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Research paper

# Preparation and infrared spectroelectrochemical studies of five-coordinate (por)Fe(OC(=O)R) compounds (por = TPP, OEP; $R = CCl_3$ , $CH_2Cl$ )

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# ABSTRACT

Three five-coordinate iron acetate porphyrin complexes, (por)Fe(OC(=O)R) (por = porphyrinato dianion;  $R = CCl_3$ ,  $CH_2Cl$ ), have been synthesized and characterized. The crystal structure of  $(TPP)Fe(OC(=O)CCl_3)$  (TPP = tetraphenylporphyrinato dianion) has been determined by X-ray crystallography. The redox behaviors of the (por)Fe(OC(=O)R) compounds have been investigated by cyclic voltammetry and infrared spectroelectrochemistry. Analysis of the data reveals that the first oxidations of the (por)Fe(OC(=O)R) compounds are porphyrin-centered processes to yield  $\pi$ -radical cations of the form (por\*)Fe(OC(=O)R), and the first reductions may facilitate the dissociation of the axial acetate ligands from the iron centers. © 2017 Elsevier B.V. All rights reserved.

# 1. Introduction

Numerous iron porphyrin complexes have been prepared as models for the studies of important roles that heme enzymes play in biological processes. The (por)Fe(*O*-ligand) (por = porphyrinato dianion) cofactor is an essential constituent of several heme proteins such as heme catalase with tyrosine axial ligands [1–4], the HasA [5,6] and IsdB [7] heme-binding proteins, and in some natural mutant hemoglobins such as Hb M Boston [ $\alpha$ 58(E7)His $\rightarrow$ Tyr] (i.e., alkoxide ligation) and Hb M Milwaukee [ $\beta$ 67(E11)Val $\rightarrow$ Glu] (i.e., carboxylate ligation) [8]. Consequently, there is continued interest in the preparation and examination of the redox behavior of such (por)Fe(*O*-ligand) species, especially for synthetic analogues that allow probing of porphyrin and axial *O*-ligand substitutions on the properties of these species.

In this paper, we report the preparation, characterization, electrochemistry, and IR spectroelectrochemistry of three (por)Fe(OC (=O)R) (por = TPP or OEP; R = CCl<sub>3</sub> or CH<sub>2</sub>Cl) compounds. Only a few other reports of the electrochemistry of iron porphyrin acetate complexes have been published [9–11]. Further, and to the best of our knowledge, this is the first report describing the infrared spectroelectrochemistry of these compounds.

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# 2. Experimental

## 2.1. General

All reactions were performed under a nitrogen atmosphere using standard Schlenk glassware and/or in an Innovative Technology Labmaster 100 Dry Box. Hexane and CH<sub>2</sub>Cl<sub>2</sub> were distilled from CaH<sub>2</sub> under nitrogen just prior to use.

# 2.2. Chemicals

Trichloroacetic acid (99%), chloroacetic acid (99%) and NBu<sub>4</sub>PF<sub>6</sub> (98%) were purchased from Aldrich Chemical Company. The oxodimer precursors [(por)Fe]<sub>2</sub>( $\mu$ -O) (por = TPP, OEP) [12,13] were prepared by published methods and their identities confirmed by IR spectroscopy.

#### 2.3. Instrumentation

Electrochemical measurements were performed using a BAS CV-50W instrument (Bioanalytical Systems, West Lafayette, IN). For cyclic voltammetry, a three-electrode cell with a 3 mm diameter Pt disk working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode were utilized. The solutions for all electrochemical experiments were 1.0 mM in analyte, in 10 mL  $CH_2CI_2$  solution containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub> as support electrolyte. The solutions were deaerated by purging with prepurified nitrogen for





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10 min before each set of measurements, and then the nitrogen atmosphere was maintained during the measurements which were performed at room temperature ( $\sim$ 20 °C). Scan rates of 200–1000 mV/s were used, but no significant differences in the cyclic voltammogram profiles were noted.

Infrared spectra for the synthetic work were collected on a Bio-Rad FT-155 FTIR spectrometer. For infrared spectroelectrochemistry, the experimental setup consisted on the same cell utilized for the cyclic voltammetry measurements, with the 3 mm Pt disk working electrode serving as the mirror for the fiber optic mid-IR dip probe, as described previously [14–16]. The resulting IR spectra were recorded using a Bruker Vector 22 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector (Remspec Corporation, Sturbridge, MA, USA). UV–Vis spectra were recorded on a Hewlett-Packard model 8453 diode array instrument.

