectra of **1** in CD_2Cl_2 between 200 and 400 K shows that the coalescence temperature of these four methylene signals lies, as in the variable-temperature ^1H NMR spectrum of **1'** in $C_2D_2Cl_4$,[4] at about 370 K. Hence, the conformations of **1** and **1'** must also be very similar in solution.

The molar magnetic susceptibility of **1** was measured on a powder sample between 2 and 293 K with a SQUID magnetometer (Quantum Design MPMS). Figure 2 shows the temperature dependence of the effective magnetic moment per molecule of **1**. The effective magnetic moment of 5.78 μ_B is only slightly lower than the spin-only value for a pure $S = 5/2$ state ($2(S(S+1))^{1/2}\mu_B = 5.92\,\mu_B$). The data were analyzed by means of the spin-Hamiltonian formalism, which gave a zero-field splitting of $D = 10.2$ cm^{-1} and an isotropic g tensor of 1.954. The latter value, being smaller than 2, indicates minor quantum-mechanical mixing of the $S = 5/2$ and $S = 3/2$ spin states.[19]

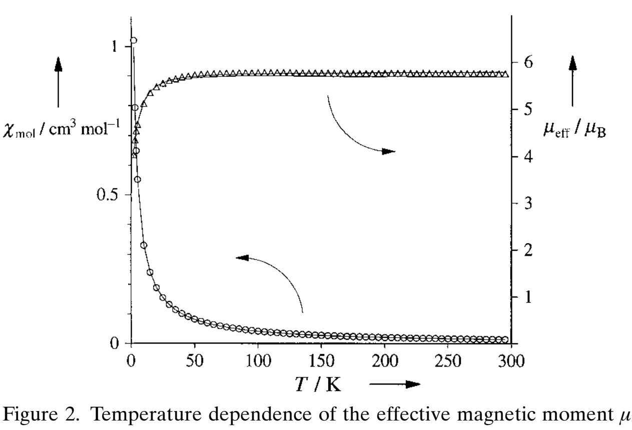

Figure 2. Temperature dependence of the effective magnetic moment μ_{eff} of a powder sample of **1** as derived from the molar magnetic susceptibility χ_{mol} in a field of 1 T. The measured data are corrected for diamagnetic contributions ($\chi_{dia} = -592 \times 10^{-6}$ cm^{3}mol^{-1}). The solid line represents a spin-Hamiltonian simulation with a zero-field splitting of $D = 10.2$ cm^{-1}, the rhombicity parameter $E/D = 0.025$ (from the EPR analysis), and an isotropic g tensor with $g = 1.954$.

The EPR spectra of **1** were recorded with a conventional X-band spectrometer (Bruker 200D SRC) equipped with a helium-flow cryostat (ESR 910, Oxford Instruments). The measurements at 10 K were performed at a frequency of 9.646 GHz, a microwave power of 20 µW, a modulation amplitude of 5 G, and a modulation frequency of 100 kHz. The spectra were analyzed under the assumption of a Lorentzian line shape. Figure 3 shows the EPR spectrum of **1** in frozen 2-MeTHF measured at 10 K (a) and a simulation (b), which yielded the effective g values $g_y^{eff} = 6.55$, $g_x^{eff} = 5.28$ ($g_\perp^{eff} = 5.92$), and $g_z^{eff} = 1.976$. A less well resolved spectrum recorded in frozen CH_2Cl_2 yielded by simulation the following effective g values: $g_y^{eff} = 6.34$, $g_x^{eff} = 5.28$ ($g_\perp^{eff} = 5.81$), and $g_z^{eff} = 1.992$. The effective g values obtained in both frozen solutions are characteristic for an $S = 5/2$ ground state with a positive zero-field splitting D, a small rhombicity ($E/D = 0.02 - 0.03$), and a small quantum-chemical admixture of the $S = 3/2$ state. According to Maltempo and Moss,[6] the reduction of the average $g_\perp^{eff}$ value due to quantum-chemical 5/2,3/2 spin mixing is given by $g_\perp^{eff} = 6(a_{5/2})^2 + 4(b_{3/2})^2$. The coefficient $(a_{5/2})^2$ can be directly expressed in terms of effective $g_\perp$ value by $(a_{5/2})^2 = (g_\perp^{eff} - 4)/2$. Hence, the degree of spin mixing in **1** lies between 4% in 2-MeTHF ($(a_{5/2})^2 = 0.96$) and 10% in CH_2Cl_2 ($(a_{5/2})^2 = 0.90$).

