



Synthesis, molecular structure, and properties of six-coordinate iron(III) porphyrin, [OEPFe(Pz)₂]ClO₄

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ABSTRACT

The effect of pyrazine as axial ligand on the formation and coordination of heme analogue has been studied. A new six coordinate and stable iron(III) heme analogue, [OEPFe^{III}(Pz)₂]ClO₄, where OEP is octaethylporphyrin and Pz is pyrazine, has been isolated. The compound has been characterized by different spectroscopic methods ¹H NMR, UV–Vis, IR as well as elemental analysis. ¹H NMR spectroscopy and magnetic moment measurements show that [OEPFe^{III}(Pz)₂]ClO₄ is paramagnetic and iron is six coordinate. The structure of [OEPFe^{III}(Pz)₂]ClO₄ has been determined by X-ray diffraction analysis. The four Fe–N_p bond distances have average values of 1.985 Å.

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1. Introduction

The main thrust of the initial studies on metalloporphyrins arises from the biological functions of cytochrome P₄₅₀ enzymes that contain an iron porphyrin unit and are present in most organisms [1]. The iron porphyrin compounds play important roles as an oxygen transfer and storage agent in hemoglobin and myoglobin and as an electron carrier in the cytochrome. Metalloporphyrins have a square-planar geometry in which a metal ion is chelated by the four nitrogens of a porphine ring with open coordination sites for axial ligation [2]. There have been several recent investigations of the effect of the relative orientations of planar axial ligands, and π -acceptor properties of axial ligands [3–5], on the structural and spectroscopic properties of Fe(III) porphyrinates [6]. The biological significance and rich chemistry of these compounds have promoted extensive research on model metalloporphyrins [2].

The vast majority of metalloporphyrins is mononuclear compounds and contains iron. Although most of the synthetic metalloporphyrins have no direct applications to biological systems, the studies on the model compounds, especially iron containing porphyrins, will help scientists to gain a fundamental understanding of the molecular mechanism and related chemistry such as affinity of oxygen binding and the rate of electron transfer in biological reactions [1,7,8].

The rich redox chemistry of metalloporphyrins makes them ideal templates for the design of new electron-transfer catalysts. Attaching redox active metalloporphyrins to electrodes simplifies their electrochemical study and facilitates their use as catalysts in electrochemical cells [9]. These compounds also find other applications as sensors for vapor detection [10] organometallic catalysts for hydrocarbon activation [11], sorbents for chemical analysis [12], and nonlinear optical materials [13].

We recently, reported isolation of heme analogues with weakly coordinated anion and cyanamide ligands [14,15]. Here, we report the synthesis of a new heme analogue with pyrazine ligand, [OEPFe^{III}(Pz)₂]ClO₄. As we will describe later this ligand could stabilize six coordinate iron(III) with a low spin electronic configuration. Also we report the molecular structure of [OEPFe^{III}(Pz)₂]ClO₄.

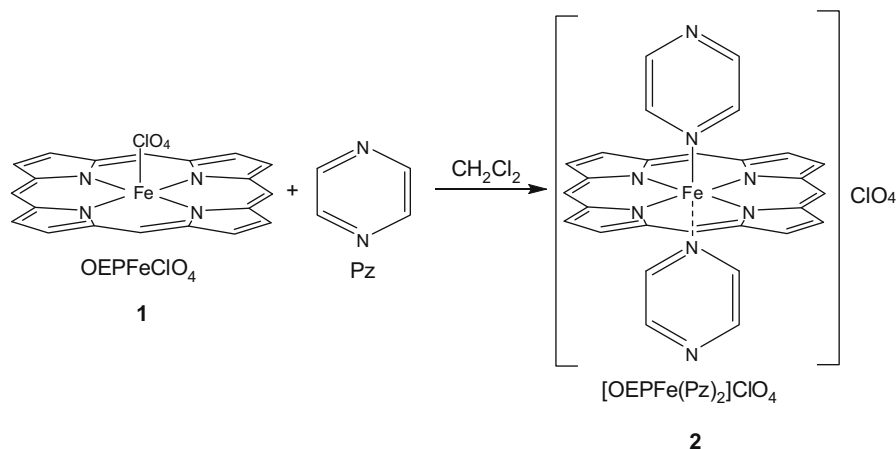
2. Experimental

[OEPFeClO₄] was synthesized by previous method [16]. All solvent were dried by refluxing for several days over Na and benzophenone under Ar and distilled immediately before use. Purified N₂ (99.9%) was used without further treatment. All reagent and solvent used in this study were obtained from Merck and Aldrich Chem. Co.

UV–Vis spectra were recorded on an analytikjena SPE-CORD S100 spectrometer with photodiode array detector. IR spectra were recorded as KBr disks on a Shimadzu IR instrument. NMR experiments were recorded at room temperature in CDCl₃ on a Bruker AV-500 spectrometer using an internal deuterated solvent lock.

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Scheme 1.