#### 2.4. Synthesis

Three iron porphyrin acetate compounds were prepared in a manner similar to that used for the preparation of (por)Fe(OC (=O)R) analogues [17]. The following is representative:

(**TPP**)**Fe**(**OC**(=**O**)**CCl<sub>3</sub>** (**1**). To a CH<sub>2</sub>Cl<sub>2</sub> solution (15 mL) of [(TPP) Fe]<sub>2</sub>( $\mu$ -O) (0.033 g, 0.024 mmol) was added trichloroacetic acid (0.010 g, 0.06 mmol). The mixture was stirred for 45 min, during which time the color of the solution changed from green to brown. The solvent was reduced to ~3 mL and hexane (10 mL) was added. The solution was slowly concentrated under reduced pressure until precipitation of the product occurred. The dark brown precipitate was collected by filtration, washed with hexane (2 × 15 mL), and dried in *vacuo* to give (TPP)Fe(OC(=O)CCl<sub>3</sub>) (0.020 g, 0.024 mmol, 50% isolated yield). Slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane (1:1 ratio; 4 mL) solution of the product at room temperature gave suitable crystals for X-ray diffraction studies. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $v_{OCO}(asym) = 1704$ . IR (KBr, cm<sup>-1</sup>):  $v_{OCO}(asym) = 1709$ . UV–vis ( $\lambda$  (relative  $\varepsilon$ , mM<sup>-1</sup>cm<sup>-1</sup>), 2 × 10<sup>-5</sup> M in CH<sub>2</sub>Cl<sub>2</sub>): 411 (138), 509 (14), 571 (8), 681 (4) nm.

The other iron acetate porphyrin complexes were generated similarly using the respective porphyrin and acid precursors.

(**TPP**)**Fe**(**OC**(=**O**)**CH**<sub>2</sub>**CI**) (2). Isolated yield: 60%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $v_{OCO}(asym) = 1684$ . IR (KBr, cm<sup>-1</sup>):  $v_{OCO}(asym) = 1692$ . UV-vis ( $\lambda$  (relative  $\varepsilon$ , mM<sup>-1</sup>cm<sup>-1</sup>), 1 × 10<sup>-5</sup> M in CH<sub>2</sub>Cl<sub>2</sub>): 351 (36), 412 (109), 507 (8), 573 (9), 656 (7) nm.

**(OEP)Fe(OC(=0)CCl<sub>3</sub>) (3)** [18]. Isolated yield: 65%. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $v_{OCO}(asym) = 1704$ . IR (KBr, cm<sup>-1</sup>):  $v_{OCO}(asym) = 1711$ . UV-vis ( $\lambda$  (relative  $\varepsilon$ , mM<sup>-1</sup>cm<sup>-1</sup>), 8 × 10<sup>-6</sup> M in CH<sub>2</sub>Cl<sub>2</sub>): 381 (98), 506 (7), 533 (7), 634 (3) nm.

# 2.5. X-ray crystallography

A black plate-shaped crystal of (TPP)Fe(OC(=O)CCl<sub>3</sub>) (1) of dimensions  $0.28 \times 0.26 \times 0.05$  mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector [19,20] and graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a non-linear least squares fit of 8508 peaks in the range 2.21 <  $\theta$  < 27.37°. A total of 62935 data were measured in the range 1.689 <  $\theta$  < 28.456° using  $\phi$  and  $\omega$  oscillation frames. The data were corrected for absorption by the semi-empirical method [21] giving minimum and maximum transmission factors of 0.833 and 0.967. The data were merged to form a set of 9144 independent data with R(int) = 0.1583 and a coverage of 100.0%.

The monoclinic space group  $P2_1/n$  was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on  $F^2$  [22,23]. Hydrogen atom positions were initially determined by geometry and refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the displacement parameters of the bonded atoms. A total of 505 parameters were refined against 9144 data to give wR( $F^2$ ) = 0.1638 and S = 1.012 for weights of w = 1/[ $\sigma^2(F^2)$  + (0.0680 P)<sup>2</sup> + 1.9000 P], where P = [ $F_0^2 + 2F_c^2$ ]/3. The final R(F) was 0.0655 for the 5690 observed, [ $F > 4\sigma(F)$ ], data.

The largest shift/s.u. was 0.003 in the final refinement cycle. The final difference map had maxima and minima of 0.616 and  $-0.876 \text{ e/Å}^3$ , respectively. Displacement ellipsoids in Fig. 1 are drawn at the 35% probability level. Details of the crystal data and refinement are given in Table 1. CCDC 1444107 contains the crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or by emailing deposit@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033

(a)



**Fig. 1.** (a) Molecular structure of (TPP)Fe(OC(=O)CCl<sub>3</sub>) (1). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 35% probability level. (b) Perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean porphyrin plane. Selected bond lengths (in Å) and angles (in deg): Fe-N1 = 2.044(3), Fe-N2 = 2.046(3), Fe-N3 = 2.046(3), Fe-N4 = 2.054(3), Fe-O1 = 1.917(2),  $\angle$ Fe-O1-C45 = 133.2(2).

Table 1	1
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Crystal data and structure refinement for 1.

