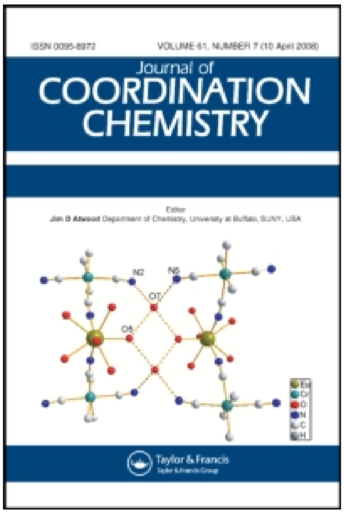

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Reactivity of verdoheme, [(OEOP)Fe^{II}(py)$_2$]Cl, toward HX (X=F, CF$_3$CO$_2$, CF$_3$SO$_3$)

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Reactivity of verdoheme, [(OEOP)$Fe^{II}(py)_2$]Cl, toward HX (X=F, CF_3CO_2, CF_3SO_3)

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Reaction of verdoheme, [(OEOP)$Fe^{II}(py)_2$]Cl, where OEOP is the monoanion of octaethyloxoporphyrin, with HX (X = F, CF_3CO_2, CF_3SO_3) has been studied in the presence of air, producing six-coordinate iron(III) product, [OEOP$Fe^{III}X_2$] (X = F (**2**), CF_3CO_2 (**3**)) or five-coordinate iron(II) oxoporphyrin compound, [OEOP$Fe^{II}(CF_3SO_3)$] (**4**). Compounds **2**, **3** and **4** have been isolated and characterized by spectroscopic methods. ^{1}H NMR spectroscopy and magnetic measurements reveal that [OEOP$Fe^{III}X_2$] (X = F and CF_3CO_2) are paramagnetic (S = 5/2) and [OEOP$Fe^{II}(CF_3SO_3)$] (**4**) is also paramagnetic (S = 2).

Keywords: Verdoheme; Octaethyloxoporphyrin; Weakly coordinating anion; Fluoride

1. Introduction

Transition metal complexes with weakly coordinating anions that act as good leaving groups are important industrial catalysts [1, 2]. Likely candidates as leaving groups include perchlorate (ClO_4^-) [3], tetrafluoroborate (BF_4^-) [4], fluorosulfate (FSO_3^-) [5], trifluoromethanesulfonate ($CF_3SO_3^-$) [5] and trifluoroacetate ($CF_3CO_2^-$) [6].

Reaction of iron(II) porphyrins with dioxygen in the presence of a reducing agent such as ascorbic acid or hydrazine in pyridine produces a deep green solution that has been known since 1930 to contain a diamagnetic iron complex, verdoheme and an iron biliverdin complex (coupled oxidation process). The coupled oxidation process has been extensively employed as a model for the heme oxidase reaction (scheme 1) [7–9].

We recently reported isolation of a new class of verdoheme analogues with weakly coordinating anions [10, 11]. Here we report the reaction of verdoheme, [(OEOP)$Fe^{II}(py)_2$]Cl, where OEOP is the monoanion of octaethyloxoporphyrin, with HX (X = F, CF_3CO_2, CF_3SO_3) in the presence of air. [(OEOP)$Fe^{II}(py)_2$]Cl reacts with HX (X = F, CF_3CO_2) to produce six-coordinate iron(III) product, [OEOP$Fe^{III}X_2$]

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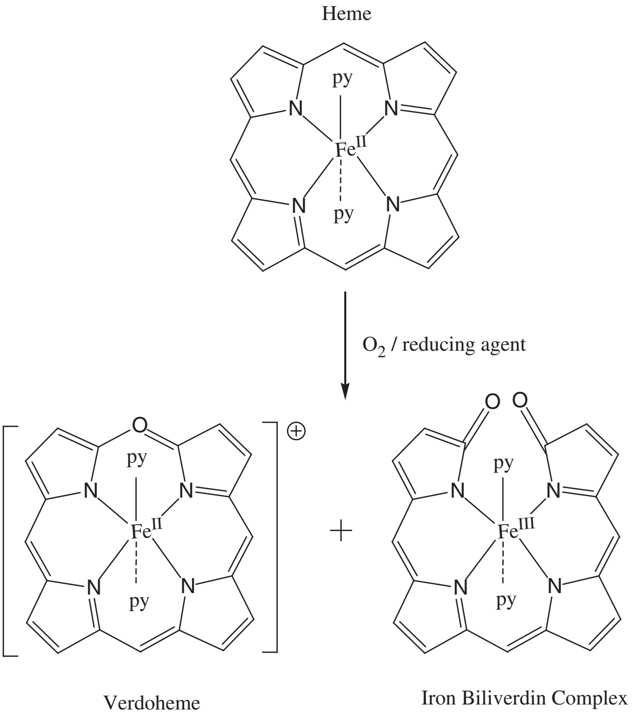


Scheme 1. The coupled oxidation process.

