

# Molecular Structure of the Chloroiron(III) Derivative of the *meso*-Unsubstituted 2,7,12,17-Tetramethyl-3,8,13,18-tetramesitylporphyrin and Weak Ferromagnetic Exchange Interactions in the $A_{1u}$ Oxoiron(IV) Porphyrin $\pi$ Radical Cation Complex

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**Abstract:** The molecular structure of the chloroiron(III) porphyrinate [Fe<sup>III</sup>Cl(tmtmp)] (**1**) is described. The doming of the bifacially encumbered tmtmp dianionic ligand present in **1** is characterized by a separation of 0.09(1) Å between the mean plane of the four pyrrole nitrogens (4N<sub>p</sub>) and that of the porphyrin core. The coordination polyhedron of the five-coordinate iron atom is a square pyramid of C<sub>4v</sub> symmetry. The metal is displaced by 0.44(1) Å from the 4N<sub>p</sub> mean plane towards the axial chloro ligand. The Fe–N<sub>p</sub> and Fe–Cl bond lengths are 2.057(6)

and 2.223(5) Å, respectively. Upon treatment of [Fe<sup>III</sup>Tf(tmtmp)] (**2**) with *m*-chloroperoxybenzoic acid, the green oxoferryl  $\pi$  radical cation complex [Fe<sup>IV</sup>=O(tmtmp<sup>•+</sup>)]<sup>+</sup> (**3**) is obtained. It has been studied by EPR, Mössbauer, and resonance Raman spectroscopy. It exhibits an EPR spectrum strikingly similar

to those of compounds I of *Micrococcus lysodeikticus* catalase (MLC-I) and ascorbate peroxidase (APX-I). The exchange interactions between the spins of the radical cation and the ferryl iron are of the ferromagnetic type and are the weakest ever found for a synthetic compound I model. The shift of +22 cm<sup>-1</sup> in the radical marker band  $\nu_2$  in the resonance Raman spectra upon oxidation of **2** to **3** confirms that the electronic state of the porphyrin  $\pi$  radical cation is predominantly  $^2A_{1u}$  in this tmtmp compound I model.

## Keywords

electronic structure · exchange coupling · heme proteins · iron complexes · porphyrins

## Introduction

In their ferric resting states, heme-containing peroxidases and catalases are oxidized by two equivalents of peroxides or hydroperoxides to yield transient intermediates called compound I.<sup>[1–4]</sup> Based on UV/Vis, resonance Raman, EPR, and Mössbauer studies, they have been formulated as oxoiron(IV) porphyrin  $\pi$  radical cation complexes.<sup>[5–8]</sup> The proximity of the

$S_1 = 1$  iron(IV) center to the  $S_2 = 1/2$  ligand-centered  $\pi$  radical cation creates the possibility of metal–ligand exchange interactions. Since the first report of a green oxoferryl  $\pi$  radical cation species generated from a *meso*-tetramesitylporphyrinatoiron(III) derivative, the electronic structures of compound I models of *meso*-tetraaryl(tetrapyrrolic) ligands have been studied in detail.<sup>[9–16]</sup> In all the synthetic model systems studied to date, the exchange interactions (represented by the term  $-J(S_1 \cdot S_2)$  in the spin Hamiltonian) were found to be ferromagnetic and moderate in magnitude.<sup>[12–14]</sup> By contrast, in the compounds I of chloroperoxidase (CPO), horseradish peroxidase (HRP), *Micrococcus lysodeikticus* catalase (MLC), and ascorbate peroxidase (APX), the exchange interactions range from weakly anti-ferromagnetic to weakly ferromagnetic.<sup>[17–20]</sup>

Oxoiron(IV)  $\pi$  radical cation species of synthetic pyrrole  $\beta$ -tetramethyl- $\beta$ -tetraaryl-substituted porphyrins, such as 2,7,12,17-tetramethyl-3,8,13,18-tetramesitylporphyrin (tmtmpH<sub>2</sub>, Fig. 1) and 2,7,12,17-tetramethyl-3,8,13,18-tetrakis(2,6-dichlorophenyl)porphyrin (tmtcphH<sub>2</sub>), have recently been reported.<sup>[21,22]</sup> In these porphyrins, the *meso* positions are unsubstituted as in *heme-b*, the prosthetic group present in CPO-I, HRP-I, MLC-I, and APX-I. The long-standing question of the electronic ground state of the porphyrin radical in these enzymic and model compound I intermediates was approached recently by using theoretical and spectroscopic methods.<sup>[23,24]</sup> Forma-