Formula $C_{46}F_{128}C_{13}FeV_4O_2$ Formula weight       830.92         T (K)       100(2)         Crystal system       monoclinic         Space group $P_2_1/n$ Unit cell dimensions       11.300(3)         a (Å)       22.877(6)         c (Å)       22.877(6)         c (Å)       22.877(6)         c (Å)       14.761(4) $\alpha, \gamma$ (°)       90, 90 $\beta$ (°)       106.053(6)         Volume (Å^3)       3667.1(17)         Z, Z'       4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505         F(0 0 0)       1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data) $R_1$ = 0.0655         Goodness-of-fit on $F^2$ 1.012         Observed data) $R_1$ = 0.0655         Goodness-of-fit on $F^2$ 1.012	Formerale	
Formula weight $830.92$ T (K) $100(2)$ Crystal system       monoclinic         Space group $P2_1/n$ Unit cell dimensions $11.300(3)$ $a$ (Å) $11.300(3)$ $b$ (Å) $22.877(6)$ $c$ (Å) $14.761(4)$ $\alpha$ , $\gamma$ (°) $90$ , $90$ $\beta$ (°) $106.053(6)$ Volume (Å <sup>3</sup> ) $3667.1(17)$ $Z$ , $Z'$ $4, 1$ $D_{calc}$ (g/cm <sup>3</sup> ) $1.505$ $F(0 \ 0)$ $1700$ Absorption coefficient (mm <sup>-1</sup> ) $0.678$ Max. and min. transmission $0.967$ and $0.833$ $\theta$ range for data collection (°) $1.689$ to $28.456$ Reflections collected $62935$ Independent reflections $9144$ [ $R_{int} = 0.1583$ ]         Data / restraints / parameters $9144/0/505$ wR ( $F^2$ all data) $wR_2 = 0.1638$ $R$ (F observed data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ $1.012$ Observed data ( $b_{2} \ge \sigma(0)$ $5600$	Formula	$C_{46}H_{28}CI_3FeN_4O_2$
T (k)       100(2)         Crystal system       monoclinic         Space group $P2_1/n$ Unit cell dimensions       11.300(3)         b (Å)       22.877(6)         c (Å)       14.761(4) $\alpha, \gamma$ (°)       90, 90 $\beta$ (°)       106.053(6)         Volume (Å <sup>3</sup> )       3667.1(17)         Z, Z'       4, 1         D <sub>calc</sub> (g/cm <sup>3</sup> )       1.505 $F(0 \ 0 \ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       91444 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ 1.012         Observed data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ 1.012	Formula weight	830.92
Crystal system       monoclinic         Space group $P2_1/n$ Unit cell dimensions       11.300(3) $a$ (Å)       11.300(3) $b$ (Å)       22.877(6) $c$ (Å)       14.761(4) $\alpha, \gamma$ (°)       90, 90 $\beta$ (°)       106.053(6)         Volume (Å <sup>3</sup> )       3667.1(17)         Z, Z'       4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505 $F(0 \ 0 \ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data)       wR <sub>2</sub> = 0.1638 $R$ (F observed data) $R_1$ = 0.0655         Goodness-of-fit on $F^2$ 1.012         Observed data ( $h^2$ ) $2 \sigma(h)$ 5600	T (K)	100(2)
Space group $P2_1/n$ Unit cell dimensions         11.300(3) $a$ (Å)         11.300(3) $b$ (Å)         22.877(6) $c$ (Å)         14.761(4) $\alpha, \gamma$ (°)         90, 90 $\beta$ (°)         106.053(6)           Volume (Å <sup>3</sup> )         3667.1(17)           Z, Z'         4, 1 $D_{calc}$ (g/cm <sup>3</sup> )         1.505 $F(0 \ 0)$ 1700           Absorption coefficient (mm <sup>-1</sup> )         0.678           Max. and min. transmission         0.967 and 0.833 $\theta$ range for data collection (°)         1.689 to 28.456           Reflections collected         62935           Independent reflections         9144 [R <sub>int</sub> = 0.1583]           Data / restraints / parameters         9144/0/505           wR ( $F^2$ all data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ 1.012           Observed data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ 1.012	Crystal system	monoclinic
Unit cell dimensions       11.300(3) $a$ (Å)       11.300(3) $b$ (Å)       22.877(6) $c$ (Å)       14.761(4) $\alpha$ , $\gamma$ (°)       90, 90 $\beta$ (°)       106.053(6)         Volume (Å <sup>3</sup> )       3667.1(17) $Z$ , $Z'$ 4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505 $F(0 \ 0 \ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data)       wR <sub>2</sub> = 0.1638 $R$ (F observed data) $R_1$ = 0.0655         Goodness-of-fit on $F^2$ 1.012         Observed data) $Z = 0$	Space group	$P2_1/n$
$a$ (Å)       11.300(3) $b$ (Å)       22.877(6) $c$ (Å)       14.761(4) $\alpha, \gamma$ (°)       90, 90 $\beta$ (°)       106.053(6)         Volume (Å <sup>3</sup> )       3667.1(17) $Z, Z'$ 4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505 $F(0 \ 0 \ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data)       wR <sub>2</sub> = 0.1638 $R$ ( $F$ observed data) $R_1$ = 0.0655         Goodness-of-fit on $F^2$ 1.012         Observed data ( $\Delta \pm 2 \sigma(0)$ )       5600	Unit cell dimensions	
$b$ (Å)       22.877(6) $c$ (Å)       14.761(4) $\alpha$ , $\gamma$ (°)       90, 90 $\beta$ (°)       106.053(6)         Volume (Å <sup>3</sup> )       3667.1(17) $Z$ , $Z'$ 4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505 $F(0 \ 0 \ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ 1.012         Observed data ( $f_{2} \ge \sigma(f_{1})$ 5600	a (Å)	11.300(3)