(X = F (**2**), CF_3CO_2 (**3**)). Five-coordinate iron(II) oxoporphyrin compound, [OEOPFe^{II}(CF_3SO_3)] (**4**), is produced from reaction of verdoheme with CF_3SO_3H. Compounds **2**, **3** and **4** have been isolated and characterized by IR, UV–Vis, paramagnetic ^1H NMR, and elemental analysis.

2. Experimental

All solvents were dried by refluxing for several days over Na and benzophenone under Ar and distilled immediately before use. Purified N_2 (99.99%) was used without further treatment. All reagents and solvents used in this study were obtained from Merck & Aldrich Chem. Co. [OEOPFe^{II}(py)$_2$]Cl was synthesized by our previous method [12].

IR spectra were recorded as KBr disks on a Shimadzu IR instrument. UV–Vis spectra were recorded on an Analytik Jena SPECORD S-100 spectrometer with photodiode array detector. NMR experiments were recorded at room temperature in $CDCl_3$ on a Bruker AV-500 spectrometer using an internal deuterated solvent lock.

2.1. *Syntheses*

2.1.1. Reaction of [(OEOP)Fe^{II}(py)$_2$]Cl with HF, [OEOPFe^{III}F$_2$] (2). To a solution of [(OEOP)Fe^{II}(py)$_2$]Cl (20 mg) in dichloromethane (20 mL) excess HF (10 mL/40%) was added and shaken for 30 min in air. The green solution was filtered to remove insoluble material, and the filtrate was washed with two 50 mL portions of water. The resulting green solution was dried by passage through a 5 cm thick layer of anhydrous sodium sulfate. The sample was evaporated to dryness under vacuum to give a green residue. The resulting green solid was recrystallized by dissolving it in a minimum volume of dichloromethane and slowly adding diethyl ether to precipitate the product as green crystals (Yield 14 mg, 80%). Anal. Calcd for $C_{35}H_{43}N_4OFeF_2$: C, 66.54; H, 6.81; N, 8.87. Found : C, 66.28; H, 6.64; N, 8.67. UV/Vis absorption : λ_{max}, nm (ε, $cm^{-1}M^{-1}$), 717 (1.5×10^4), 649 (1.8×10^4), 544 (7×10^3), 362 (6.1×10^4). ^1H NMR ($CDCl_3$) ppm (intensity) *meso*-H 34.85(1), 37.66(2); methylene-H 40.72(4), 42.01(4), 43.55(4), 45.93(4); methyl-H 6.19(6), 6.71(6), 7.06(6), 7.66(6).

2.1.2. Reaction of $[(OEOP)Fe^{II}(py)_2]Cl$ with CF_3CO_2H, $[OEOPFe^{III}(CF_3CO_2)_2]$ (3). Compound **3** was prepared by the procedure used for $[OEOPFe^{III}F_2]$ except that hydrogen fluoride was replaced with trifluoroacetic acid ($CF_3CO_2H : H_2O$, 20 : 80). Anal. Calcd for $C_{35}H_{43}N_4OFe(CF_3CO_2)_2$: C, 57.27; H, 5.26; N, 6.85. Found : C, 57.05; H, 5.09; N, 6.58. UV/Vis absorption spectrum : λ_{max}, nm (ε, $cm^{-1}M^{-1}$), 717 (1.6×10^4), 623 (2.0×10^4), 478 (6×10^3), 372 (5.8×10^4). ^1H NMR ($CDCl_3$) ppm (intensity) *meso*-H 38.60(2), 41.22(1); methylene-H 33.74(4), 43.80(4), 47.55(4), 59.72(4); methyl-H 6.47(6), 6.51(6), 7.03 (6), 7.35 (6), IR (KBr) : $\upsilon(CF_3CO_2) = 1689, 1535, 1399, 1186, 1130, 878\ cm^{-1}$.

