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Effect of the Ruffled Porphyrin Ring on Electronic Structures: Structure and Characterization of [Fe(TalkylP)(OCIO₃)] and [Fe(TPrP)(THF)₂](ClO₄) (alkyl = Ethyl, Et and *n*-Propyl, Pr)

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Abstract

We report the synthesis of Fe(TalkylP)(OCIO₃) (alkyl = ethyl and propyl) and [Fe(TPrP)(THF)₂](ClO₄), which are characterized by UV-vis, EPR, X-ray crystallography, and solid-state magnetic susceptibilities. The macrocycles of all three complexes are ruffled, all of the structural features for [Fe(TETP)(OCIO₃)] and [Fe(TPrP)(OCIO₃)] are characteristic of the nearly pure *S* = 3/2 state, while the structural parameters for [Fe(TPrP)(THF)₂](ClO₄) feature a pure intermediate-spin (*S* = 3/2) state, which are all consistent with EPR and magnetic data. It is clear from these studies that the ruffled conformation plays a significant role in affecting the extent of *S* = 3/2 character.

Introduction

Physical and chemical properties of metalloporphyrins are mediated by the electronic configuration of the central metal ion. Iron(III) porphyrinate complexes that are best described as a quantum admixture (*S* = 3/2, 5/2) have been known for many years.^{1,2} Previous studies of the admixed-spin complexes indicate that the nature of the axial ligand can govern the degree of *S* = 3/2 character; the magnetochemical series ranking of ligand field strengths was developed by Reed and co-workers based on spin states of iron(III) tetraphenylporphyrin complexes.³ Recently, more attention has been focused on the role of the porphyrin ring conformation in determining the extent of *S* = 3/2 character.⁴

Conformational flexibility of the porphyrin macrocycle has been considered as a means of affecting the redox, spectroscopic and catalytic properties of metalloporphyrins and can be involved in controlling of the electronic configuration of iron porphyrins.^{5–7} Rath and Ghosh⁸ reported that there are two different iron spin states in μ -hydroxodiiron(III) bisporphyrin complex, one is the high-spin state (*S* = 5/2), the other is the admixed spin-state (*S* = 5/2, 3/2), and which is possibly caused by the differing extent of the ruffling distortion of the two porphyrin rings. Moreover, the ground electronic state of chloro(porphyrinato)iron(III) complexes is typically high-spin; however, [Fe(OMTPP)(Cl)]

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Supporting Information Available. Crystallographic details (Tables S1–S3) are given in the supplementary material. This material is available free of charge via the Internet at <http://www.worldscinet.com/jpp/jpp.shtml>. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC 896004 - 896006. Copies can be obtained on request, free of charge, via www.ccdc.cam.ac.uk/datarequest/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

and $[\text{Fe}(\text{OETPP})(\text{Cl})]$,^{9,10,11} are known to have an admixed intermediate spin, but in distinctly varying amounts.

Compared to well-documented tetraarylporphyrin complexes, tetraalkylporphyrin complexes have shown greater differences in physiochemical properties thanks to their nonplanar core conformations.^{12–21} Nakamura and co-workers utilized the NMR technique to determine electronic structures in a series of five- and six-coordinate (*meso*-tetraalkylporphyrinato)iron(III) complexes.^{20,22,23} We have previously studied neutral and π -cation radical derivatives of $[\text{Fe}(\text{TalkylP})(\text{Cl})]$ (alkyl = ethyl, *n*-propyl and *n*-hexyl), which revealed intermolecular π - π interactions controlled by the alkyl groups at the *meso*-positions.²⁴ In this paper, we explore the effect of the core conformation on the electronic structures. The present paper reports the synthesis of $[\text{Fe}(\text{TalkylP})(\text{OCIO}_3)]$ (alkyl = Ethyl and propyl) and $[\text{Fe}(\text{TPrP})(\text{THF})_2]\text{ClO}_4$, which are characterized by UV-vis, EPR, X-ray crystallography, and solid-state magnetic susceptibilities and explore effect of the substituents on *meso*-positions on core conformation. It is clear from these studies that the ruffling conformation plays a significant role in affecting the extent of $S = 3/2$ character.