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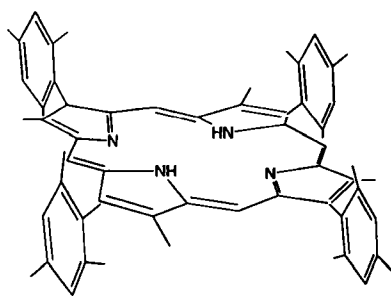
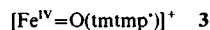
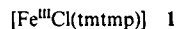


Fig. 1. Schematic representation of the structure of tmtmpH<sub>2</sub>.

tion of a  $\pi$  radical cation from *meso*-unsubstituted porphyrins is expected to proceed by electron abstraction from the  $a_{1u}$  molecular orbital. However, the assignment of an  $^2A_{1u}$  electronic state for the oxoferryl porphyrin  $\pi$  radical cations of (tmtmp)H<sub>2</sub> and (tmtcnp)H<sub>2</sub> complexes rests, to date, only on the distribution of unpaired electron spin density inferred from <sup>1</sup>H hyperfine shifts of *meso* and pyrrole  $\beta$ -methyl protons.<sup>[22]</sup> By contrast, the predominantly  $^2A_{2u}$  electronic state of the *meso*-tetramesitylporphyrin (TMP)  $\pi$  radical cation in [Fe<sup>IV</sup>=O(tmp<sup>•+</sup>)]<sup>+</sup> is firmly established by an array of theoretical and spectroscopic investigations.<sup>[10–12]</sup> Moreover, the influence of the electronic ground state on the magnitude of the exchange interactions in compounds **1** and their models so far remains poorly understood.

We report here the X-ray structure of the chloroiron(III) porphyrinate **1**, the generation of the compound **1** analogue **3** from **2**, and the characterization of **3** by EPR, Mössbauer, and



resonance Raman spectroscopy. Our resonance Raman studies confirm the assignment of the  $^2A_{1u}$  electronic state for the porphyrin  $\pi$  radical cation present in **3**. Ferromagnetic exchange interactions, smaller in magnitude than for any hitherto reported synthetic compound **1** analogue, are established by EPR and Mössbauer spectroscopy and found to be similar to the exchange interactions reported recently for MLC-I and APX-I.<sup>[17–20]</sup>

## Experimental Section

**Materials:** Methylene chloride and butyronitrile were distilled prior to use from calcium hydride and sodium carbonate, respectively. *m*-Chloroperoxybenzoic acid (85%) was purchased from Aldrich, extracted with methylene chloride, and recrystallized prior to use. The free bases tmtmpH<sub>2</sub> and tmtcnpH<sub>2</sub> were prepared according to published methods [29]. Metalation by the standard FeCl<sub>2</sub>/DMF procedure [30] yielded **1**. The trifluoromethanesulfonate complex **2** was used as precursor of **3**, and was obtained from the chloroferric derivative **1** by metathesis with silver triflate (RT, 1.2 equiv in THF) followed by extraction with distilled methylene chloride.

**X-Ray analysis:** Single crystals of the chloroferric complex of tmtmpH<sub>2</sub> were obtained by slow diffusion of pentane into a chloroform solution of [Fe<sup>III</sup>Cl(tmtmp)]·CH<sub>3</sub>OH (**1**·CH<sub>3</sub>OH). Crystal data: C<sub>61</sub>H<sub>64</sub>N<sub>4</sub>OClFe, *M<sub>r</sub>* = 960.5, dark red crystals, tetragonal, *a* = *b* = 14.845(4), *c* = 24.559(6) Å, *V* = 5412.2 Å<sup>3</sup>, *Z* = 4, *d<sub>calc</sub>* = 1.18 g cm<sup>-3</sup>,  $\mu$  = 30.147 cm<sup>-1</sup>, space group *P4/mnc*. A suitable crystal of **1**·CH<sub>3</sub>OH (0.40 × 0.40 × 0.06 mm<sup>3</sup>) was used for data collection on a PW1100/16 diffractometer at -100 °C using CuK $\alpha$  graphite monochromated radiation ( $\lambda$  = 1.5418 Å). 3445 reflections ( $3 < \theta < 52^\circ$ ) were collected. Three standard reflections measured every hour during the data collection period showed no decay. The raw data were converted to intensities and corrected for Lorentz and polarization factors. The structure was determined by direct methods using the Nonius VAX/Mo-