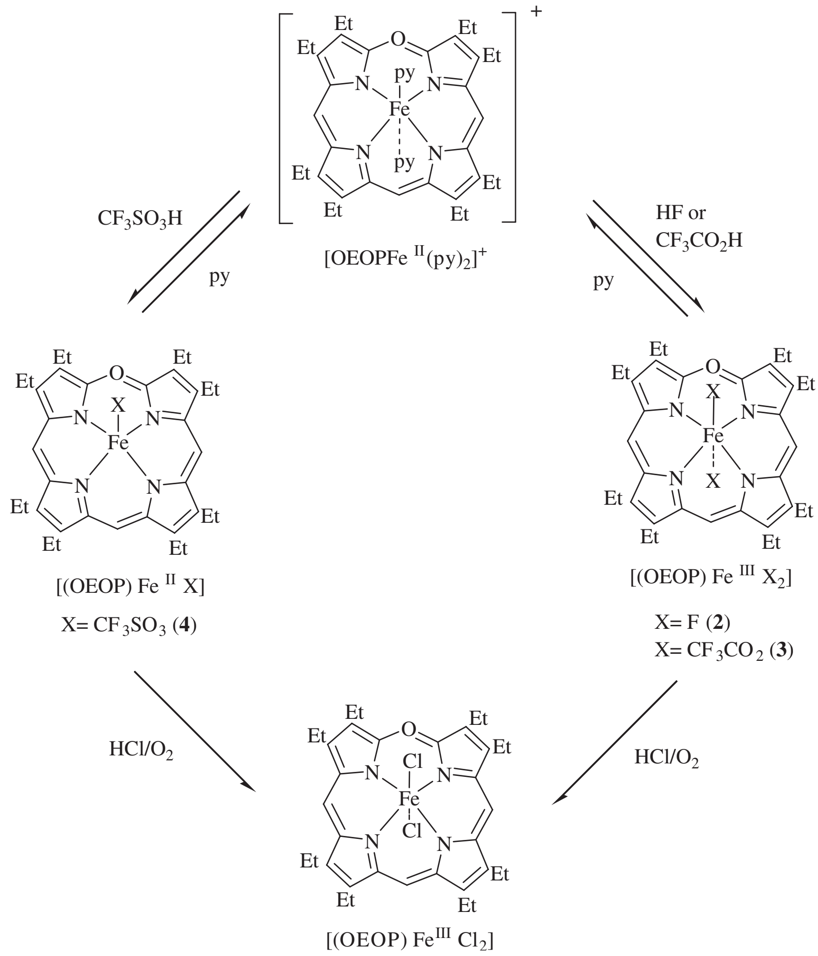
2.1.3. Reaction of $[(OEOP)Fe^{II}(py)_2]Cl$ with CF_3SO_3H, $[OEOPFe^{II}(CF_3SO_3)]$ (4). Compound **4** was prepared by the procedure used for $[OEOPFe^{III}F_2]$ except that hydrogen fluoride was replaced with trifluoromethanesulfonic acid ($CF_3SO_3H : H_2O$, 20 : 80). Anal. Calcd for $C_{35}H_{43}N_4OFe(CF_3SO_3)$: C, 58.36; H, 5.81; N, 7.57. Found : C, 58.15; H, 5.32; N, 7.25. UV/Vis absorption : λ_{max}, nm (ε, $cm^{-1}M^{-1}$), 663 (5.5×10^4), 390 (8.9×10^4). ^1H NMR ($CDCl_3$) ppm (relative intensity) : *meso*-H 37.27(2), 47.27(1); methylene-H 34.55(2), 41.82(2), 43.18(2), 44.55(2), 55.00(2), 57.95(2), 58.18(2), 64.09(2); methyl-H 6.29(6), 7.10(6), 7.73(6), 8.20 (6). IR (KBr) : $\upsilon(CF_3SO_3) = 1457, 1374, 635\ cm^{-1}$.

3. Results and discussion

3.1. *Reaction of $[(OEOP)Fe^{II}(py)_2]Cl$ with HF and CF_3CO_2H*

Reaction of $[(OEOP)Fe^{II}(py)_2]Cl$ with HX ($X = F$, CF_3CO_2) produces a six-coordinate iron(III) product, $[OEOPFe^{III}X_2]$ ($X = F$ (**2**), CF_3CO_2 (**3**)) (scheme 2). Compounds **2** and **3** are stable in air and have good solubility in dichloromethane.