Experimental Section

General Information

All manipulations were carried out under argon using a double mani-fold vacuum line, Schlenkware, and cannula techniques. Dichloromethane was distilled over CaH_2 , tetrahydrofuran (THF) and hexanes were distilled over sodium benzophenone. All other chemicals were used as received from Aldrich or Fisher. *meso*-Tetra-*n*-propylporphyrin (H_2TPrP) was prepared according to Neya's method,²⁵ while *meso*-tetraethylporphyrin (H_2TEtP) was prepared according to Lindsey's method.²⁶ The chloroiron(III) derivatives $[\text{Fe}(\text{TPrP})(\text{Cl})]$ and $[\text{Fe}(\text{TEtP})(\text{Cl})]$ were synthesized by literature methods.²⁷

Preparation of $[\text{Fe}(\text{TalkylP})(\text{OCIO}_3)]$ (alkyl = Et and Pr) complexes

$[\text{Fe}(\text{TPrP})(\text{Cl})]$ (20 mg, 0.035 mmol) and AgClO_4 (11 mg, 0.054 mmol) were placed in a 100-mL Schlenk flask, and dichloromethane (~20 mL) was added. The solution was stirred for 20 hrs and filtered/transferred into another small flask. The filtrate was layered with hexane. Red-purple crystals formed after ~4 days. UV-vis and IR spectra were measured on samples comprised of selected crystals. UV-vis (CH_2Cl_2 solution): λ_{max} : 394, 524, 708 nm. IR(KBr): $\nu(\text{ClO}_4)$ 1161(s), 1080(s), 638(m) cm^{-1} . $[\text{Fe}(\text{TEtP})(\text{OCIO}_3)]$: UV-vis (CH_2Cl_2 solution): λ_{max} : 401, 522, 706 nm. IR(KBr): $\nu(\text{ClO}_4)$ 1161(s), 1080(s), 626(m) cm^{-1} .

Preparation of $[\text{Fe}(\text{TPrP})(\text{THF})_2]\text{ClO}_4$

$[\text{Fe}(\text{TPrP})(\text{Cl})]$ (20 mg, 0.035 mmol) and AgClO_4 (11 mg, 0.054 mmol) were placed in a 100-mL Schlenk flask, and THF (~20 mL) was added. The solution was stirred overnight and filtered/transferred into a small Schlenk flask. The filtration solution was layered with hexane. Dark-purple crystals formed after ~5 days. UV-vis (THF): λ_{max} : 394, 533, 703 nm. IR(KBr): $\nu(\text{ClO}_4)$ 1145(s), 1116(s), 1080(s, br), 637(m), 624(m) cm^{-1} .

X-Ray Structure Determinations

X-ray diffraction data for $[\text{Fe}(\text{TPrP})(\text{OCIO}_3)]$, $[\text{Fe}(\text{TEtP})(\text{OCIO}_3)]$ and $[\text{Fe}(\text{TPrP})(\text{THF})_2]\text{ClO}_4$ complexes were collected on a Nonius FAST area-detector diffractometer. Our detailed methods and procedure for small molecular X-ray data collection have been described previously.²⁸

All structures were solved by direct methods.²⁹ Subsequent difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. All non-hydrogen atoms were

refined anisotropically by full-matrix least-squares method³⁰ except one oxygen atom [O(2a) and O(2b)] in [Fe(TPrP)(OCIO₃)] and three oxygen atoms [O(4a) and O(4b), O(5a) and O(5b), O(6a) and O(6b)] in [Fe(TPrP)(THF)₂]ClO₄. Hydrogen atoms of the porphyrin ligands and the solvent molecule were idealized with the standard SHELXL idealization methods. Brief crystallographic data for all complexes are listed in Table 1.

Physical Characterization

UV/visible spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer and IR spectra on a Perkin-Elmer model 883 or on a Perkin-Elmer Paragon 1000 as KBr pellets. Magnetic susceptibility measurements were obtained on ground samples in the solid state over the temperature range 6–300 K on a Quantum Design MPMS SQUID susceptometer. All samples were immobilized in Dow Corning silicone grease. Measurements at two fields (2 and 20 kG) showed that no ferromagnetic impurities were present. χ_M was corrected for the underlying porphyrin ligand diamagnetism according to previous experimentally observed values;³¹ all remaining diamagnetic contributions (χ_{dia}) were calculated using Pascal's constants.^{32,33} All measurements included a correction for the diamagnetic sample holder and diamagnetic immobilizing agent.