len package. Hydrogen atoms were introduced as fixed contributors, C-H = 0.95 Å and *B<sub>H</sub>* = 1.3 *B<sub>eq</sub>*(C). Semiempirical absorption corrections were applied before anisotropic refinements. 999 independent reflections with  $I > 3\sigma(I)$  were used in full least-squares refinements against  $|F|$ . *R*(*F*) = 0.086, *R<sub>w</sub>*(*F*) = 0.106, GOF = 1.539, final residual electron density = 0.19 e Å<sup>-3</sup>. 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-1220-19. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223) 336-033; e-mail: teched@chem-cryst.cam.ac.uk).

**Sample preparation:** [Fe<sup>IV</sup>=O(tmtmp<sup>•+</sup>)]<sup>+</sup> (**3**) was generated in methylene chloride/[D<sup>4</sup>]methanol or butyronitrile/[D<sup>4</sup>]methanol 85:15 by addition of *m*-chloroperoxybenzoic acid (mCPBA, 2 masequiv, ca. 10-fold molar excess) to the ferric triflate complex **2**. The NMR (CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>OD) and EPR (CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>OD or C<sub>6</sub>H<sub>6</sub>N/CD<sub>3</sub>OD) samples were generated directly in the tubes. The UV/Vis samples (CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>OD or C<sub>6</sub>H<sub>6</sub>N/CD<sub>3</sub>OD) were obtained in a cryostated UV/Vis cell kept at -80 °C. The Mössbauer samples (C<sub>6</sub>H<sub>6</sub>N/CD<sub>3</sub>OD) were prepared in a delrin cup stuck to a glass tube forming a reaction vessel that could be conveniently immersed in a cold bath. The Raman samples (CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>OD) were generated in a spinning quartz cell maintained at -80 °C by a home-made cryostat.

**Spectroscopy:** UV/Vis spectra were recorded on a Cary 5E spectrophotometer equipped with an Oxford Instrument cryostat, and using a quartz cuvette with a 0.1 cm path length. <sup>1</sup>H NMR data were recorded on a Bruker AC300 spectrometer at 300 MHz. EPR spectra were recorded on a Bruker ER 200 D-SRC spectrometer equipped with an Oxford Instrument liquid-helium cryostat. The Mössbauer spectrometer, equipped with helium-bath cryostats, were operated in the conventional constant acceleration mode. Resonance Raman signals were detected by an optical multichannel analyzer (EG & G Princeton Applied Research Corp., Model 1215/1216).

## Results and Discussion

Slow diffusion of pentane into a chloroform solution of [Fe<sup>III</sup>Cl(tmtmp)] (**1**) gave single crystals of the chloroferric complex **1**·CH<sub>3</sub>OH. The methanol molecule of solvation present in the unit cell comes from residual methanol introduced during the purification procedure. Per unit cell, these crystals contain four molecules of **1** lying on a crystallographic fourfold symmetry axis. This arrangement imposes *C<sub>4v</sub>* symmetry on the coordination polyhedron of iron (Fig. 2). The bifacially encumbered tmtmp dianionic ligand present in **1** displays a domed conformation characterized by a separation of 0.09(1) Å between the mean plane of the four pyrrole nitrogens (4N<sub>p</sub>) and that of the porphyrin core. The iron atom is displaced by 0.44(1) Å out of the 4N<sub>p</sub> mean plane towards the axial chloro ligand. The Fe-N<sub>p</sub> and Fe-Cl bond lengths are 2.057(6) and 2.223(5) Å, respectively. The methyl groups of the tmtmp mesityl rings, which lie

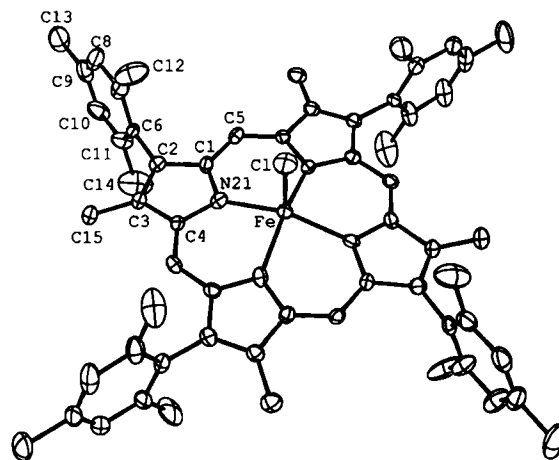


Fig. 2. Structure of [Fe<sup>III</sup>Cl(tmtmp)] (**1**) in the crystals of **1**·CH<sub>3</sub>OH (stick plot, hydrogen atoms are omitted).