The UV–Vis spectra of dichloromethane solutions of **2** and **3** show typical verdoheme features [7–9, 12] with intense Soret band at 362 and 372 nm, respectively, and Q-bands, low energy absorptions in the range 440–720 nm. The UV–Vis spectra of dichloromethane solutions of **2** and **3** are very similar to those of other iron(III) complexes of octaethyloxoporphyrin, such as $[OEOPFe^{III}Cl_2]$ [12], and are clearly different from iron(II) octaethyloxoporphyrin complexes, $[OEOPFe^{II}X]$ ($X = Cl$, PF_6, AsF_6, SbF_6, ClO_4, BF_4) [10–12].



Scheme 2. Reaction of $[(OEOP)Fe^{II}(py)_2]Cl$ with HX (X = F, CF_3CO_2, CF_3SO_3).

The IR spectra of **2** and **3** are similar to each other except for vibrations of CF_3CO_2 in **3**. The $\upsilon(CF_3CO_2)$ values (1689, 1535, 1399, 1186, 1130, 878 cm^{-1}) in this complex are similar to those of a related species with coordinated trifluoroacetate [13–15].

All resonances in the ^1H NMR spectra of **2** and **3** were assigned on the basis of their intensities, line widths, and chemical shifts at room temperature and are similar to each other. Figure 1 shows, for example, the spectrum of $[OEOPFe^{III}F_2]$ (**2**) in $CDCl_3$ at room temperature. The methylene and methine protons show strong paramagnetic shifts that place them in the downfield region. The ^1H NMR spectra of $[OEOPFe^{III}X_2]$ [X = F (**2**), CF_3CO_2 (**3**)] shows four clearly resolved, equally intense methylene resonances for the six-coordinate Fe(III) complexes, while eight are observed for five-coordinate Fe(II) compounds. Four equally intense methylene resonances are found which span the range 40 to 46 ppm for **2** and 33 to 60 ppm for **3**. Since the iron is six-coordinate (vide infra), each of the two methylene protons of the four unique

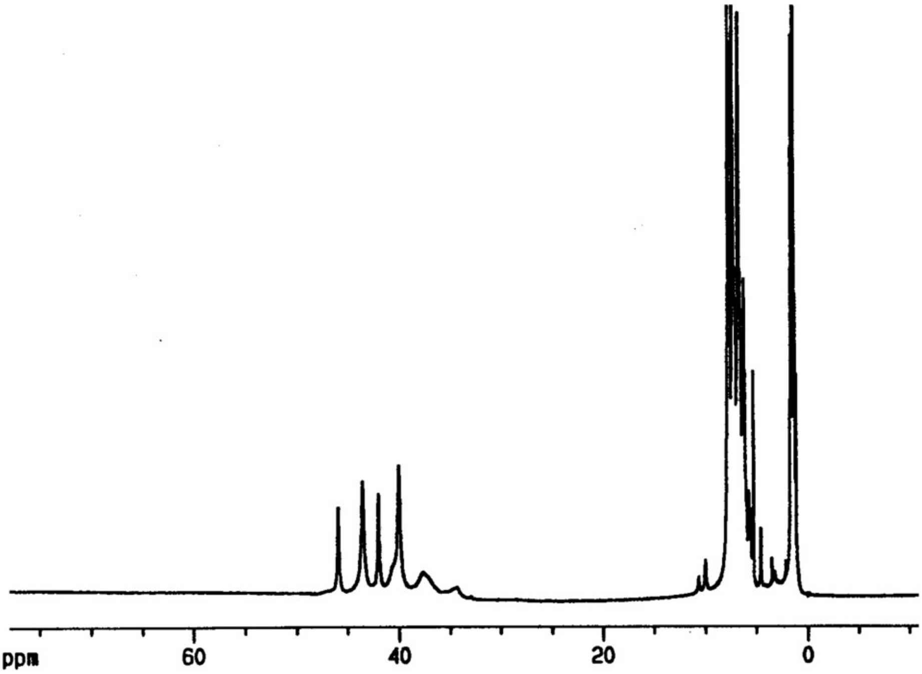


Figure 1. 500-MHz ^{1}H NMR spectrum of [OEOPFe^{III}F$_2$] in chloroform-d at r.t.

