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Electronic structure of low-spin ferric chlorins: characterization of bis(1-methylimidazole)(*meso*-tetraphenylchlorinato)iron(III) triflate

Gérard Simonneaux,*[a] Marwan Kobeissi[a] and Loïc Toupet[b]

[a] *Laboratoire de Chimie Organométallique et Biologique, Université de Rennes 1, UMR CNRS 6509, 35042 Rennes cedex, France. E-mail: simonnea@univ-rennes1.fr*
[b] *Groupe de Physique Cristalline, Université de Rennes 1, UA CNRS 040804, Campus de Beaulieu, 35042 Rennes Cedex, France*

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The synthesis and characterization of the trifluoromethanesulfonato derivative of bis(1-methylimidazole)tetrakis-(phenyl)chlorinatoiron(III) [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 **1** are reported. The crystal structure of complex **1** has been determined. The X-ray structure shows that the porphyrinate rings are weakly distorted. The metal–nitrogen distances to the reduced pyrrole N(2), 2.016 (6) Å and to the pyrrole *trans* to it N(4), 2.032 (5) Å are longer than the remaining two nitrogens: N(1), 2.005 (6) Å and N(3), 1.972 (6) Å leading to a core-hole expansion of the macrocycle due to the reduced pyrrole. The two axial ligand planes are parallel. The ^{1}H NMR isotropic shifts at 20 °C of the different pyrrole protons of **1** varied from −8.6 ppm to −42.6 ppm according to bis-ligated complexes of low-spin ferric chlorins. The EPR spectrum of [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 **1** in solution is rhombic and shows the principal *g*-values $g_1 = 2.47$, $g_2 = 2.42$ and $g_3 = 1.78$ ($\Sigma g^2 = 15.1$). These spectroscopic observations are indicative of a metal-based electron in the d_π orbital for the [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 (**1**) complex with a $(d_{xy})^2$ $(d_{xz}d_{yz})^3$ ground state at any temperature.

Introduction

The essential objective of hemoprotein research is the elucidation of the structural and electronic factors that control the different functional properties of the active site heme group. The nature of axial ligands that are ligated to the heme group is the major determinant of reactivity. However, even in many cases where imidazole serves as the axial ligand, wide variation in reactivity is present as a result of small changes in orientation or in the presence of a nearby residue. Thus, imidazole is one of the most studied ligands in five- and six-coordinate derivatives of iron porphyrins. This is largely due to the fact that physiologically relevant ligands provided by the protein include the imidazole side chain of histidine which can be found in many hemoproteins such as hemoglobins,[1,2] cytochromes c,[3] cytochromes *b*[4] and cytochromes *f*.[5] Two limiting orientations of the axial ligand planes have been implicated in the structures of cytochromes having two axial imidazole ligands, either the imidazole planes are oriented parallel to each other (cytochrome b_5[4]) or the imidazole planes are oriented perpendicular to each other (cytochrome c_3[6] and cytochrome bc_1[7]).

In contrast, the electronic structure of iron chlorins still represents a recently active and challenging area[8] because iron chlorins have been found as the prosthetic groups of a number of heme proteins in recent years. Cytochrome *bd* oxidase is a bacterial terminal oxidase that contains three cofactors: a low-spin heme (*b558*), a high spin heme (*b595*) and a chlorin *d*.[9–11] Whereas X-ray structures have been published for several heme-copper cytochrome c oxidases,[12] no crystal structure is available yet for the cytochrome *bd* family. The molecular mechanism of the enzyme action has been studied in much less detail[13,14] than the heme-copper oxidases and the nature of the axial ligand of heme *d* is still unknown. Heme d has also been found in catalases, such as hydroperoxidase II, from *Escherichia coli* (*E. coli*).[15] In contrast to cytochrome *bd* oxidase, the crystal structure of catalase HP II from *E. coli* has been determined showing a heme *d* prosthetic group with a *cis*-hydroxychlorin γ-spirolactone[16] and a tyrosine as the proximal ligand.[17] A heme *d* prosthetic group with the same configuration has also been found in the crystal structure of *Penicillium vitale* catalase.[18] Evidence favoring coordination of a tyrosinate proximal ligand to the chlorin iron of *E. coli* Hp II catalase was previously proposed by Dawson *et al*.[19]