2.44(1) Å above the porphyrin core mean plane, form a cavity preventing dimerization to [(tmtmp)Fe-O-Fe(tmtmp)], through  $\mu$ -oxo bond formation. The structure demonstrates that, as expected, the tmtmp ligand is able to form metal complexes in which the symmetry of the coordination polyhedron of the metal is effectively  $C_{4v}$ .

Upon addition of a tenfold molar excess of mCPBA in deuterated methanol to solutions of the ferric triflate [Fe<sup>III</sup>Tf(tmtmp)] (**2**) in methylene chloride or in butyronitrile at  $-78^\circ\text{C}$ , the green oxoferryl  $\pi$  radical cation species **3** was formed.<sup>[25]</sup> The UV/Vis and NMR spectra show a clean conversion of **2** into **3**. The absorption maxima and the <sup>1</sup>H NMR chemical shifts are similar to those reported elsewhere for **3**<sup>[22]</sup> (UV/Vis (173 K, CH<sub>2</sub>Cl<sub>2</sub>:CD<sub>3</sub>OD):  $\lambda_{\text{max}}$  = 623.0, 559.5, 387.0 nm; <sup>1</sup>H NMR (173 K, CD<sub>2</sub>Cl<sub>2</sub>:CD<sub>3</sub>OD):  $\delta$  = 117.3 ( $\beta$ -methyl), 43.1 (*meso*), 13.8, 12.9 (*meta*-phenyl)).

A general feature of the synthetic oxoferryl porphyrin  $\pi$  radical cations known to date is that the exchange interactions between the spins of the ferryl iron ( $S_1 = 1$ ) and of the porphyrin  $\pi$  radical cation ( $S_2 = 1/2$ ) are of the ferromagnetic type with  $J > 0$ . EPR signals arise from the transitions within the  $M_s = \pm 1/2$  Kramers doublet of the  $S_1 = 3/2$  ground state. The spectra of the oxoferryl tetraarylporphyrin  $\pi$  radical cation derivatives typically display rhombic splittings with  $g_x$  and  $g_y$  values in the range 4.2 to 4.6 and 3.4 to 3.8, respectively, and  $g_z$  values close to 2.0.<sup>[11–15]</sup> The absorption derivative spectrum of [Fe<sup>IV</sup>=O(tmtmp)]<sup>+</sup> (**3**) deviates from this usual pattern inasmuch as it exhibits only a single broad signal centered at an apparent  $g^{\text{eff}} = 3.5$  together with a narrow intense line at  $g^{\text{eff}} = 2$  (Fig. 3). Although, the quasi-axial appearance of the

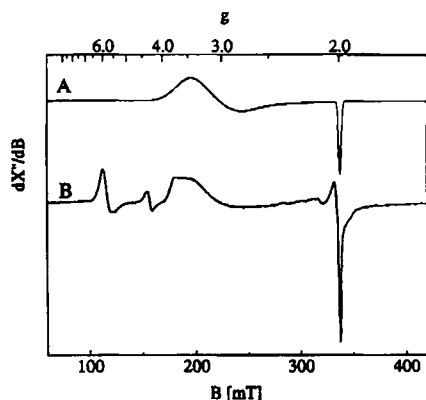


Fig. 3. A: Absorption derivative EPR spectrum of **3** in C<sub>4</sub>H<sub>7</sub>N/CD<sub>3</sub>OD (85:15) at 10 K extending from  $g = 3.5$  to 2 (intense negative line). B: EPR spectrum of reaction mixture generated from **2**. About 90% of **2** was converted. Spin quantification reveals about 60% generation of compound **1**,  $\approx 2\%$  of non-heme iron of decomposed complex (signal at  $g = 4.3$ ),  $\approx 2\%$  of “free radical” (positive line at  $g = 2$ ). Some neutral oxoferryl complex (EPR silent) is also present in the preparation. Conditions: Microwave frequency: 9.432 GHz, power: 20  $\mu\text{W}$ , modulation amplitude: 3.2 mT, modulation frequency: 100 kHz.