ethyl groups is chemically equivalent and hence there are four methylene resonances. Also, ^{1}H NMR spectra of **2** and **3** show four signals for CH$_2$ at low temperature ($-60°$C). The two methine resonances observed in the spectra of these complexes show an intensity ratio of 1 : 2 and greater line widths, consistent with the fact that they are closest to the iron center and most affected by dipolar relaxation. Line widths increase in the order methyl > methylene > meso, consistent with a dominant dipolar contribution to the line width (which is proportional to r^{-6}) [12] (r is the distance between the proton and the paramagnetic center) since the distance between the oxoporphyrin protons and the iron center follow an inverse order (i.e., meso > methylene > methyl). Four methyl resonances corresponding to 24 protons are seen in the 6–8 ppm region at room temperature. These spectra are consistent with the structure shown in scheme 2.

The [OEOPFe^{III}X$_2$] (X = F, CF$_3$CO$_2$) species are paramagnetic. In chloroform solution at 25°C, as measured by the Evans technique [16], **2** and **3** have magnetic moments of 5.48 and 5.43 μ_B, respectively, consistent with a high-spin (S = 5/2) electronic configuration of iron(III) in these species.

Binding of basic, hard axial ligands such as fluoride is expected to stabilize metal-centered oxidation. The six-coordinate iron(III) porphyrin complexes with two bound fluorides are well known [17].

Our results show that the reactivity of verdoheme to HF and CF$_3$CO$_2$H is very similar to the reactivity of verdoheme with HCl [12]. In all cases, six-coordinate iron(III) oxoporphyrin is formed.

3.2. *Reaction of [(OEOP)Fe^{II}(py)$_2$]Cl with CF_3SO_3H*

Trifluoromethanesulfonic acid is a stronger acid than perchloric acid [18]. Unlike perchlorate, CF_3SO_3 anion is not an oxidizing anion [19]. In water, CF_3SO_3H ionizes completely to H_3O^+ and $CF_3SO_3^-$.

[(OEOP)Fe^{II}(py)$_2$]Cl reacts with CF_3SO_3H in the presence of air to produce five-coordinate iron(II) product, [OEOPFe^{II}(CF_3SO_3)] (**4**) (scheme 2). Compound **4** is stable in air and has good solubility in dichloromethane.

The UV–Vis spectrum of dichloromethane solution of **4** shows Soret and Q bands at 663 and 390 nm, respectively. The UV–Vis spectrum (figure 2) of dichloromethane solution of **4** is clearly different from those of iron(III) complexes of octaethyl-oxoporphyrin, such as [OEOPFe^{III}Cl$_2$] [12], whereas very similar to those of [(OEOP)Fe^{II}(py)$_2$]Cl and [OEOPFe^{II}X] (X = Cl, PF_6, AsF_6, SbF_6, ClO_4, BF_4) [10–12].

Compound **4** was also characterized by infrared spectroscopy. Unambiguous assignments of vibrational modes of $CF_3SO_3^-$ are not possible due to mixing of CF_3 and SO_3 vibrational modes and accidental coincidences of these modes arising particularly in the stretching region [20]. An assignment of the IR spectrum of ionic $CF_3SO_3^-$ as the Ag^+ salt has been made [21] and IR spectroscopy has been used to identify bound or ionic $CF_3SO_3^-$ [22, 23]. Characteristically, the band near 1280 cm^{-1} for ionic $CF_3SO_3^-$ is shifted to higher wavenumber, appearing near 1380 cm^{-1} for monodentate trifluoromethanesulfonate [24, 25].

The vibrations from CF_3SO_3 for [OEOPFe^{II}(CF_3SO_3)] (**4**) appear at 1457, 1374 and 635 cm^{-1}, consistent with monodentate trifluoromethanesulfonate. The $\upsilon(CF_3SO_3)$ values in this complex are similar to those of [TPPFe(OSO_2CF_3)], which has bands at 1340, 1205 and 630 cm^{-1} [3].

The ^{1}H NMR spectrum of **4** is different from **2** and **3**; figure 3 shows the spectrum of **4** in $CDCl_3$ at room temperature with eight methylene resonances for the five-coordinate Fe(II) complex, while four are observed for the six-coordinate Fe(III) compounds. The methylene and methine protons show strong paramagnetic shifts that place them in the downfield region. The two methine resonances at 37.25 and 47.27 ppm are readily assigned on the basis of their intensity. Four methyl resonances with intensity corresponding to 24 protons are seen in the 6–8.5 ppm region at room temperature. Eight equally intense methylene resonances are found which span the range 34 to 65 ppm. Since the iron is five-coordinate (vide infra), each methylene proton of the four unique ethyl groups is chemically distinct and hence there are eight methylene resonances. These spectra are consistent with the structure shown in scheme 2.