Iron chlorins are porphyrin-derived iron-containing prosthetic groups in which one of the peripheral double bonds of the porphyrin ring has been reduced to yield a dihydroporphyrin. Although some investigations of the NMR and EPR spectra of low-spin iron(III) complexes of reduced porphyrins have been investigated by us[20,21] and others,[22–32] the nature of the electronic ground state is not always clear and more information is needed with these systems. Magnetic circular dichroism spectroscopy has also been shown to be of great utility in the identification of proximal and distal axial ligands in chlorin-containing proteins.[33,34] However, only a limited number of iron chlorin complexes such as high-spin ferrous,[35,36] high spin ferric[31,37] (μ-oxo)bis[(tetraphenylchlorin)iron(III)],[38] and low-spin ferric tetraphenylporphyrin[20] species have been investigated with X-ray crystallography. We now report the first X-ray structure and ^{1}H NMR analysis of the bis(1-methylimidazole) adduct of ferric tetraphenylporphyrin, as a low-spin complex. The purpose of this study is to extend the coverage of iron chlorin models with physiological nitrogenous ligands such as imidazole.

Results and discussion

Preparation of compound 1

The synthesis of the [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 compound is achieved by displacement of coordinate triflate from Fe(TPC)-CF_3SO_3[21] according to eqn. (1).

$$Fe(TPC)CF_3SO_3 + 2(1\text{-MeIm}) \longrightarrow [Fe(TPC)(1\text{-MeIm})_2]CF_3SO_3 \quad (1)$$

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Table 1 Selected bond distances (Å) and angles (°) for [Fe(TPC)-(1-MeIm)$_2$]CF_3SO_3

Bond	Distance/Å	Bond	Distance/Å
Fe1–N1	2.005 (6)	Fe1–N7	2.002 (6)
Fe1–N2	2.016 (6)	C2–C3	1.320 (11)
Fe1–N3	1.971 (6)	C7–C8	1.444 (12)
Fe1–N4	2.032 (5)	C12–C13	1.390 (10)
Fe1–N5	1.958 (5)	C17–C18	1.408 (11)
Angle	**Degrees**	**Angle**	**Degrees**
N1–Fe1–N3	178.4 (3)	N3–Fe1–N5	91.2 (2)
N1–Fe1–N5	89.8 (2)	N3–Fe1–N7	88.9 (2)
N1–Fe1–N7	90.1 (2)	N4–Fe1–N5	90.4 (2)
N2–Fe1–N4	178.3 (2)	N4–Fe1–N7	89.4 (2)
N2–Fe1–N5	91.2 (2)	N5–Fe1–N7	179.7 (3)
N2–Fe1–N7	89.1 (2)		

In solution, the complex has a green–brown color, as reported for the bis(dimethylphenylphosphine) adduct,[20] and shows a visible spectrum with λ_{max} at 417, 595 and 634 nm. During the synthesis, the two major difficulties are the oxidation of the chlorin ring to the porphyrin ring and a possible autoreduction of the ferric state.

Crystal structure of [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3

The molecule is a six-coordinate iron with four nitrogen atoms of the porphyrin and two nitrogen atoms of the axial ligands. An ORTEP diagram of the complex is shown in Fig. 1, along with the atom numbering scheme. The most interesting bond distances and angles are summarized in Table 1.

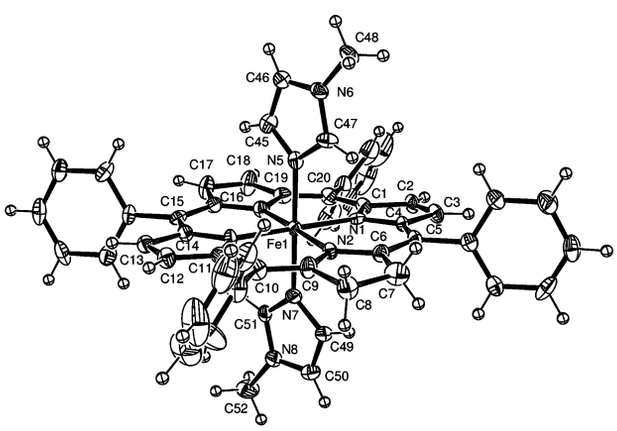

Fig. 1 Atom labels and perspective view for the cation **1**.