spectrum seems to be consistent with the putative high symmetry of the iron environment in **3**, the strong angular dependence of the line shapes in the  $g_{\perp}$  and  $g_{\parallel}$  directions is more in accord with a distribution of subspectra, resulting from distributions of spin-Hamiltonian parameters. A preliminary fit of the main feature (80% of total intensity) with a simple tensorial line-shape model yielded  $\Gamma_x = 39$  mT,  $\Gamma_y = 30$  mT,  $\Gamma_z = 5$  mT, and  $g_x = 3.48$ ,  $g_y = 3.02$ ,  $g_z = 1.995$ . The in-plane  $g$  value is the lowest ever observed for an oxoferryl porphyrin  $\pi$  radical cation complex,<sup>[10–15]</sup> and is similar to those reported for MLC-I and

APX-I in which the exchange interactions are also described as being weakly ferromagnetic.<sup>[19,20]</sup> The first-derivative EPR spectra of MLC-I and APX-I are characterized by broad signals at  $g_{\perp}^{\text{eff}} = 3.32$  and 3.27, respectively, and  $g_{\parallel}^{\text{eff}} = 2$  and 1.99, respectively. Spin expectation diagrams correlating the effective ( $g_{\perp}^{\text{eff}}$ )<sup>2</sup> and ( $g_{\parallel}^{\text{eff}}$ )<sup>2</sup> values with the ratio  $|J|/D$  have been developed for such spin-coupled systems.<sup>[17,26]</sup> This correlation, gives a value of  $|J|/D \approx 0.5$  for **3**, which represents the smallest ever reported for a synthetic compound **1** analogue and which lies in the range of the  $|J|/D$  values obtained by this approach for the weakly ferromagnetically coupled protein species MLC-I ( $|J|/D = 0.4$ ) and APX-I ( $|J|/D = 0.28$ ).<sup>[19,20,31]</sup>

Mössbauer isomer shifts and quadrupole splittings of **3** could be determined in spite of the presence of a small amount of reduced species [Fe<sup>IV</sup>=O(tmtmp)] in the sample. The parameters determined from zero-field measurements at 77 K are  $\delta = 0.10$  and  $\Delta E_Q = 1.72$  mm s<sup>-1</sup> (in butyronitrile) and lie in the normal range for oxoferryl porphyrins. The magnetic field spectra, however, deviate significantly from those of other synthetic compound **1** analogues, mainly because of short spin relaxation times, which approach the regime of the Larmor precession time (10<sup>-9</sup> s). In weak fields (20–150 mT), therefore, “intermediate relaxation spectra” with partially collapsed magnetic splittings were observed, even at temperatures down to 1.5 K. Only in strong applied fields (6–7 T), where a single magnetic sublevel ( $m_s = -1/2$ ) is populated at 1.5 K, could “static” spectra be measured (Fig. 4). Overall magnetic splittings are less than

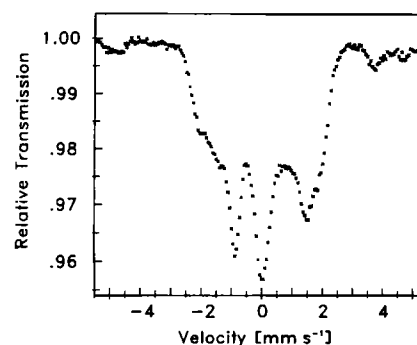


Fig. 4. Magnetic Mössbauer spectrum of **3** in C<sub>4</sub>H<sub>7</sub>N/CD<sub>3</sub>OD, recorded at 1.5 K with 7 T field applied perpendicular to the  $\gamma$  rays. The sample was about 90% enriched with <sup>57</sup>Fe. The weak lines at  $-5$  and  $+3.5$  mm s<sup>-1</sup> belong to an underlying subspectrum from contamination with non-oxidized ferric starting material.

those of the known synthetic oxoferryl porphyrin radical complexes, presumably owing to stronger mixing of the  $S_1 = 3/2$  electronic ground state and the  $S_1 = 1/2$  excited state; this implies a small  $D$  and therefore a small  $J$ . The characteristic four-line pattern of the spectra, however, is still present. The pattern results from the combined effects of ferryl iron quadrupole interaction and “ $S_1 = 3/2$ ” magnetic hyperfine interaction and therefore corroborates the nature of the electronic ground state, which, as mentioned above, is affected by the close-lying excited state. A full analysis of field- and temperature-dependent spectra is in progress, in conjunction with spin-Hamiltonian simulations of the EPR spectra.