$c$ (Å)       14.761(4) $\alpha, \gamma$ (°)       90, 90 $\beta$ (°)       106.053(6)         Volume (Å <sup>3</sup> )       3667.1(17)         Z, Z'       4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505 $F(0 \ 0 \ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR (F <sup>2</sup> all data)       wR <sub>2</sub> = 0.1638         R (F observed data) $R_1$ = 0.0655         Goodness-of-fit on F <sup>2</sup> 1.012         Observed data (b 2.2 cf(b)       5600	b (Å)	22.877(6)
$\alpha, \gamma(^{\circ})$ 90, 90 $\beta(^{\circ})$ 106.053(6)         Volume (Å <sup>3</sup> )       3667.1(17)         Z, Z'       4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505 $F(0 \ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data) $R_1$ = 0.0655         Goodness-of-fit on $F^2$ 1.012         Observed data (data)       5600	c (Å)	14.761(4)
$\beta$ (°)       106.053(6)         Volume (Å <sup>3</sup> )       3667.1(17)         Z, Z'       4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505 $F(0 \ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data)       wR <sub>2</sub> = 0.1638         R (F observed data) $R_1$ = 0.0655         Goodness-of-fit on $F^2$ 1.012         Observed data / $\Delta = 2 \sigma(D)$ 5600	α, γ (°)	90, 90
Volume ( $\hat{A}^3$ )       3667.1(17)         Z, Z'       4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505         F(0 0 0)       1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [ $R_{int} = 0.1583$ ]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data)       wR <sub>2</sub> = 0.1638         R (F observed data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ 1.012         Observed data ( $J_2 \gtrsim C(D)$ )       5600	β (°)	106.053(6)
Z, Z'       4, 1 $D_{calc}$ (g/cm <sup>3</sup> )       1.505 $F(0\ 0\ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR (F <sup>2</sup> all data)       wR <sub>2</sub> = 0.1638         R (F observed data)       R <sub>1</sub> = 0.0655         Goodness-of-fit on F <sup>2</sup> 1.012         Observed data (data)       5600	Volume (Å <sup>3</sup> )	3667.1(17)
$D_{calc} (g/cm^3)$ 1.505 $F(0\ 0\ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data) $R_1$ = 0.0655         Goodness-of-fit on $F^2$ 1.012         Observed data ( $J_{2,2} = C(D)$ )       5600	Z, Z'	4, 1
$F(0\ 0\ 0)$ 1700         Absorption coefficient (mm <sup>-1</sup> )       0.678         Max. and min. transmission       0.967 and 0.833 $\theta$ range for data collection (°)       1.689 to 28.456         Reflections collected       62935         Independent reflections       9144 [R <sub>int</sub> = 0.1583]         Data / restraints / parameters       9144/0/505         wR ( $F^2$ all data) $R_1$ = 0.0655         Goodness-of-fit on $F^2$ 1.012         Observed data / $E_2 = 0$ (0)       5600	$D_{calc}$ (g/cm <sup>3</sup> )	1.505
Absorption coefficient $(mm^{-1})$ 0.678Max. and min. transmission0.967 and 0.833 $\theta$ range for data collection (°)1.689 to 28.456Reflections collected62935Independent reflections9144 [R <sub>int</sub> = 0.1583]Data / restraints / parameters9144/0/505wR ( $F^2$ all data)wR2 = 0.1638R (F observed data)R1 = 0.0655Goodness-of-fit on $F^2$ 1.012Observed data / $22 = 0$ 5600	F(0 0 0)	1700
Max. and min. transmission0.967 and 0.833 $\theta$ range for data collection (°)1.689 to 28.456Reflections collected62935Independent reflections9144 [ $R_{int} = 0.1583$ ]Data / restraints / parameters9144/0/505wR ( $F^2$ all data)wR2 = 0.1638R (F observed data)R1 = 0.0655Goodness-of-fit on $F^2$ 1.012Observed data / 2.2 cf(D)5600	Absorption coefficient (mm <sup>-1</sup> )	0.678
$\theta$ range for data collection (°)1.689 to 28.456Reflections collected62935Independent reflections9144 [ $R_{int} = 0.1583$ ]Data / restraints / parameters9144/0/505wR ( $F^2$ all data)w $R_2 = 0.1638$ R ( $F$ observed data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ 1.012Observed data ( $L_2 \supset C(D)$ )5600	Max. and min. transmission	0.967 and 0.833
Reflections collected62935Independent reflections9144 [ $R_{int} = 0.1583$ ]Data / restraints / parameters9144/0/505wR ( $F^2$ all data)w $R_2 = 0.1638$ R ( $F$ observed data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ 1.012Observed data ( $L_2 \supset C(D)$ )5600	$\theta$ range for data collection (°)	1.689 to 28.456
Independent reflections $9144 [R_{int} = 0.1583]$ Data / restraints / parameters $9144/0/505$ wR ( $F^2$ all data) $wR_2 = 0.1638$ R ( $F$ observed data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ $1.012$ Observed data ( $L_2 \supset C(D)$ )5600	Reflections collected	62935
Data / restraints / parameters $9144/0/505$ wR ( $F^2$ all data)w $R_2 = 0.1638$ R ( $F$ observed data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ $1.012$ Observed data ( $f_2 = 0$ ) $F_2 = 0.000$	Independent reflections	$9144 [R_{int} = 0.1583]$
wR ( $F^2$ all data)wR2 = 0.1638R (F observed data)R1 = 0.0655Goodness-of-fit on $F^2$ 1.012Observed data ( $F_2$ = 0.000	Data / restraints / parameters	9144/0/505
$R$ (F observed data) $R_1 = 0.0655$ Goodness-of-fit on $F^2$ 1.012Observed data $U > 2\pi(D)$ 5600	wR ( $F^2$ all data)	$wR_2 = 0.1638$
Goodness-of-fit on $F^2$ 1.012Observed data $U_2 2 \pi (U)$ 5600	R (F observed data)	$R_1 = 0.0655$
Observed data $[1 > 2\pi(b)]$ 5600	Goodness-of-fit on $F^2$	1.012
	Observed data $[I > 2\sigma(I)]$	5690
Largest difference of peak and hole $(e/Å^3)$ 0.616 and -0.876	Largest difference of peak and hole $(e/Å^3)$	0.616 and -0.876