A convenient measure of the orientation of imidazole ligands in metalloporphyrin complexes is to use the dihedral angle ϕ between the imidazole plane and a plane perpendicular to the porphinato core and passing through a porphinato nitrogen atom.[39,40] As shown in Fig. 2A, the two axial ligand planes are coplanar with a unique ϕ angle of 21.8°. This is different from the analog porphyrin complex [Fe(TPP)(1-MeIm)$_2$]ClO_4 in which the axial ligands form ϕ angles of 22° and 32° with an angle of 10° separating the ligand planes.[41] ϕ values between 0° and 20° are however a common feature of six-coordinate imidazole-ligated metalloporphyrins.[42] Thus preferred orientation of imidazole ligands in iron porphyrins has been largely discussed by Scheidt group on the basis of analysis of many X-ray structure determinations.[40] Charge iterative extended Hückel theory calculations on electronic effects for a large group of representative systems indicate an orientational preference in the M–N(imidazole) bond which favors eclipsed orientation.

The pyrrole and pyrroline atoms are only slightly displaced

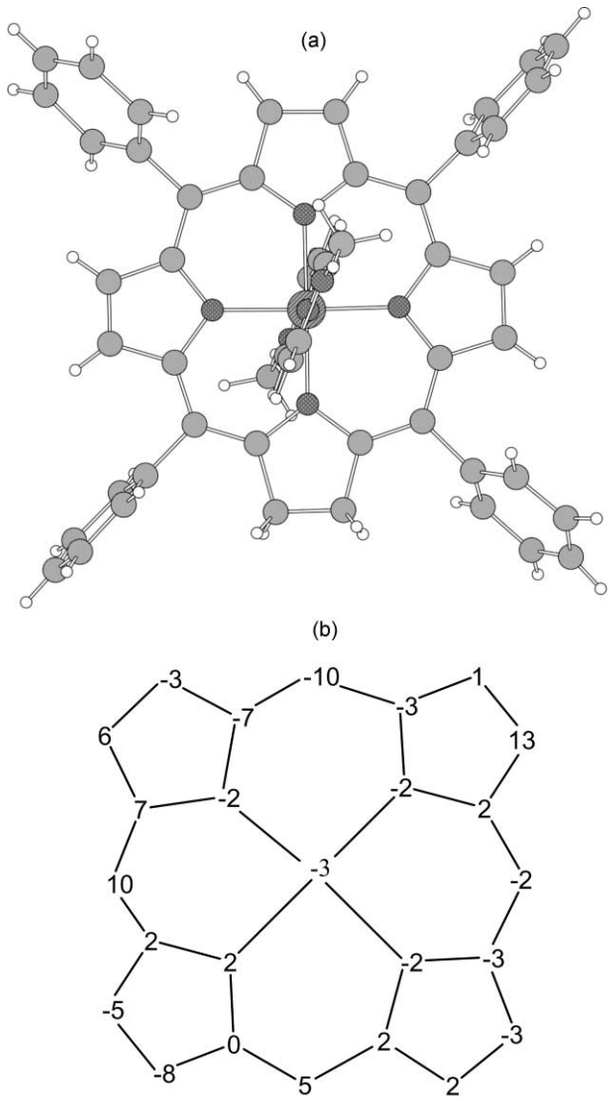

Fig. 2 A, Formal diagram of the porphinato core in [Fe(TPC)-(1-MeIm)$_2$]CF_3SO_3 showing the relative orientations of the axial ligands with each other and the Fe–Np vectors. B, Also displayed in the diagram are the displacements of each atom, in units of 0.01, from the best plane of the 24-atom porphinato core.

above and below the mean plane of the chlorin (maximum displacement 0.15 (2) Å). Fig. 2B gives out of plane distances for the atoms in the chlorin core from the mean chlorin plane. Thus the conformation of the chlorin macrocycle can be described as weakly distorted and indicates that the ground state is largely $(d_{xy})^2(d_{xz}d_{yz})^3$ (*vide infra*).

The C(7)–C(8) (1.444(12) Å) distance in the pyrroline ring is longer than the usual values of the three remaining pyrroles (average value of 1.373(10) Å) and reflects the sp^3 hybridization of the corresponding pyrroline atoms. Such a situation was previously observed with three iron chlorins: the low-spin complex [Fe(TPC)(PMe_2Ph)$_2$]CF_3SO_3 (C–C distance: 1.446 (16) Å),[20] the ferrous octaethylchlorin (OEC)Fe (C–C distance: 1.508(7) Å)[36] and the μ-oxo complex [(TPC)Fe]$_2$O (C–C distance: 1.419(9) Å).[38]