Resonance Raman samples of **3** were generated from the triflate complex **2** at  $-78^\circ\text{C}$  in CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>OD (85:15). The assignments of the radical marker bands  $\nu_2$  and  $\nu_4$  are based on polarization studies with excitation at 3564 Å. Oxidation was accompanied by band broadening and shifting, along with decreased intensity, as expected for generation of a porphyrin  $\pi$  radical cation species (Fig. 5 and Table 1).<sup>[27]</sup> The  $\nu_2$  band at

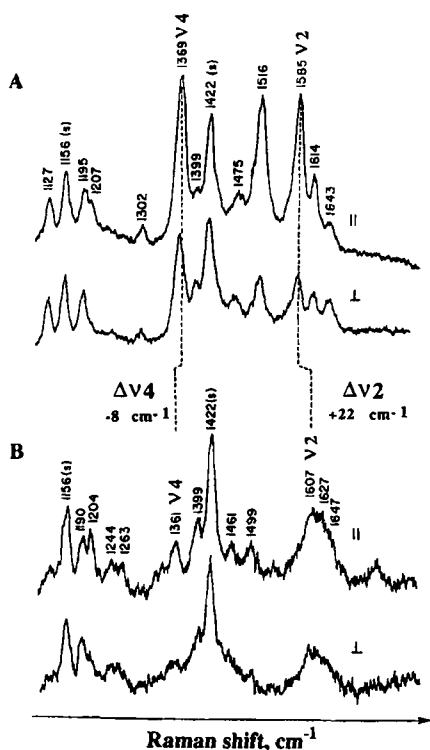


Fig. 5. Resonance Raman spectra of 2 (A) and 3 (B) formed by mCPBA oxidation of the sample shown in (A) at  $-78^{\circ}\text{C}$  (S: solvent). Band intensities in parallel and perpendicular polarizations are normalized to the intensities of the depolarized bands (band assignments are listed in Table 1).

Table 1. Band assignments in the resonance Raman spectra of 2 and 3 (in  $\text{cm}^{-1}$ ).

	2	3	2	3
$\tilde{\nu}_{10}$	1643	1647	$\tilde{\nu}_{20}$	1399
$\tilde{\nu}_{\text{phenyl}}$	1614	1627	$\tilde{\nu}_4$	1369
$\tilde{\nu}_2$	1585	1607	$\tilde{\nu}_1$	1207
$\tilde{\nu}_3$	1516	1499	$\tilde{\nu}_{14}$	1195
$\tilde{\nu}_{28}$	1475	1461	$\text{CH}_2\text{Cl}_2$	1156
$\text{CH}_2\text{Cl}_2$	1422	1422	$\tilde{\nu}_{30}$	1127

$1585\text{ cm}^{-1}$  in the non-radical ferric precursor 2 shifts in frequency to  $1607\text{ cm}^{-1}$  (+  $22\text{ cm}^{-1}$ ) on oxidation to 3. Also,  $\nu_4$  shifts down, from  $1369\text{ cm}^{-1}$  in the precursor 2 to  $1361\text{ cm}^{-1}$  in the compound I model 3. The shift of  $\nu_2$  is highly sensitive to the symmetry state, shifting up in frequency in  $^2A_{1u}$  radicals and down in  $^2A_{2u}$  radicals. The correlation of  $\nu_4$  is less certain, but a shift to lower frequency is expected for an  $^2A_{1u}$  electronic state of a  $\pi$  radical cation derivative. The shift of +  $22\text{ cm}^{-1}$  in  $\nu_2$  and -  $8\text{ cm}^{-1}$  in  $\nu_4$  are thus in complete accord with the  $^2A_{1u}$  electronic state assignment for the porphyrin  $\pi$  radical cation of 3.<sup>[22, 31]</sup>