Results and Discussion

We report the synthesis and characterization (including UV-Visible and EPR spectra, magnetic susceptibility data and crystal structures) of [Fe(TEtP)(OCIO₃)], [Fe(TPrP)(OCIO₃)] and [Fe(TPrP)(THF)₂]ClO₄. Labeled ORTEP diagram of [Fe(TEtP)(OCIO₃)] and [Fe(TPrP)(OCIO₃)] are shown in Figure 1 and 2. Table 2 lists selected bond lengths and angles for both complexes. The coordination environments of the iron atoms in [Fe(TEtP)(OCIO₃)] and [Fe(TPrP)(OCIO₃)] are similar. The axial Fe–O and average Fe–N_p distances are 2.0840(15) and 1.974(5) Å for [Fe(TEtP)(OCIO₃)], and 2.0631(18) and 1.972(4) Å for [Fe(TPrP)(OCIO₃)].

The average Fe–N_p distances are in accord with those expected for an intermediate-spin state of dominant $S = 3/2$ character and not the high-spin state. The Fe–N_p values observed here are dramatically shorter than the average Fe–N_p distances of 2.001(5) Å in [Fe(TPP)(OCIO₃)]³⁴ and 1.994(10) Å in [Fe(OEP)(OCIO₃)],³⁵ which are both admixed-intermediate spin complexes, but are comparable to 1.978(3) Å in [Fe(TPP)(FSbF₅)] with 98% $S = 3/2$ character.³⁶ All of the structural features for [Fe(TEtP)(OCIO₃)] and [Fe(TPrP)(OCIO₃)] are characteristic of the nearly pure $S = 3/2$ state. This observation is reflected in their EPR spectra and in solid-state magnetic data.

The EPR spectra of both complexes in the solid state at 77 K show a broad peak with $g_{\perp} = 4.2$ for [Fe(TEtP)(OCIO₃)] and $g_{\perp} = 4.3$ for [Fe(TPrP)(OCIO₃)], the apparent $g_{\perp}$ is quite distinct from the range of typical high-spin ferric ($g_{\perp} \approx 6$), and close to the value predicted for intermediate-spin iron (III) porphyrin ($g_{\perp} = 4$). The effective magnetic moments (μ_{eff}) of 4.36 μ_B in [Fe(TEtP)(OCIO₃)] and 4.53 μ_B in [Fe(TPrP)(OCIO₃)] at 300K lie between theoretical spin-only values (μ_{eff}) of high-spin (5.92 μ_B) and intermediate-spin (3.87 μ_B), therefore, suggesting a predominant contribution of the $S = 3/2$ spin state to both complexes. These values are also smaller than those found in the admixed-spin systems [Fe(TPP)(OCIO₃)] (5.2 μ_B)³⁴ and [Fe(OEP)(OCIO₃)] (4.8 μ_B).³⁵

The temperature-dependent effective magnetic moments of both complexes are plotted in Figure 3, and can be fitted with a modified admixed intermediate-spin Maltempo model,³⁷

$$H = H_o + \zeta(\vec{L} \cdot \vec{S} + \vec{L}' \cdot \vec{S}') + g\beta\vec{H} \cdot (\vec{S} + \vec{S}') - 2J(\vec{S} \cdot \vec{S}')$$

where H_o is the splitting between the sextet and quartet states, and ζ is the spin-orbit coupling parameter. The fit is the solid and dashed lines in Figure 3, yielding an 8% – 11% admixture of $S = 5/2$ character in [Fe(TPrP)(OCIO₃)] and an admixture of only 1% $S = 5/2$ character in [Fe(TEtP)(OCIO₃)].

The coupling constants derived from fitting the magnetic data for both complexes imply that there is an antiferromagnetic magnetic exchange interaction of the iron(III) centers, the Fe–Fe exchange interaction in [Fe(TEtP)(OCIO₃)] is slightly bigger ($J = -1.2 \text{ cm}^{-1}$) than in [Fe(TPrP)(OCIO₃)] ($J = -0.9 \text{ cm}^{-1}$). The Fe–Fe interaction is consistent with their respective Fe...Fe distances of 5.44 and 6.07 Å in a pairwise π - π interaction.