The metal–nitrogen distance to the reduced pyrrole, N(2) (2.016 (6) Å), and the nitrogen N(4) (2,014 (6) Å) are longer than and the two remaining nitrogens: N(1) and N(3) (average Fe–N distance: 1.988 (6) Å). These values are different to those found for [Fe(TPP)(1-MeIm)$_2$]ClO_4[41] in which the four Fe–N distances average to 1.981 (3) Å. Thus there is a core-hole expansion of the macrocycle due to the reduced pyrrole. Such a situation, but to a lesser extent, has been recently reported by us[20] with the comparison of the two complexes [Fe(TPC)-(PMe_2Ph)$_2$]CF_3SO_3 and [Fe(TPP)(PMe_2Ph)$_2$]CF_3SO_3.[43] It

Table 2 Observed and isotropic shifts of [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 **1** (δ, CD_2Cl_2, ppm)

Proton chlorin	H_o	$H_{o'}$	H_m	$H_{m'}$	H_p	$H_{p'}$	H_{pyrro}	H_{pyr1}	H_{pyr2}	H_{pyr3}
$(\Delta H/H)^a$	6.17	6.17	7.22	7.11	7.11	6.91	39.14	−1	−10	−35
$(\Delta H/H)^b$	7.6	7.8	7.6	7.6	7.6	7.6	4.35	7.6	8.2	7.6
$(\Delta H/H)_{iso}{}^c$	−1.43	−1.63	−0.38	−0.49	−0.49	−0.69	34.79	−8.6	−18.2	−42.6

Proton ligand	H_2	H_4	H_5	Me
$(\Delta H/H)^a$	−5.73	1.78	3.11	12.6
$(\Delta H/H)$	−0.8	0.4	4.0	1.6
$(\Delta H/H)_{iso}{}^d$	−4.9	1.3	−0.9	11

[a] Chemical shift of [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 **1** at 298 K with TMS as internal reference. [b] Chemical shift of [Fe(TPC)(PMe_2Ph)$_2$] at 298 K with TMS as internal reference. [c] Isotropic shift of **1** with diamagnetic complex [Fe(TPC)(PMe_2Ph)$_2$] as reference. We used a medium value of 7.8 ppm for the chemical shifts of the diamagnetic pyrroles since the relative assignment was not possible at this stage. [d] Isotropic shift of **1** with diamagnetic ruthenium(II) mesoporphyrin dimethyl ester complex Ru(MPDME))(CO)(1-MeIm) as reference.[48]

should also be noted that the equatorial Fe–Np bonds that are approximately perpendicular to the imidazole ring planes in [Fe(TPP)(1-MeIm)$_2$]ClO_4 are significantly shorter than the set that are approximately parallel to the imidazole plane, the respective averaged values are 1.973 and 1.991 Å.[41] This rhombic effect which is due to the π-donating ability of the imidazole ligand to the half-filled d_{yz} orbital of the metal was also noted for [Fe(TPP)(Him)$_2$]Cl.[44] With the [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 complex, the expected rhombic distortion due to the reduced ring results in an axial ligand orientation nearly along the Fe–N (pyrroline) bond. This situation may result from competition between the chlorin ring and imidazole ligand to π-donate to the iron(III).

The axial Fe–N(5) and Fe–N(7) distances are 1.958 (5) and 2.002 (6) Å, respectively. Thus, the average axial Fe–N(Im) distance of 1.9805 Å is slightly longer than in the iron(III) complex of TPP containing the same ligand [Fe(TPP)(1-MeIm)$_2$]-ClO_4 (1.974(6) Å)[41] and is typical of distances observed previously with unhindered imidazole derivatives.

^{1}H NMR spectroscopy

The ^{1}H NMR spectrum of [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 at 298 K is shown in Fig. 3. The peaks for the phenyl protons

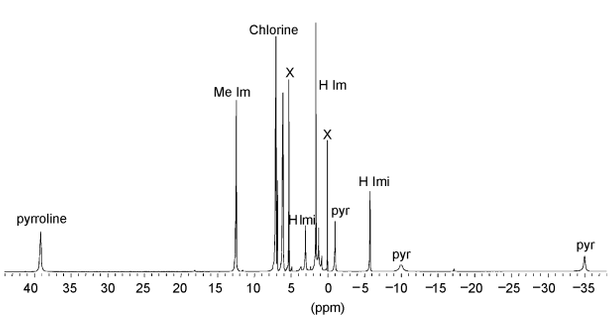

Fig. 3 ^{1}H NMR spectrum of [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 recorded at 283 K in CD_2Cl_2.