## 3. Results and discussion

#### 3.1. Preparation and crystallography

The (por)Fe(OC(=O)R) compounds (por = OEP or TPP; R = CCl<sub>3</sub> or CH<sub>2</sub>Cl) were prepared in a manner similar to that used for the preparation of other (por)Fe(OC(=O)R) analogues. Reactions of the respective acetic acids with the  $\mu$ -oxo dimers [(por)Fe]<sub>2</sub>( $\mu$ -O) generated, after appropriate workup, the desired products in 50–65% isolated yields (Eq. (1)). These compounds are moderately stable as solids in air, as judged by the lack of changes in their IR spectra over several days.

$$[(por)Fe]_2(\mu-0) + 2RC(=0)OH \rightarrow 2(por)Fe(O(C(=0)R) + H_2O$$
(1)

1: por = TPP,  $R = CCl_3$ 2: por = TPP,  $R = CH_2Cl_3$ 

**3**: por = OEP, 
$$R = CCl_3$$
 [18]

The IR spectra of the (por)Fe(OC(=O)R) compounds display bands attributed to the coordinated carboxylates; for **1** ( $v_{OCO}(asym)$  1704 cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub>) and 1709 cm<sup>-1</sup> (KBr)), for **2** ( $v_{OCO}(asym)$  1684 cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub>) and 1692 cm<sup>-1</sup> (KBr)), and for **3** ( $v_{OCO}(asym)$  1704 cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub>) and 1711 cm<sup>-1</sup> (KBr)). Clearly, the  $v_{OCO}(asym)$  band positions are more reflective of the carboxy-late R substitution rather than the type of porphyrin macrocycle (i.e., TPP vs. OEP). In line with this, iron porphyrin analogues with more electron-rich carboxylate ligands (OC(=O)CH<sub>3</sub>, OC(=O)C<sub>6</sub>H<sub>5</sub>, OC(=O)CH<sub>2</sub>CH<sub>3</sub>) have much lower  $v_{OCO}(asym)$  bands in the 1651–1670 cm<sup>-1</sup> range [17].

Single crystals of  $(TPP)Fe(OC(=O)CCl_3)$  were obtained by slow evaporation of a  $CH_2Cl_2/cyclohexane$  solution of the complex at room temperature. The molecular structure and the porphyrin atom displacements for  $(TPP)Fe(OC(=O)CCl_3)$  are shown in Fig.1 (a) and (b), respectively.

The porphyrin core is *saddled*, where diagonally positioned pyrrole moieties have their atoms above the porphyrin mean plane, and the other pyrrole atoms are below the plane [24]. There are only three other five-coordinate (por)Fe(acetate) compounds whose crystal structures have ben reported, and these are high-

spin species. A *saddle* distortion has been noted for the closely related (TPP)Fe(OC(=O)CF<sub>3</sub>) [25]. However, the compound (TTP)Fe (OC(=O)CH<sub>3</sub>) has a *domed* porphyrin core [17], whereas the (OEP) Fe(OC(=O)CCl<sub>3</sub>) [18] has varied porphyrin core deformations depending on the crystal form obtained with different solvates. The relative positioning of adjacent porphyrins is shown in Fig. 2, where a lateral shift of 3.76 Å and a porphyrin mean plane separation of 3.67 Å are observed [24].

As seen in Figs. 1 and 2, the trichloroacetate ligand in 1 binds to the Fe center through one of the acetate O atoms. The Fe–O bond distance is 1.917(2) Å, and the axial  $\angle$ Fe–O–C angle is 133.2(2)°. The Fe atom is displaced by 0.44 Å from the 24-atom mean porphyrin plane towards the acetate ligand. This apical Fe displacement is similar to that determined in high-spin (TPP)Fe(OC(=O) CH<sub>3</sub>) (+0.477(2) Å) [26] and in (TPP)Fe(OC(=O)CF<sub>3</sub>) (+0.45 Å) [27], and is in the range (0.39–0.62 Å) determined for five-coordinate high-spin ferric porphyrins as documented by Scheidt and coworkers [28]. Indeed, the Fe–N(por) and Fe–O bond parameters are also indicative of (TPP)Fe(OC(=O)CCl<sub>3</sub>) being a high-spin species in the crystal.