Comparison of structural parameters with spin state for five-coordinate complexes are summarized in Table 3. It is found that there is a clear correlation between the Fe–N_p bond length and the percent $S = 3/2$ character, the shortened Fe–N_p distance is characteristic of increased $S = 3/2$ character. This trend is attributed to the axial ligand strength and core conformation changes. As shown in Figure 4 illustrating the displacements of the macrocyclic atoms from the mean plane defined by the least-squares plane of the 24-atom porphyrin ring, both of the porphyrin rings are described as having ruffled conformation, and which is more highly ruffled than that found in [Fe(TPP)(OCIO₃)],³⁴ thus resulting in a higher population of $S = 3/2$ character due to destabilization of the $d_{x^2-y^2}$ orbital.^{4,22} The saddled complexes has a different scenario from the ruffled complexes. In addition to destabilization of the $d_{x^2-y^2}$ orbital, the saddle conformation also destabilizes the iron d_{π} (d_{xz} and d_{yz}) orbitals because of the stronger interaction between the iron d_{π} and porphyrin $3e_g$ orbitals.^{4,38}

The molecular structure of [Fe(TPrP)(THF)₂](ClO₄) is shown in Figure 5. Table 4 lists selected bond lengths and angles for [Fe(TPrP)(THF)₂](ClO₄). Two THF molecules are bonded to iron atom at the distances of 2.147(4) and 2.162(4) Å (average 2.155(7) Å), the four iron–nitrogen bond distances are almost identical, and their average value is 1.970(1) Å, which is significantly shorter than the 2.016(3) and 1.999(2) Å in the admixed intermediate spin complexes, [Fe(TPP)(THF)₂](ClO₄)^{23,39} and [Fe(OEP)(THF)₂](ClO₄)⁴⁰ respectively. A powder EPR spectrum of [Fe(TPrP)(THF)₂](ClO₄) at 77 K has a signal with $g_{\perp} = 4.00$ while that obtained in CH₂Cl₂ shows signals with $g_{\perp} = 4.16$ and $g_{\parallel} = 2.00$, indicative of an intermediate-spin ($S = 3/2$) iron(III) porphyrins. The effective magnetic moments of [Fe(TPrP)(THF)₂](ClO₄), determined in the solid state, are 3.9 μ_B at 20 K and 4.1 μ_B at 300 K, and thus shows only a little temperature dependence between 300 and 20 K. The observed moments are almost identical to the spin-only value of 3.9 μ_B for the intermediate-spin state. Therefore, the electronic structure of the iron in [Fe(TPrP)(THF)₂](ClO₄) is best described by a *pure* intermediate-spin ($S = 3/2$) state.

Figure 6 presents the formal diagram of the porphinato core of [Fe(TPrP)(THF)₂](ClO₄) displaying the perpendicular displacements of each atom from the 24-atom mean plane of the porphinato core. The porphyrin ring has a ruffled conformation, similar to those observed for [Fe(TEtP)(THF)₂](ClO₄)⁴¹ and [Fe(TⁱPrP)(THF)₂](ClO₄) (ⁱPr = isopropyl).⁴² The degree of distortion increases with increasing steric bulk at *meso*-positions, with the order of the distortion [Fe(TEtP)(THF)₂](ClO₄) < [Fe(TPrP)(THF)₂](ClO₄) < [Fe(TⁱPrP)(THF)₂](ClO₄). The average Fe–N_p distances decrease in the same order with values 2.006(3), 1.970(1) and 1.967(12) Å.

The experimental studies have indicated that the highly ruffled conformation results in the destabilization of the $d_{x^2-y^2}$ orbital due to the effective interactions between four nitrogen atoms and the iron $d_{x^2-y^2}$ orbital,⁴ consequently, the electronic configuration of the iron (III) atom tends to be the intermediate-spin state with the increase of the core distortion. As demonstrated by NMR, EPR, Mössbauer and SQUID,⁴³ $[\text{Fe}(\text{TtP})(\text{THF})_2]\text{ClO}_4$ exhibits an admixture ($S = 5/2, 3/2$), but the complexes, $[\text{Fe}(\text{T}^i\text{PrP})(\text{THF})_2]\text{ClO}_4$ and $[\text{Fe}(\text{EtPrP})(\text{THF})_2]\text{ClO}_4$ (EtPr = 1-ethylpropyl) are all pure intermediate spin-states.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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9. Abbreviations: TPP, dianion of tetraphenylporphyrin; OEP, dianion of octaethylporphyrin; OMTTP, dianion of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphyrin; OETPP, dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin; N_p , porphinato nitrogen atom; H_2TPrP , dianion of *meso*-tetra-*n*-propylporphyrin; H_2TtP , dianion of *meso*-tetraethylporphyrin; $\text{H}_2\text{T}^i\text{PrP}$, dianion of *meso*-tetra-*i*-propylporphyrin.
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Figure 1. ORTEP diagram of $[\text{Fe}(\text{TEtP})(\text{OCIO}_3)]$ displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure 2. ORTEP diagram [Fe(TPrP)(OCIO₃)] displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure 3.