2.1. Syntheses of $[\text{OEPFe}(\text{Pz})_2]\text{ClO}_4$ (**2**)

An excess amount of Pz (47.06 mg, 0.59 mmol) was added to a solution of $[\text{OEPFeClO}_4]$ (10 mg, 0.015 mmol) (**1**) in dichloromethane (25 ml), and the mixture was stirred for 12 h in air. The volume of solution was reduced to 3 ml and then 20 ml of diethyl ether was added in, to result a dark brown product. The resulting solid was recrystallized by dissolving it in a minimum volume of dichloromethane and slowly adding ether to precipitate the product as dark brown crystals. Yield: 85%. (Scheme 1). *Anal. Calc.* for $\text{C}_{44}\text{H}_{52}\text{N}_8\text{FeClO}_4$: C, 62.33; H, 6.13; N, 13.21. Found: C, 62.14; H, 6.02; N, 13.09%. UV–Vis absorption: λ_{max} , nm (ϵ , $\text{cm}^{-1}\text{M}^{-1}$), 298 (5.4×10^4), 396 (6.2×10^4), 518 (7.1×10^3). $^1\text{H NMR}$ (CDCl_3) ppm: meso-H, 41.48; methylene-H, 33.32; methyl-H 5.45; Pz-H, 18.39, 18.64. IR (KBr): $\nu(\text{ClO}_4)$ 1086, 631 cm^{-1} .

2.2. Crystallography

Crystallization of $[\text{OEPFe}^{\text{III}}(\text{Pz})_2]\text{ClO}_4$ at room temperature by diffusion of ether into their saturated dichloromethane solutions yielded brown-needle single crystals. Measurements were made on a Bruker X8 APEX diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$). The data were collected at a temperature of -100 ± 0.1 °C to a maximum 2θ value of 56.0°. The structures were solved by direct methods [17] and expanded using Fourier techniques [18]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The material crystallizes with one half-molecule in the asymmetric unit, related to another half-molecule by inversion symmetry. Additionally, the ClO_4^- counter ion is disordered about an inversion center. The disorder was modeled using restraints on bond lengths and angles to maintain reasonable geometries. The standard deviation of an observation of unit weight was 1.03. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.97 and $-1.10\text{ e}^-/\text{\AA}^3$, respectively.

Of the 17377 reflections that were collected, 4776 were unique ($R_{\text{int}} = 0.025$); equivalent reflections were merged. The linear absorption coefficient, μ , for Mo K α radiation is 4.93 cm^{-1} .

A perspective view of complex **2** is shown in Fig. 2. Crystallographic data for $[\text{OEPFe}^{\text{III}}(\text{Pz})_2]\text{ClO}_4$ are given in Table 1. Selected interaction distances and angles are given in Table 2.

2.3. Electrochemical measurement

Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) were recorded on an Electroanalyzer system Model

Table 1

Crystallographic data for $[\text{OEPFe}(\text{Pz})_2]\text{ClO}_4$.

Empirical formula	$\text{C}_{44}\text{H}_{52}\text{N}_8\text{FeClO}_4$
Formula weight	848.24
Crystal color, habit	Brown, needle
Crystal system	Triclinic
Space group	$P\bar{1}$ (#2)
<i>a</i> (Å)	10.0008(13)
<i>b</i> (Å)	10.6477(12)
<i>c</i> (Å)	11.0352(13)
α (°)	74.527(5)
β (°)	63.509(4)
γ (°)	85.082(5)
<i>V</i> (Å ³)	1012.8(2)
<i>Z</i>	1
<i>T</i> (K)	173.0(1)
<i>D</i> _{calc} (g/cm ³)	1.391
<i>F</i> (000)	447.00
μ (cm ⁻¹)	4.93
Total data collected	17377
Number of unique data	4776 ($R_{\text{int}} = 0.025$)
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.042$, $wR_2 = 0.096$
Final <i>R</i> indices (for all data)	$R_1 = 0.052$, $wR_2 = 0.102$
Goodness-of-fit	1.02

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = \sqrt{\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2}$$

Table 2

Selected bond lengths (Å) and bond angles (°) for $[\text{OEPFe}(\text{Pz})_2]\text{ClO}_4$.

Bond length(Å)	
N(1)–Fe(1)	1.9798(15)
N(2)–Fe(1)	1.9895(15)
N(3)–Fe(1)	2.0057(16)
C(1)–N(1)	1.383(2)
C(1)–C(2)	1.437(3)
C(2)–C(3)	1.359(3)
C(2)–C(11)	1.495(3)
C(3)–C(4)	1.439(2)
C(3)–C(13)	1.494(3)
C(4)–N(1)	1.377(2)
C(4)–C(5)	1.379(3)
C(5)–C(6)	1.378(3)
Bond angles (°)	
N(1)–Fe(1)–N(3)	90.02(6)
N(2)–Fe(1)–N(3)	89.31(6)
N(1)–Fe(1)–N(2)	90.20(6)
C(1)–N(1)–Fe(1)	127.79(12)
C(4)–N(1)–Fe(1)	127.44(12)
C(6)–N(2)–Fe(1)	127.26(12)
C(9)–N(2)–Fe(1)	127.62(12)

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