## Conclusion

The X-ray structure of the chloroferric complex  $[\text{Fe(III)Cl}(\text{tmtmp})]$  (1) demonstrates that the bifacially hindered, *meso*-unsubstituted tetramethyltetramesitylporphyrin (tmtmp) forms complexes in which the coordination polyhedron of the metal has a high symmetry. In the solid state, the coordination polyhedron of iron in 1 has effective  $C_{4v}$  symmetry. We have generated the corresponding oxo-ferryl  $\pi$  radical cation species,  $[\text{Fe}^{\text{IV}}=\text{O}(\text{tmtmp}^{\bullet})]^+$  (3), which has been studied by an array of

different spectroscopic techniques. As for other synthetic compound I analogues, the exchange interactions between the two spins of the ferryl and the porphyrin radical are ferromagnetic. However, EPR studies show that the magnitude of  $|J|/D$  arising in 3 is the smallest yet observed in a model compound.<sup>[30]</sup> Mössbauer studies establish that the zero-field splitting parameter  $D$  is small, requiring that  $J$  also be smaller in magnitude than the values reported for any synthetic compound I model. Assuming that dipole interactions are not contributing significantly to the exchange interactions,  $J$  is the sum of ferromagnetic  $J_F$  and antiferromagnetic  $J_{AF}$  components ( $J = J_F + J_{AF}$ ).<sup>[28]</sup> Because the symmetry of the coordination polyhedron in 3 is, most probably, higher than  $C_s$ , overlap between the singly occupied iron  $d_{xz}$  and  $d_{yz}$  atomic orbitals and the singly occupied porphyrin HOMO, whether  $a_{1u}$  or  $a_{2u}$ , is symmetry forbidden.<sup>[28]</sup> As a result, antiferromagnetic exchange terms cannot explain the small value of  $J$ . The resonance Raman studies offer an explanation by confirming the  $^2A_{1u}$  electronic state for the radical in 3. Since nodes in the  $a_{1u}$  molecular orbital at the pyrrole nitrogens concentrate the unpaired spin density mainly on the  $C_\alpha$  and  $C_\beta$  carbon atoms of the pyrrole rings and increase the average distance between the spins of iron(IV) and the porphyrin  $\pi$  radical cation, weaker exchange interactions should result when the porphyrin  $\pi$  radical cation is in the  $^2A_{1u}$  rather than in the  $^2A_{2u}$  electronic state.

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- [1] H. H. Dunford, in *Peroxidases in Chemistry and Biology II* (Eds.: J. Everse, K. E. Everse, M. B. Grisham), CRC Press, Boca Raton, 1991, pp. 1–24.
- [2] B. W. Griffin, *Peroxidases in Chemistry and Biology II* (Eds.: J. Everse, K. E. Everse, M. B. Grisham), CRC Press, Boca Raton, 1991, pp. 85–137.
- [3] G. R. Schonbaum, B. Chance, in *The Enzymes* (Eds.: P. D. Boyer, H. Lardy, K. Myrbach), Academic Press, New York, 1976, pp. 363–408.
- [4] H. R. Bosshard, H. Anni, T. Yonetani, in *Peroxidases in Chemistry and Biology II* (Eds.: J. Everse, K. E. Everse, M. B. Grisham), CRC Press, Boca Raton, 1991, pp. 51–84.
- [5] W. E. Blumberg, J. Peisach, B. A. Wittenberg, J. B. Wittenberg, *J. Biol. Chem.* 1968, 243, 1854–1862.
- [6] T. Kitagawa, Y. Mizutani, *Coord. Chem. Rev.* 1994, 135/136, 685–735.
- [7] A. X. Trautwein, E. Bill, E. L. Bominaar, H. Winkler, *Struct. Bonding* 1991, 78, 1–95.
- [8] It has also been postulated that in HRP-I and in BI CAT-I, one oxidizing equivalent is delocalized over the heme and the proximal axial ligand. See: V. Thanabal, G. N. La Mar, J. S. De Ropp, *Biochemistry*, 1988, 27, 5400–5407; W.-J. Chuang, H. E. Van Wart, *J. Biol. Chem.* 1992, 267, 13293–13301.
- [9] J. T. Groves, R. C. Haushalter, M. Nakamura, T. E. Nemo, B. J. Evans, *J. Am. Chem. Soc.* 1981, 103, 2884–2886.
- [10] B. Boso, G. Lang, T. J. McMurry, J. T. Groves, *J. Phys. Chem.* 1983, 79, 1122–1126.
- [11] E. Bill, X.-Q. Ding, E. L. Bominaar, A. X. Trautwein, H. Winkler, D. Mandon, R. Weiss, A. Gold, K. Jayaraj, W. E. Hatfield, M. L. Kirk, *Eur. J. Biochem.* 1990, 188, 665–672.
- [12] D. Mandon, R. Weiss, K. Jayaraj, A. Gold, J. Turner, E. Bill, A. X. Trautwein, *Inorg. Chem.* 1992, 31, 4404–4409.
- [13] P. Ochsenbein, D. Mandon, J. Fischer, R. Weiss, R. N. Austin, K. Jayaraj, A. Gold, J. Turner, E. Bill, M. Mütter, A. X. Trautwein, *Angew. Chem. Int. Ed. Engl.* 1993, 32, 1437–1439.
- [14] M. Mütter, E. Bill, A. X. Trautwein, D. Mandon, R. Weiss, A. Gold, K. Jayaraj, R. N. Austin, *Hyperfine Interactions*, 1994, 91, 803–808.
- [15] Z. Gross, S. Nimri, *Inorg. Chem.* 1994, 33, 1731–1732.
- [16] K. Jayaraj, J. Turner, A. Gold, D. A. Roberts, R. N. Austin, D. Mandon, R. Weiss, E. Bill, M. Mütter, A. X. Trautwein, *Inorg. Chem.* 1996, 35, 1632–1640.
- [17] R. Rutter, L. P. Hager, H. Dhonau, M. Hendrich, M. Valentine, P. Debrunner, *Biochemistry*, 1984, 23, 6809–6816.