## 3.2. Electrochemistry

The redox behaviors of the (por)Fe(OC(=O)R) compounds **1–3** have been examined by cyclic voltammetry at room temperature. The resulting cyclic voltammograms are shown in Figs. 3–5. As shown in Fig. 3, the (OEP)Fe(OC(=O)CCl<sub>3</sub>) compound (i.e., **3**) undergoes two reversible oxidations, occurring at  $E^{ov}_{ox1}$  = +0.55 and  $E^{ov}_{ox2}$  = +1.04 V versus the Cp<sub>2</sub>Fe<sup>0/+</sup> redox couple.

The separations in peak potentials (i.e.,  $\Delta E$ ) for each of the oxidations are near-identical to that for the known reversible Cp<sub>2</sub>Fe<sup>0/+</sup> couple under our electrochemical cell setup conditions, indicating that both the first and second oxidations are reversible single-electron transfer processes. In addition, the cathodic to anodic peak current ratios ( $i_{pc}/i_{pa}$ ) for both oxidations are ~1.0, suggesting that the two oxidations are chemically reversible at this scan rate. Furthermore, plots of  $i_{pa}$  versus  $v^{1/2}$  for the first and second oxidations are linear, indicative of diffusion-controlled processes for both oxidations. In contrast to the well-behaved oxidations, the reduction of **3** is quite ill-defined under our conditions, showing a broad irreversible reduction peak at  $E_{pc} = -0.99$  V; this broad feature is observed when either the positive or negative scan direction is initiated first. The electrochemistry of the related compounds



Fig. 2. Relative positions of adjacent porphyrin macrocycles in the crystal structure of 1.



Fig. 3. Cyclic voltammogram of 0.1 mM (OEP)Fe(OC(=O)CCl<sub>3</sub>) 3 in  $CH_2Cl_2$  containing 0.1 NBu<sub>4</sub>PF<sub>6</sub> at a scan rate of 0.2 V/s.



Fig. 4. Cyclic voltammograms of 0.1 mM (TPP)Fe(OC(=O)CCl\_3) 1 in  $CH_2Cl_2$  containing 0.1 NBu<sub>4</sub>PF<sub>6</sub> at a scan rate of 0.2 V/s.



Fig. 5. Cyclic voltammograms of 0.1 mM (TPP)Fe(OC(=O)CH\_2Cl) 2 in  $CH_2Cl_2$  containing 0.1 NBu<sub>4</sub>PF<sub>6</sub> at a scan rate of 0.2 V/s.

 $(por)Fe(OC(=O)CH_3)$  (por = OEP, TPP) have been reported; the acetate  $(OEP)Fe(OC(=O)CH_3)$  compound in  $CH_2Cl_2$  undergoes two reversible oxidations and a reversible reduction [10], and

 $(TPP)Fe(OC(=O)CH_3)$  also exhibits a reversible reduction [9]. It thus appears that the presence of the trichloroacetate ligand in **3** probably enhances follow-up decomposition of the reduced product.

The cyclic voltammograms of the tetraphenylporphyrin compounds, namely (TPP)Fe(OC(=O)CCl<sub>3</sub>) **1** and (TPP)Fe(OC(=O)CH<sub>2</sub>Cl) **2**, were also recorded. As shown in Fig. 4a and 5 a, and when the full oxidation scan is recorded, the first oxidations appear less fully reversible. In addition, **1** undergoes an apparent reversible second oxidation at  $E^{or}_{ox2} = +1.01$  V, but with a daughter peak at + 0.11 V. That the second oxidations of the trichloroacetate complexes and **1** and **3** are more reversible than that of the chloroacetate complex **2** is suggestive of the second oxidations of **1** and **3** also being largely porphyrin centered.

Interestingly, however, when only the first oxidations are probed, i.e., the when the direction of the scans is reversed just after the first oxidation, well-defined reversible first oxidations are observed at  $E^{\circ}_{ox1} = +0.72 \text{ V}$  (for **1**) and  $E^{\circ}_{ox1} = +0.69 \text{ V}$  (for **2**) as shown in Figs. 4b and 5b. It is not surprising that the first oxidation potential of **1** is slightly higher than that of **2**, since **1** has the more chloro-substituted axial acetate.

Further, the first oxidation of the OEP trichloroacetate derivative **3** (at  $E^{o}_{ox1} = +0.55$  V) is lower than that of the related TPP derivative **1** (at  $E^{o}_{ox1} = +0.72$  V), reflecting the fact that the OEP macrocycle is more electron-rich than the TPP macrocycle. Given the greater effect of macrocycle substitution, compared with axial acetate identity, on the oxidation potentials, we surmise that the first oxidations are largely porphyrin macrocycle based. The electrochemical data are summarized in Table 2.