Compound **4** is paramagnetic with, in chloroform solution at 25°C as measured by the Evans technique [16], a magnetic moment of 4.78 μ_B. This is consistent with a high-spin (S = 2) electronic configuration.

UV–Vis and ^{1}H NMR spectra of **4** are very similar to previously reported spectra for verdoheme analogues with weakly coordinating anions, [OEOPFe^{II}X] (X = PF_6, As F_6, SbF_6, BF_4, ClO_4) [10, 11].

3.3. *Reaction of 2, 3 and 4 with pyridine and HCl*

When **2**, **3** and **4** are dissolved in pyridine or when pyridine (more than 4 equiv) is added to dichloromethane solution of these complexes, [OEOPFe^{II}(py)$_2$]X is reformed

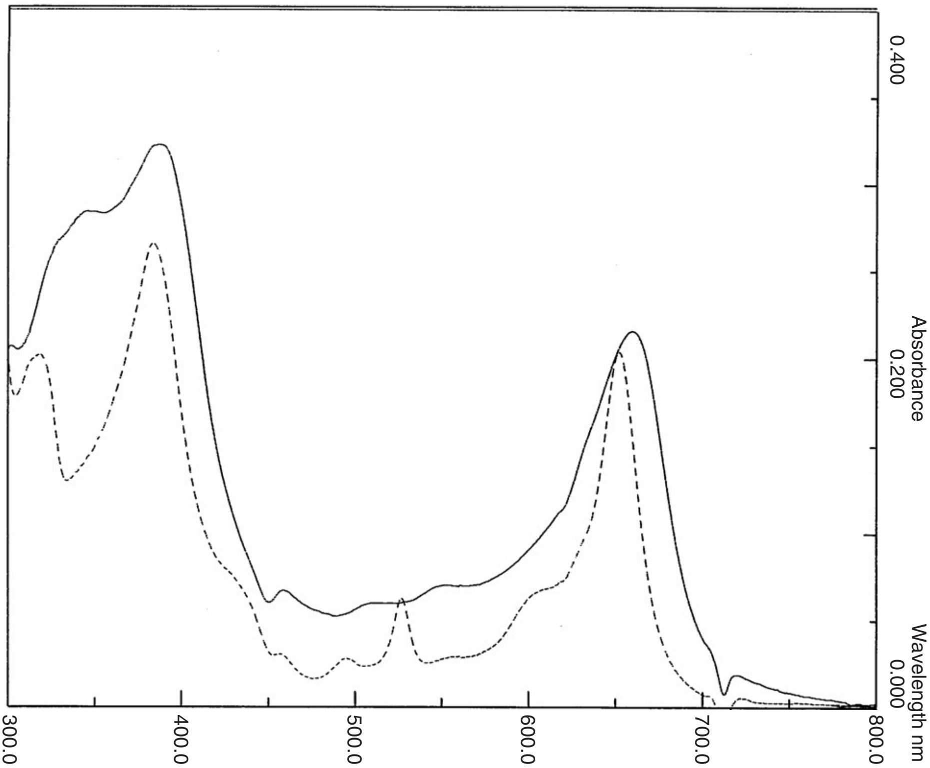


Figure 2. UV–Vis absorption spectra of [OEOPFe^{II}(CF$_3$SO$_3$)] (solid) and [OEOPFe^{II}(CF$_3$SO$_3$)] (dashed) in dichloromethane after addition of 1% pyridine ([OEOPFe^{II}(py)$_2$]$^+$).