of the porphyrin ring are assigned completely by 2D COSY spectra. For the imidazole ligands and the pyrroles, the relative intensities and 2D COSY determine the assignment. The shifts of the imidazole ligands are independent of the presence of excess ligand, and hence axial ligand dissociation does not appear to be significant at ambient temperature. Magnetic measurements using the method of Evans[45,46] were made for 0.03 M CD_2Cl_2 solutions of **1** at 297 K, employing Me_4Si as the reference. The solution magnetic moment (μ = 1.93 μ_B) is compatible with a low-spin state, S = 1/2. The hyperfine shifts, obtained by referencing the observed shift to that of the corresponding diamagnetic complex Fe(TPC)($PPh(Me)_2$)$_2$[20] are summarized in Table 2.

The hyperfine shifts for symmetrical low-spin ferric porphyrins are known to consist of large contact shifts and smaller upfield dipolar shifts due to the magnetic anisotropy. In chlorin, the symmetry is lost but La Mar and coworkers have suggested that such a situation is also highly probable with low-spin ferric chlorins.[26] It should also be underlined that spin density distributions estimated using Hückel molecular orbital calculations for [Fe(TPC)(ImH)$_2$]$^+$Cl have been recently reported.[32,47]

Pyrrole. The spectrum of [Fe(TPC)(1-MeIm)$_2$]CF_3SO_3 **1** shows the pyrrole proton signals at −1.0, −10.0 and −35.0 ppm (298 K). This is quite different from the pyrrole proton signals of two other low-spin Fe(III) chlorinates at ambient temperature: [Fe(TPC)(PMe_2Ph)$_2$]CF_3SO_3 (0.66, 0.66 and −57.8 ppm)[20] and [Fe(QTPP)(Im)]$^+$ (−12.2, −15.6 and −21.7 ppm, 293 K),[31] but close to the pyrrole proton signals of [Fe(TMC)(Im)$_2$]Cl (−2.4, −12.3 and −47.1 ppm, 203 K).[29]

Pyrroline. For the saturated pyrroline ring, the protons are expected to exhibit low-field π contact shifts.[26] The observed large low-field shift (δ = 39.1 ppm) for **1** agrees with an important π metal bonding involving a molecular orbital of the chlorin derived either from the a_{1u} orbital[25] or from the 3eπ orbital of a porphyrin.[32] This contact shift is very similar to that of the corresponding [Fe(TMC)(Im)$_2$]Cl (δ = 38.3 ppm)[29] and not too far from those of pyropheophorbide a methylester iron(III) (δ = 24 and 28 ppm).[26] Since the contact shift has been shown to arise predominantly from spin delocalization into the bonding d_{xz} and d_{yz} orbitals,[26] this result agrees with a $(d_{xy})^2(d_{xz},d_{yz})^3$ electronic structure in this imidazole derivatives (see below).

Phenyl. In contrast to the pyrrole protons, the phenyl protons show weak isotropic shifts which are found to be essentially dipolar in origin. Thus a plot $(\Delta H)_{iso}$ *vs.* $(3\cos^2 - 1)/r^3$ for all protons is linear and confirms the quasi absence of contact shift in this position.

Ligand. The chemical shifts of the protons of the 1-Me imidazole ligands of [Fe(TPP)(1-MeIm)$_2$]Cl and the isotropic shifts of the imidazole ligands of [Fe(TPP)(Im)$_2$]Cl have been reported.[48] It has been found that the imidazole ligand shifts are consistent with delocalization into the filled orbitals that have large density on the bonding nitrogen.[49] The hyperfine shifts, obtained by referencing the observed shift to that of a corresponding diamagnetic Ru(II) complex[49,50] are summarized in Table 2. The paramagnetic shifts of 4-H and 5-H are weak and reflect the balance of a positive dipolar shift and a negative contact shift. The shift of 2-H is at a stronger field (δ = −4 ppm) due to more π delocalization at that position. In comparison with the analogous complex with porphyrin, the effects are similar but to a lesser extent in the chlorin case. This decrease

is probably due to a larger contribution of iron chlorin than iron porphyrin. Thus the same conclusion can be reached: imidazoles interact with low-spin iron(III) as π donors and the mechanism of spin delocalization is 1-methylimidazole towards Fe π bonding. These results also confirm the $(d_{xy})^2$ $(d_{xz}, d_{yz})^3$ ground state, both in porphyrin and chlorin complexes