As with the (OEP)Fe(OC(=O)CCl<sub>3</sub>) compound **3** (Fig. 3), the trichloroacetate compound (TPP)Fe(OC(=O)CCl<sub>3</sub>) 1 undergoes an irreversible reduction with a broad  $E_{pc}$  value of -0.76 V (Fig. 4a), indicative of rapid decomposition of the reduction products on the cyclic voltammetry timescale. We speculated that this lack of the reversibility of the first reductions of  $(OEP)Fe(OC(=O)CCl_3)$ and  $(TPP)Fe(OC(=O)CCl_3)$  was due to the dissociation of the  $Cl_3C$ (C=O)O<sup>-</sup> anions after the reductions. Similar ligand dissociations after the first reductions of five-coordinate iron porphyrins have been reported [29,30]. On the other hand, we found that the first reduction of the chloromethyl compound (TPP)Fe(OC(=O)CH<sub>2</sub>Cl) was quite well-defined at the scan rate of 0.2 V/s, showing reversible behavior ( $E^{0}$  = -0.78 V) (Fig. 5c), which indicates that the Fe-O bond stays intact in the reduction process. Similar reversible reductions of the non-halogenated axially coordinated (TPP)Fe(OC(=O)CH<sub>3</sub>) and (OEP)Fe(OC(=O)CH<sub>3</sub>) compounds have been reported previously [9,10].

# 3.3. Infrared spectroelectrochemistry

In order to further investigate the redox processes of these compounds, difference IR spectra were recorded using a fiber-optic dip probe [14–16] at room temperature while the electrode was held at the potential just past the potential of the forward peak. To the best of our knowledge, there are no reports describing the infrared spectroelectrochemistry of five-coordinate iron acetate porphyrin complexes.

Table 2

Redox potentials ( $E^{o}$ , in V vs Cp<sub>2</sub>Fe<sup>0/+</sup>) for oxidations and reductions of the (por)Fe(OC(=O)R) compounds in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub>.

Compounds	1st oxid.	2nd oxidation	reduction
(TPP)Fe(OC(=O)CCl <sub>3</sub> ) <b>1</b>	0.72	1.01	$-0.76^{\circ}$
(TPP)Fe(OC(=O)CH <sub>2</sub> Cl) <b>2</b>	0.69	1.13 <sup>°</sup>	$-0.78^{\circ}$
(OEP)Fe(OC(=O)CCl <sub>3</sub> ) <b>3</b>	0.55	1.04	$-0.99^{\circ}$

<sup>\*</sup> Irreversible redox process; the forward peak potential  $E_p$  is reported instead.

For (OEP)Fe(OC(=O)CCl<sub>3</sub>) **3**, the electrode potential was held at +0.85 V to generate a measurable quantity of the first oxidation product on the electrode surface. The difference IR spectrum is shown in Fig. 6a. The  $v_{OCO}(asym)$  band at 1704 cm<sup>-1</sup> of the starting compound disappeared, and a new  $v_{OCO}(asym)$  at 1776 cm<sup>-1</sup> formed assigned to the oxidation product. In addition, a new band at 1535 cm<sup>-1</sup> appeared in the spectrum assigned to the formation of an OEP-containing  $\pi$ -radical cation, indicating that the first oxidation occurs at the porphyrin ring, a spectral conclusion that is consistent with the results from the cyclic voltammograms. Characteristic IR bands in the region of 1520–1570 cm<sup>-1</sup> are diagnostic for OEP-containing  $\pi$ -radical cations as detailed elsewhere [31,32].

The reduction of (OEP)Fe(OC(=O)CCl<sub>3</sub>) **3** was also probed by IR spectroelectrochemistry, where the electrode potential was held at -1.17 V. As shown in Fig. 6b, the reduction of **3** results in loss of  $v_{OCO}(asym)$  at 1704 cm<sup>-1</sup> of the starting compound and the appearance of a new band at 1687 cm<sup>-1</sup> was assigned to the accumulation of the dissociated Cl<sub>3</sub>C(C=O)O<sup>-</sup> anion at the electrode surface. This assignment was further confirmed by the  $v_{OCO}(asym)$  (at 1687 cm<sup>-1</sup>) of independently synthesized [(15-crown-5)Na](OC(=O)CCl<sub>3</sub>) [33–36] added to CH<sub>2</sub>Cl<sub>2</sub> containing the support electrolyte.