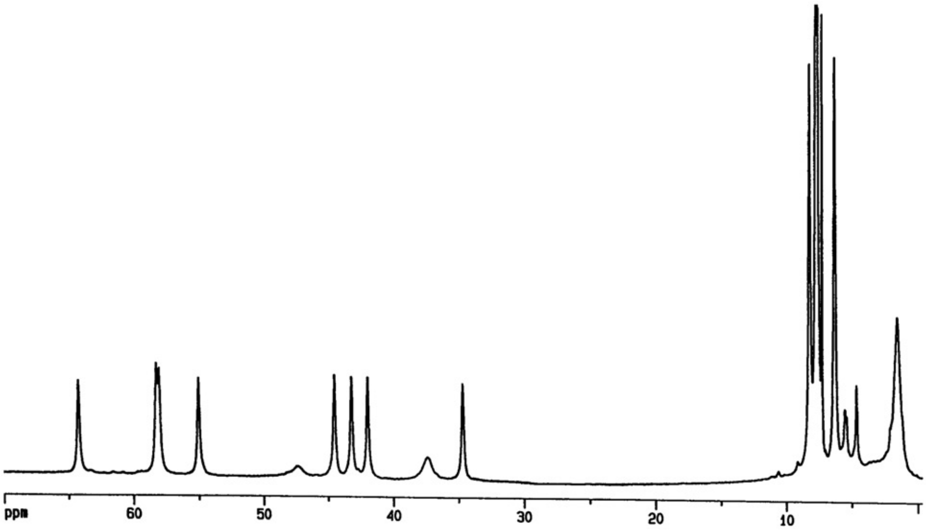


Figure 3. 500-MHz ^{1}H NMR spectrum of [OEOPFe^{II}(CF$_3$SO$_3$)] in chloroform-d at r.t.

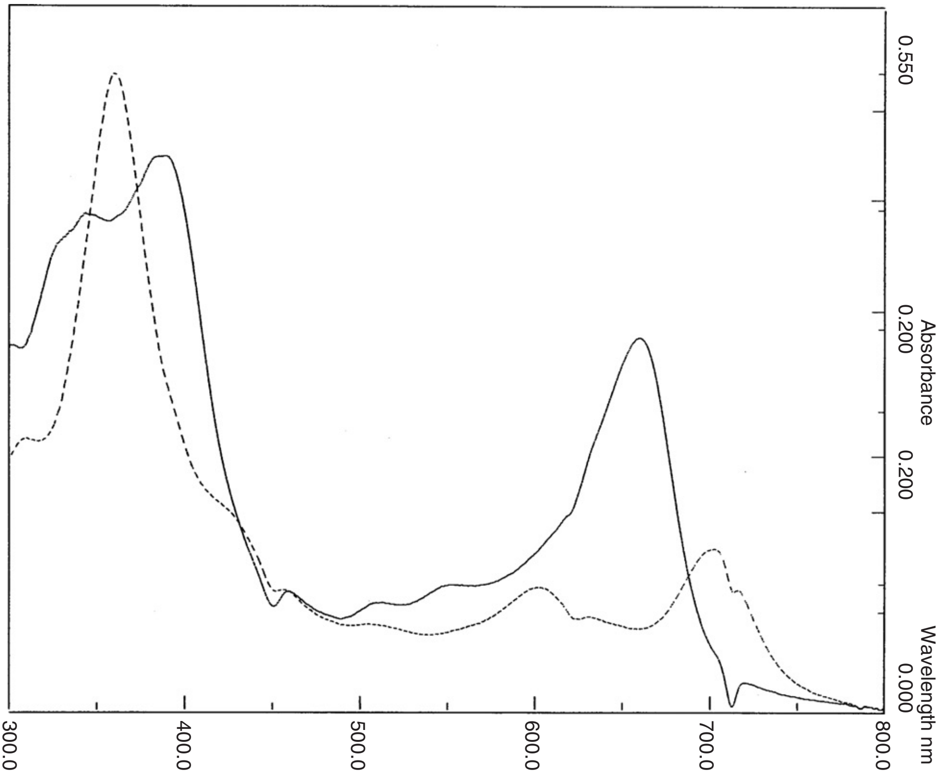


Figure 4. UV–Vis absorption spectra of [OEOPFe^{II}(CF$_3$SO$_3$)] (solid) and [OEOPFe^{II}(CF$_3$SO$_3$)] (dashed) in dichloromethane after addition of HCl ([OEOPFe^{III}Cl$_2$]).

as revealed by UV–Vis; similar auto-reduction reactions for **2** and **3** have been observed in reaction of [OEOPFe^{III}Cl$_2$] with excess pyridine [12].

When HCl is added to aerobic dichloromethane solution of **2**–**4**, [OEOPFe^{III}Cl$_2$] is produced. These *in situ* reactions have been monitored by changes in the UV/Vis absorption. Figures 2 and 4 show reactions of [OEOPFe^{II}(CF$_3$SO$_3$)] (**4**) with pyridine and HCl.

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