Analysis of the curve in the Curie plot was made for the $[Fe(TPC)(1\text{-}MeIm)_2]CF_3SO_3$ complex. The temperature dependence of the chemical shifts of the protons in CD_2Cl_2 are shown in Fig. 4. A magnetically simple molecule is expected to

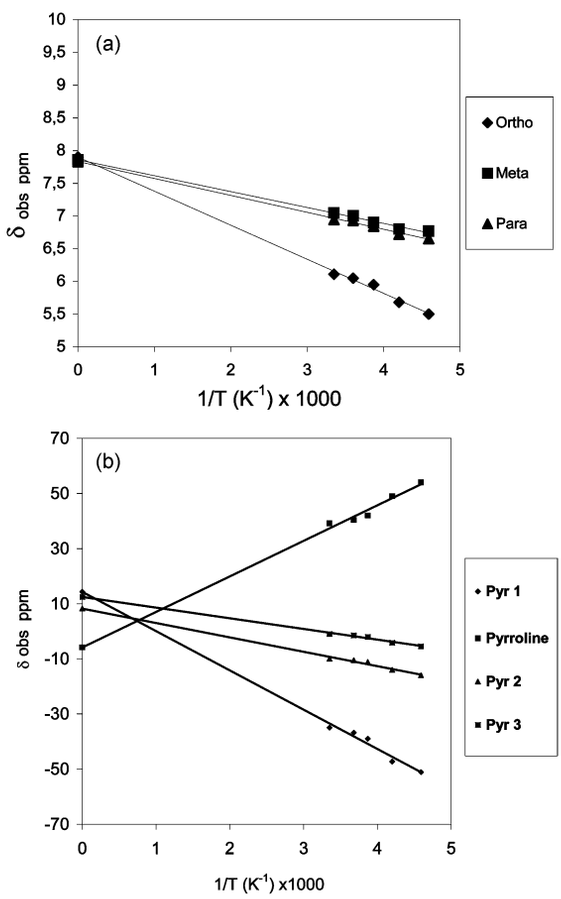

Fig. 4 Curie plot of the chemical shifts *vs*. reciprocal temperature of $[Fe(TPC)(1\text{-}MeIm)_2]CF_3SO_3$ in CD_2Cl_2. A: phenyl protons; B: pyrrole and pyrroline protons.

follow Curie-law behavior in that a plot of the chemical shifts *vs*. $1/T$ is linear with an intercept equal to the resonance in the diamagnetic complex. Plots of *ortho*, *meta* and *para* signals of *meso*-aryl protons of the chlorin ring are reasonably linear which intercepts at 8.03, 7.4, and 7.34 ppm respectively (Fig. 4A). However these protons show only small temperature dependence, consistent with a weak spin density on the *meso* position. For the pyrrole resonances, the chemical shifts vary linearly with $1/T$, but the extrapolated lines do not pass through the diamagnetic value at $1/T = 0$ Fig. 4B).

EPR spectroscopy

Among the heme proteins, the paramagnetic states of iron are particularly amenable to spectroscopic investigations by electron paramagnetic resonance (EPR).[51] Thus EPR spectroscopy has been used for classifying low-spin ferriheme proteins and model porphyrin complexes on the basis of a crystal field analysis developed by Griffith.[52] For low-spin ferrihemes, Blumberg and Peisach used the tetragonality Δ/λ and rhombicity V/Δ parameters which are obtained from the three *g*-values of the typically rhombic EPR spectra with λ being the spin-orbit coupling.[51] However, continuous wave EPR yields only absolute values of the components of the *g*-tensors and not their orientation with respect to the molecular frame. Since, it was found recently [32] that the orientation and electronic ground states are not necessarily those expected on the basis of the Taylor analysis,[53] which assumes that the rhombicity must be less than 2/3, our proposition cannot be considered as definitive. However the EPR results, strongly suggest a $(d_{xy})^2$ $(d_{xz}, d_{yz})^3$ ground state. Thus the EPR spectrum of CH_2Cl_2 frozen solutions of complex **1** (Fig. 5) shows EPR signals with the