Comparison of observed and calculated values of $\mu_{\text{eff}}/\text{monomer}$ vs T for $\text{Fe}(\text{TEtP})(\text{OCIO}_3)$ (∇) and $[\text{Fe}(\text{TPrP})(\text{OCIO}_3)]$ ($\circ$). The lines (solid or dashed) are model calculations assuming pairwise spin coupling. The parameters used were, for $\text{Fe}(\text{TEtP})(\text{OCIO}_3)$, mixed spin ($5/2, 3/2$) with the $3/2$ excited-state multiplet at 380 cm^{-1} , spin-orbit coupling $\zeta = 35 \text{ cm}^{-1}$, and antiferromagnetic coupling with $J = -1.2 \text{ cm}^{-1}$; for $[\text{Fe}(\text{TPrP})(\text{OCIO}_3)]$, with the $3/2$ excited-state multiplet at 310 cm^{-1} , spin-orbit coupling $\zeta = 118 \text{ cm}^{-1}$, and antiferromagnetic coupling with $J = -0.9 \text{ cm}^{-1}$.

Figure 4.

Formal diagrams of the porphinato core displaying perpendicular displacements, in units of 0.01 Å, of the core atoms from the 24-atom mean plane. Also entered on the diagrams are the values of the averaged bond distances (Å) and angles (°). [Fe(TeTP)(OCIO₃)] (top) and [Fe(TPrP)(OCIO₃)] (bottom).

Figure 5. ORTEP diagram [Fe(TPrP)(THF)₂]⁺ displaying the atom labeling scheme. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure 6.

Formal diagrams of the porphinato core displaying perpendicular displacements, in units of 0.01 Å, of the core atoms from the 24-atom mean plane for [Fe(TPrP)(THF)₂](ClO₄). Also entered on the diagrams are the values of the averaged bond distances (Å) and angles (°).

Table 1

Brief crystallographic data and data collection parameters

	[Fe(TEtP)(OCIO ₃)]	[Fe(TPrP)(OCIO ₃)]	[Fe(TPrP)(THF) ₂ ClO ₄]
Formula	C ₂₈ H ₂₈ ClFeN ₄ O ₄	C ₃₂ H ₃₆ ClFeN ₄ O ₄	C ₄₀ H ₅₂ ClFeN ₄ O ₆
FW	575.84	631.95	848.26
<i>a</i> , Å	10.2565(4)	10.8344(10)	23.085(2)
<i>b</i> , Å	10.9066(9)	11.889(2)	18.8929(5)
<i>c</i> , Å	12.5276(13)	12.0571(9)	9.4840(4)
α , deg	111.095(12)	88.145(11)	90
β , deg	96.075(8)	80.165(11)	90
γ , deg	105.626(7)	72.371(10)	90
<i>V</i> , Å ³	1226.66(17)	1458.0(3)	4136.4(4)
<i>Z</i>	2	2	4
Space group	<i>P</i> $\bar{1}$	$\bar{P}$	<i>Pna</i> 2 ₁
<i>D_c</i> , g/cm ³	1.559	1.439	1.362
<i>F</i> (000)	598	662	1804
μ , mm ⁻¹	0.769	0.654	0.485
Radiation (λ , Å)	0.71073	0.71073	0.71073
Temperature, K	130(2)	130(2)	130(2)
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0464 <i>wR</i> ₂ = 0.1211	<i>R</i> ₁ = 0.0561 <i>wR</i> ₂ = 0.1249	<i>R</i> ₁ = 0.0797 <i>wR</i> ₂ = 0.1967
Final R indices [for all data]	<i>R</i> ₁ = 0.0525; <i>wR</i> ₂ = 0.1252	<i>R</i> ₁ = 0.0714 <i>wR</i> ₂ = 0.1337	<i>R</i> ₁ = 0.0984 <i>wR</i> ₂ = 0.2131

Table 2Selected bond lengths(Å) and angles(°) for [Fe(TEtP)(OCIO₃)] and [Fe(TPrP)(OCIO₃)]