The IR difference spectra of the first oxidations for the (TPP)Fe(OC(=O)CCl<sub>3</sub>) **1** and (TPP)Fe(OC(=O)CH<sub>2</sub>Cl) **2** complexes show that the  $v_{OCO}(asym)$  bands of the oxidized products shifted by + 72 and + 76 cm<sup>-1</sup>, respectively, from their neutral precursors (Figs. 7a and 8a). In addition, an IR band shift from 1600 cm<sup>-1</sup> to ~1585 cm<sup>-1</sup> for **1**, and 1600 cm<sup>-1</sup> to ~1588 cm<sup>-1</sup> for **2**, are observed in the difference IR spectra of the two complexes. Similar shifts are detected for one-electron porphyrin centered oxidation of tetraphenyl-based metalloporphyrins, due to the phenyl mode absorption changes [37]. The oxidized tetraarylporphyrin  $\pi$ -radical cations have characteristic IR bands in the region of 1270–1295 cm<sup>-1</sup> [31]. Unfortunately, we could not identify this band because of the strong absorption of our solvent system in this

(OEP)Fe(OC(=O)CCl<sub>3</sub>) (a) 1st oxid 1776 cm<sup>-1</sup> 1704 cm<sup>-1</sup> (b) 1687 cm<sup>-1</sup> 1st red 1704 cm<sup>-1</sup>

1900 1800 1700 1600 1500 Wavenumber (cm<sup>-1</sup>)

**Fig. 6.** Difference IR spectra showing the products from (a) the first oxidation, and (b) first reduction of (OEP)Fe(OC(=O)CCl<sub>3</sub>) **3** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub>, with the potential held at + 0.85 V and -1.17 V, respectively, vs the Cp<sub>2</sub>Fe<sup>0/+</sup> couple.



**Fig. 7.** Difference IR spectra showing the products from the (a) first oxidation, and (b) first reduction of (TPP)Fe(OC(=0)CCl<sub>3</sub>) **1** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub>, with the potentials held at + 0.91 V and -0.87 V, respectively, vs the Cp<sub>2</sub>Fe<sup>0/+</sup> couple.



**Fig. 8.** Difference IR spectra showing the products from the (a) first oxidation, and (b) first reduction of (TPP)Fe(OC(=O)CH<sub>2</sub>Cl) **2** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub>, with the potentials held at + 0.92 V and -1.03 V, respectively, vs the Cp<sub>2</sub>Fe<sup>0/+</sup> couple.

region. However, the OCO shifts of the two TPP derivatives are comparable with that of the OEP derivative. We thus assign the first oxidations of  $(TPP)Fe(OC(=O)CCl_3)$  and  $(TPP)Fe(OC(=O)CH_2Cl)$  to also be porphyrin based.

Similar to the (OEP)Fe(OC(=O)CCl<sub>3</sub>) **3** compound described earlier in Fig. 6, the reduction of (TPP)Fe(OC(=O)CCl<sub>3</sub>) **1** results in the loss of the  $v_{OCO}(asym)$  band at 1704 cm<sup>-1</sup> and the appearance of a new band at 1688 cm<sup>-1</sup>, suggesting the dissociation of the acetate anion from the iron center of the porphyrin (Fig. 7b).

In the case of the reduction of (TPP)Fe(OC(=O)CH<sub>2</sub>Cl), the difference IR spectrum also shows the disappearance of the original  $v_{OCO}(asym)$  band at ~1684 cm<sup>-1</sup>, but the appearance of two new bands at  $1643 \text{ cm}^{-1}$  and  $1624 \text{ cm}^{-1}$  (Fig. 8b). It is interesting that the cyclic voltammogram of (TPP)Fe(OC(=O)CH<sub>2</sub>Cl) 2 shows a reversible reduction on the cyclic voltammetry timescale (Fig. 5c). These two new  $v_{OCO}(asym)$  bands indicate that the reduction product undergoes a slow but detectable decomposition on the IR spectroelectrochemical timescale. In addition, the solution IR spectrum of the salt [(15-crown-5)Na](OC(=O)CH<sub>2</sub>Cl) shows a  $v_{OCO}(asym)$  band at ~1620 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>. Thus, the 1624 cm<sup>-1</sup> band is assigned to the  $v_{OCO}(asym)$  band of the dissociated chloroacetate anion and the 1643 cm<sup>-1</sup> band is assigned to the  $v_{OCO}(asym)$  band of the bound chloroacetate anion still attached to Fe in the reduction product. The IR data thus suggests that the (TPP)Fe(OC(=0)CH<sub>2</sub>Cl) **2** compound undergoes a fast electron transfer followed by a structural change that involves loss of the chloroacetate anion from the metal center. Consistent with the cyclic voltammetry results, we find that axial ligand loss after the first reduction of (TPP)Fe(OC(=O)CH<sub>2</sub>Cl) **2** is much slower than those of the trichloroacetate compounds  $(TPP)Fe(OC(=O)CCl_3)$  1 and  $(OEP)Fe(OC(=O)CCl_3)$  **3** in this study.

## 4. Conclusion

We have prepared three five-coordinate iron acetate porphyrins: (TPP)Fe(OC(=O)CCl<sub>3</sub>) **1**, (TPP)Fe(OC(=O)CH<sub>2</sub>Cl) **2**, and (OEP)Fe(OC(=O)CCl<sub>3</sub>) **3** [18]. We have also determined the X-ray crystal structure of (TPP)Fe(OC(=O)CCl<sub>3</sub>). The electrochemistry and IR spectroelectrochemistry of theses iron acetate porphyrin complexes have been investigated. The first reversible oxidations of these compounds are porphyrin based, resulting in +71–76 cm<sup>-1</sup> shifts of the  $v_{OCO}(asym)$  bands of the acetate groups. The reductions of these compounds result in eventual dissociation of the acetate anions from the Fe centers.

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