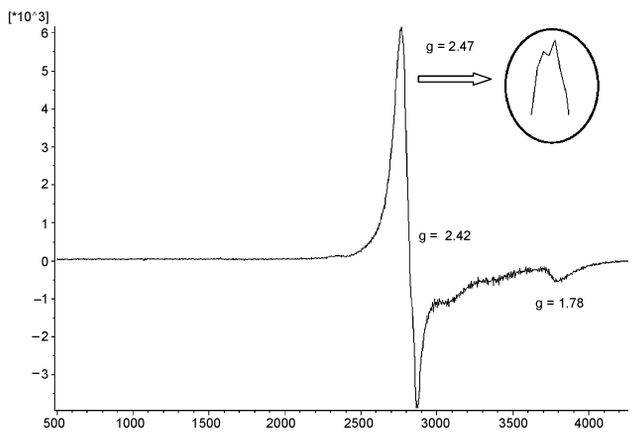

Fig. 5 EPR spectrum of $[Fe(TPC)(1\text{-}MeIm)_2]CF_3SO_3$ in a CH_2Cl_2 glass, recorded at 4 K.

principal *g*-values $g_1 = 2.47$, $g_2 = 2.42$ and $g_3 = 1.78$ ($\Sigma g^2 = 15.1$). The electronic structure of **1** is rhombic and is described in terms of crystal field parameters as rhombic (Δ/λ) and tetragonal (V/λ) components normalized to the spin-orbit coupling constant (λ). These values can be determined from the principal EPR *g* values using the expressions given by Taylor.[53] Using the values of complex **1** yields $V/\lambda = 3.8$ and $\Delta/\lambda = 2.3$ ($V/\Delta = 1.6$) with the largest magnitude *g* value assigned to the heme normal independent of the value of V/Δ. The principal *g* values for a similar complex, $[Fe(TPC)(Im)_2]Cl$ are $g_1 = 2.49$, $g_2 = 2.39$ and $g_3 = 1.75$ ($\Sigma g^2 = 15.0$).[32] In contrast, for $[Fe(TPC)(CN\text{-}t\text{-}Bu)_2]Cl$, where $\Sigma g^2 = 13.1$ is much lower, a considerable amount of orbital angular momentum is quenched in this complex according to a $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground state.[21] This interpretation is also supported by a recent EPR results on $[Fe(TPC)(Im)_2]Cl$ reported by Walker *et al*. showing that the highest *g* value is g_z in this complex with a $(d_{xy})^2$ $(d_{xz}, d_{yz})^3$ ground state.[32]

Geiger *et al*. have suggested that magnetic properties in iron(III) porphyrins can depend on the rotational orientation of the axial ligands with respect to the equatorial $M–N_p$ bonds of the porphyrin.[42] Walker *et al*. have also studied the possible effect of the relative axial ligand orientation on the EPR and 1H NMR of bis(imidazole)iron(III) porphyrinates as models of cytochromes b.[54] It is reported that a perpendicular orientation of the two axial ligands leads to an unusual EPR spectrum which was called "large g_{max}" (*g* value > 3.3).[55] In contrast, the EPR spectrum of complex **1** in solution agrees with a parallel orientation which is also observed in the X-ray structure.

Conclusion

In conclusion, these spectroscopic observations are indicative of a metal-based electron in the d_π orbitals of the $[Fe(TPC)(1\text{-}MeIm)_2]CF_3SO_3$ complex at any temperature. Thus the change in ground state of low-spin Fe(III) from the usual $(d_{xy})^2$ $(d_{xz},d_{yz})^3$ to the unusual $(d_{xz},d_{yz})^4$ $(d_{xy})^1$ electron configuration which was previously suggested to occur from porphyrin to chlorin macrocycles [51] is not observed with 1-methylimidazole ligands. However, the unusual $(d_{xz},d_{yz})^4$ $(d_{xy})^1$ electron configur-

ation of low-spin Fe(III) is possible both with porphyrin and chlorin macrocycles but seems largely related to the π-acceptor properties[56] of the ligands such as isocyanide[57–60] and phosphonite.[61]

Experimental

General information

As a precaution against the formation of the μ-oxo dimer $[Fe(TPC)]_2O$,[38,62] all reactions were carried out in dried solvents in Schlenk tubes under an Ar atmosphere. Solvents were distilled from appropriate drying agents and stored under argon. ^1H NMR spectra were recorded on a Bruker AC 300P spectrometer in CD_2Cl_2 or $CDCl_3$ at 300 MHz. Tetramethylsilane was used as the internal reference. The temperatures are given within 1 K. EPR spectra were recorded in CH_2Cl_2 on a Bruker EMX 8/2,7 spectrometer operating at X-band frequencies. Samples were cooled to 4.2 K in a stream of helium gas in frozen CH_2Cl_2, the temperature of which was controlled by an Oxford Instruments ESR 900 cryostat. Visible spectra were measured on a Uvikon 941 spectrometer in CH_2Cl_2.