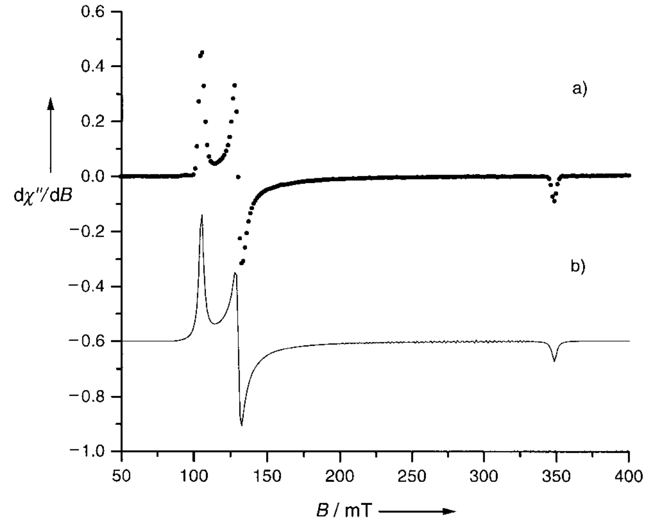

Figure 3. a) EPR spectrum of **1** in 2-MeTHF at $T = 10$ K; b) simulated spectrum under the assumption of Lorentzian line shape with $g_y^{eff} = 6.55$, $g_x^{eff} = 5.28$, and $g_z^{eff} = 1.976$ and line widths $\Gamma_y = 3.7$ mT, $\Gamma_x = 3.7$ mT, and $\Gamma_z = 3.8$ mT. Experimental conditions: Microwave frequency 9.646 GHz, modulation frequency 100 kHz, modulation amplitude 10 G, microwave power 20 µW.

A Mössbauer spectrum of a powder sample was recorded with a conventional spectrometer in the constant-acceleration mode. Isomer shifts are relative to α-Fe at room temperature. The spectrum was analyzed by a least-squares fit with a Lorentzian line shape. The Mössbauer spectrum of **1** (Figure 4) at 280 K exhibits an asymmetric doublet because of relaxation effects. The Mössbauer parameters ($\delta = 0.35\,\mathrm{mm\,s^{-1}}$ and $\Delta E_Q = 0.95\,\mathrm{mm\,s^{-1}}$) compare well with those of other high-spin iron(III) porphyrins, whereas the quadrupole splitting is considerably smaller than those of iron(III) porphyrin complexes which exhibit a substantial $S = 3/2$ admixture.[13–15, 19]

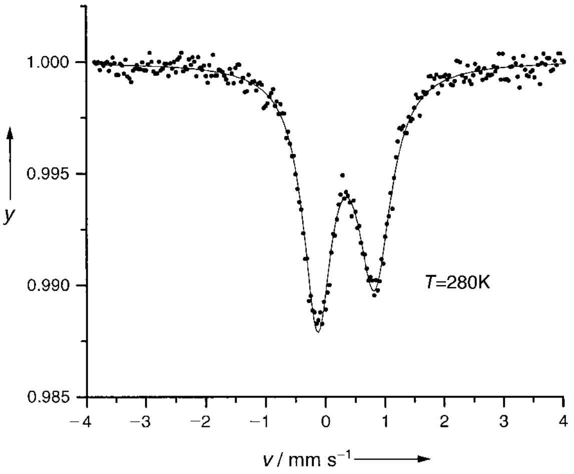

Figure 4. Mössbauer spectrum of a powder sample of **1** at 280 K in a field of 10 mT applied perpendicular to the γ beam. Two single lines of Lorentzian shape were used to fit the asymmetry of the spectrum, which is caused by relaxation effects: $\delta = 0.35\,\mathrm{mm\,s^{-1}}$, $\Delta E_Q = 0.95\,\mathrm{mm\,s^{-1}}$, $\Gamma_1 = 0.68\,\mathrm{mm\,s^{-1}}$, and $\Gamma_2 = 0.57\,\mathrm{mm\,s^{-1}}$. y = relative transmission, v = velocity.

In conclusion, a significantly smaller quantum-mechanical $S = 3/2$ spin admixture is present in the [Fe^{III}Cl(oetpp)] complex prepared by us (4–10%), as compared to that in the [FeCl(oetpp)] complex prepared by Cheng et al. (ca. 40%),^{849} despite similar ring deformations in both complexes in solution and in the solid state.

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[17] a) Crystal data for **1**: $C_{60}H_{60}N_4ClFe$, $M_r = 928.5$, monoclinic, space group $C2/c$, $a = 17.737(5)$, $b = 24.456(7)$, $c = 15.588(4)$ Å, $\beta = 111.24(2)°$, $V = 6302$ Å^3, $Z = 4$, $\rho_{calcd} = 0.978\,\mathrm{g\,cm^{-3}}$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.7107$ Å, 6791 reflections ($2 < \theta < 26°$) were collected at 20°C on a dark blue crystal of dimensions 0.35 × 0.30 × 0.25 mm. Semi-empirical absorption corrections were applied. A total of 3537 reflections with $I > 3\sigma(I)$ were used in the refinements; 299 refined parameters, $R = 0.073$, $R_w = 0.120$, GOF 1.036, final residual electron density 0.13 Å^3; b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118960. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Transition Metal Induced Pentamerization of a Phosphaalkyne**

Peter Kramkowski and Manfred Scheer*

Dedicated to Professor Manfred Regitz
on the occasion of his 65th birthday

The chemistry of the phosphaalkynes has been intensively investigated over the past 15 years in their various aspects of organoelement chemistry[1] and coordination chemistry.[2] The basis for this immense development was the first synthesis of kinetically stabilized tBuC≡P by G. Becker in 1981[3, 4] and the improved preparation by M. Regitz and G. Becker.[5] Most of the studies into the reactivity of phosphaalkynes have been carried out on this compound, whereas the supermesitylphosphaalkyne Mes*C≡P (Mes* = 2,4,6-$t\mathrm{Bu_3C_6H_2}$) and the

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