	[Fe(TEtP)(OCIO ₃)]	[Fe(TPrP)(OCIO ₃)]
Bond Lengths (Å)		
Fe(1)–N(1)	1.9775(17)	1.973(2)
Fe(1)–N(2)	1.9732(16)	1.9773(19)
Fe(1)–N(3)	1.9788(16)	1.971(2)
Fe(1)–N(4)	1.9672(16)	1.9678(19)
Fe(1)–O(1)	2.0840(15)	2.0631(18)
Bond Angles(°)		
N(1)–Fe(1)–N(2)	89.29(7)	88.91(8)
N(1)–Fe(1)–N(3)	162.90(7)	165.38(8)
N(1)–Fe(1)–N(4)	89.39(7)	88.93(8)
N(2)–Fe(1)–N(3)	89.09(7)	89.25(8)
N(2)–Fe(1)–N(4)	169.33(7)	166.22(8)
N(3)–Fe(1)–N(4)	89.06(7)	89.41(8)
N(1)–Fe(1)–O(1)	102.04(7)	97.62(8)
N(2)–Fe(1)–O(1)	92.49(6)	93.40(7)
N(3)–Fe(1)–O(1)	95.04(6)	96.97(8)
N(4)–Fe(1)–O(1)	98.15(7)	100.37(7)

Table 3

Stereochemical/spin-state relationships for five-coordinate complexes.

Complex	Fe-N _{TP} , Å	Fe-A _{ax} , Å	Δ _r , Å	% S=3/2	core conformation	ref.
[Fe(TPP)(Cl)]	2.070(9)	2.211(1)	0.59	0	planar	44
1, 2-bis[Fe(OEP)- (OCIO ₃) ₂]ethane ^c	2.063(9)	1.873(9)	0.11	0	saddled	45
	2.057(9)	1.940(7)	0.11	0	saddled	45
[Fe(TPP)(OCOCF ₃)]	2.054(5)	1.921(4)	0.48	0	saddled	46
[Fe(OEP)(OCOCCl ₃)] ^b	2.033(5)	1.975(9)	0.38	22	ruffled	47
[Fe(OMTPP)(Cl)]	2.034(6)	2.247(3)	0.51	35	saddled	10
[Fe(OETPP)(Cl)]	2.031(5)	2.2418(23)	0.43	40	saddled	10
[Fe(TPP)(OCIO ₃)]	2.001(5)	2.029(4)	0.30	65	ruffled	34
[Fe(OEP)(OCIO ₃)]	1.994(10)	2.067(9)	0.26	82	planar	35
[Fe(TEP)(OCIO ₃)]	1.974(5)	2.0840(15)	0.26	99	ruffled ^d	tw
[Fe(THP)(OCIO ₃)]	1.972(4)	2.0631(18)	0.29	~91	ruffled	tw
[Fe((OETPP)(OCIO ₃)]	1.963(7)	2.059(6)	0.25	100	saddled	49

^aIron atom displacement from 24-atom core.

^bTwo crystalline forms.

^c1,2-bis[perchloratoiron(III) 5-(2,3,7,8,12,13,17,18-octaethylporphyrinyl)]ethane.

^dThere is a minor saddling component as well.

Table 4Selected bond lengths(Å) and angles(°) for [Fe(TPrP)(THF)₂]ClO₄

Bond Lengths (Å)			
Fe(1)–N(1)	1.970(4)	Fe(1)–N(4)	1.970(4)
Fe(1)–N(2)	1.971(4)	Fe(1)–O(1)	2.147(4)
Fe(1)–N(3)	1.970(4)	Fe(1)–O(2)	2.162(4)
Bond Angles (°)			
N(1)–Fe(1)–N(2)	89.82(17)	N(2)–Fe(1)–O(1)	93.20(18)
N(1)–Fe(1)–N(3)	179.49(19)	N(3)–Fe(1)–O(1)	89.70(17)
N(1)–Fe(1)–N(4)	89.92(17)	N(4)–Fe(1)–O(1)	88.19(17)
N(2)–Fe(1)–N(3)	89.97(17)	N(1)–Fe(1)–O(2)	91.32(17)
N(2)–Fe(1)–N(4)	178.59(19)	N(2)–Fe(1)–O(2)	88.73(17)
N(3)–Fe(1)–N(4)	90.31(17)	N(3)–Fe(1)–O(2)	89.14(17)
N(1)–Fe(1)–O(1)	89.84(18)	N(4)–Fe(1)–O(2)	89.89(17)
O(1)–Fe(1)–O(2)	177.75(16)		