Reagents

The following iron chlorins were prepared by literature methods: Fe(TPC)Cl[63] and $Fe(TPC)CF_3SO_3$.[21] 1-Methylimidazole is commercially available. Abbreviations used: TPC = 7,8-dihydro-5,10,15,20-tetraphenylporphyrin dianion (tetraphenylchlorin), TMC = 7,8-dihydro-5,10,15,20-tetra(2,4,6-trimethylphenyl)porphyrin dianion (tetramesitylchlorin); QTPP = quinoxalinotetraphenylporphyrin, TPP = 5,10,15,20-tetraphenylporphyrin dianion.

Synthesis

$[Fe(TPC)(1\text{-}MeIm)_2]CF_3SO_3$ **1**. To a solution of 0.1 g (0.12 mmol) of $[Fe(TPC)]$ CF_3SO_3 in 5 ml of dichloromethane was added 2.5 equiv. (13 μl) of 1-methylimidazole by a syringe under stirring at room temperature. After stirring for 15 min, the solution became green. Then 10 ml of pentane was added and the solution was set aside overnight for crystallization at 0 °C. Purple crystals of $[Fe(TPC)(1\text{-}MeIm)_2]CF_3SO_3$ were collected by filtration and washed with hexane. The yield was 0.097 g (83 %). UV-vis (CH_2Cl_2): λ_{max}/nm 417 (ε 60.7 dm^3 $mmol^{-1}$ cm^{-1}), 595 (ε 4.6), 634 (ε 10.5); FAB MS (*m*/*z*) : 670, $[M - 2\,(1\text{-}MeIm) - CF_3SO_3]^+$.

Single-crystal structure determination on $[Fe(TPC)(1\text{-}MeIm)_2]CF_3SO_3$

The X-ray study was carried out on a NONIUS Kappa CCD diffractometer using graphite monochromatized Mo Kα radiation. The cell parameters were obtained with Denzo and Scalepack[64] with 10 frames (Φ rotation: 1° per frame). Crystallographic data are presented in Table 3. Crystals of the compound were obtained as reported above. The data collection ($2\theta_{max}$ = 60°, 151 frames *via* 2.0° ω rotation and 18 s per frame, range *h,k,l*: *h* 0.11, *k* −13.13, *l* −17.17 gave 14197 reflections. The data reduction with Denzo and Scalepack[64] leads to 5427 independent reflections from which 5114 reflections satisfied $I > 2.0\sigma(I)$. The structure was solved with SIR-97 which reveals the non-hydrogen atoms of the structure, the triflate anions and some residual solvents.[65] Near the cation and the counterion, there are some residual density peaks identified as a non-stoichiometric disordered ether molecule (about 20%). After anisotropic refinement, many hydrogen atoms were found with a Fourier difference. The whole structure was refined by using full-matrix least-square techniques[66] (use of *F* magnitude; *x*, *y*, *z*, $\beta_{i,j}$ for Fe, N and C atoms; *x, y, z*, $\beta_{i,j}$ for triflate anions and riding mode for hydrogen atoms; 627 variables and 5114 observations with $I > 2.0\sigma(I)$; calc $w = 1/[\sigma^2(F_o)^2 + (0.159P)^2 + 1.58P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.068$, $R_w = 0.194$ and $S_w = 1.059$ (residual $\Delta\rho < 1.51$ eA^{-3}). Atomic scattering factors were from the International Tables for X-ray Crystallography.[67] ORTEP views were realized with PLATON98.[68]

Table 3 Crystallographic data for $[Fe(TPC)(1\text{-}MeIm)_2]CF_3SO_3$

Empirical formula	$FeC_{53}H_{42}N_8F_3O_3S$
FW	984.04
Crystal system	Triclinic
Space group	*P*1
a/Å	9.1730 (3)
b/Å	10.6674 (4)
c/Å	13.3392 (5)
α/deg	80.497 (2)
β/deg	79.141 (2)
γ/deg	75.696 (2)
V/Å^3	1232.48 (8)
Z	1
ρ_{calcd}/g cm^{-3}	1.326
μ/cm^{-1}	4.03
T/K	150
R_w	0.194
Final *R*	0.068

CCDC reference number 184540.

See http://www.rsc.org/suppdata/dt/b2/b204006a/ for crystallographic data in CIF or other electronic format.

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