- [18] C. E. Schulz, R. Rutter, J. T. Sage, P. G. Debrunner, L. P. Hager, *Biochemistry* **1984**, *23*, 4743–4754.
- [19] M. J. Benecky, J. E. Frew, N. Scowen, P. Jones, B. M. Hoffman, *Biochemistry* **1993**, *32*, 11929–11933.
- [20] W. R. Patterson, T. L. Poulos, D. B. Goodin, *Biochemistry* **1995**, *34*, 4342–4345.
- [21] H. Fujii, K. Ichikawa, *Inorg. Chem.* **1992**, *31*, 1110–1112.
- [22] H. Fujii, *J. Am. Chem. Soc.* **1993**, *115*, 4641–4648.
- [23] P. Du, G. H. Loew, *Biophys. J.* **1995**, *68*, 69–80.
- [24] S. Hashimoto, Y. Mizutani, Y. Tatsuno, T. Kitagawa, *J. Am. Chem. Soc.* **1991**, *113*, 6542–6549.
- [25] The same procedure was applied to the chloroferric derivative of the  $\beta$ -tetramethyl- $\beta$ -tetrakis(2,6-dichlorophenyl)porphyrin (tmdcphp<sub>2</sub>). UV/Vis and NMR data are similar to those reported in ref. [21]; [Fe<sup>IV</sup>=O(tmdcphp<sup>+</sup>)]<sup>+</sup> (**5**): UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>:CD<sub>3</sub>OD, 173 K):  $\lambda_{\text{max}}$  = 647.0, 590.0, 399.0 nm<sup>-1</sup>; <sup>1</sup>H NMR (173 K, CD<sub>2</sub>Cl<sub>2</sub>:CD<sub>3</sub>OD):  $\delta$  = 135.9 ( $\beta$ -methyl), –4.0 (*meso*), 10.6, 9.3 (*meta*-phenyl). A preliminary EPR spectrum of **5** is similar to that of **3**, with  $g_{\perp}$  = 3.5 and  $g_{\parallel}$  = 1.99 at 10 K, giving a similar  $J/D$  ratio of 0.5.
- [26] M. Mütter, PhD dissertation, **1996**, Medizinische Universität Lübeck (Germany)
- [27] T. Kitagawa, Y. Mizutani, *Coord. Chem. Rev.* **1994**, *135/136*, 685–735
- [28] C. A. Reed, R. D. Orosz, in *Research Frontiers in Magnetochemistry* (Ed.: C. J. O'Connor), World Scientific Publishing, **1993**.
- [29] N. Ono, H. Kawamura, M. Bougaishi, K. Maruyama, *Tetrahedron*, **1990**, *46*, 7483–7496.
- [30] J. W. Büchler in *The Porphyrins* (Ed.: D. Dolphin), Academic Press, New York, **1979**, pp. 389–483.
- [31] Note added in proof: Since the submission of this manuscript, two publications appeared giving EPR and resonance Raman results for [Fe<sup>IV</sup>=O(tmtmp<sup>+</sup>)]<sup>+</sup> (**3**) similar to those reported in this paper: H. Fujii, T. Yoshimura, H. Kamada, *Inorg. Chem.* **1996**, *35*, 2373–2377; K. Czarnecki, M. L. Proniewicz, H. Fujii, J. R. Kincaid, *J. Am. Chem. Soc.* **1996**, *118*, 4680–4685.