Synthesis, Characterization and Solid State Molecular Structures of Five- and Six-Coordinate Primary Amide Manganese Porphyrin Complexes

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1. Introduction

Primary amides are a class of organic compounds, containing the -C(=O)NH_2 functional group. Acrylamide is one of the simplest primary amides, and is the building block for polyacrylamide used in the manufacturing of plastics and polymers. Acrylamide formation in the human diet can result from high temperature food treatments.[1] The oxidation of asparagine by hydrogen peroxide also produces acrylamide at physiological conditions in vitro.[2] It is known that acrylamide is neurotoxic, and potentially carcinogenic in humans.[3] Thus, the interactions of acrylamide with heme proteins have been studied intensively.[4-7] Interestingly, an acrylamide analog (A-778935) has been reported as a nitric oxide (NO) independent soluble guanylyl cyclase (sGC) activator.[8] The binding site of the acrylamide analog to sGC was proposed to be located away from the heme moiety; however a nitric oxide (NO)-like direct heme interaction can not be excluded.

Synthetic manganese porphyrin complexes have been prepared and studied as models for heme-containing proteins.[9-14] Fukuzumi and coworkers reported the formation of a primary amide adduct of manganese porphyrin complexes in solution.[15] A tertiary amide manganese porphyrin complex has been prepared and structurally characterized.[16] Curiously, no heme acrylamide model complex has been reported to date. Consequently, we are very interested in investigating the interactions of acrylamide with manganese porphyrin complexes, and obtaining structural information that would help inform our understanding of these species.

We have prepared and characterized both five- and six-coordinate acrylamide and acetamide manganese porphyrin complexes. The X-ray crystal structures of these complexes

have been obtained and reveal the sole O-binding mode of the acetamide and acrylamide as ligands. In addition, the electro-reduction of the acrylamide porphyrin adducts were studied. As far as we know, these compounds represent the first series of structurally characterized primary amide metalloporphyrin complexes.

2. Experimental Section

All reactions were performed under an atmosphere of prepurified nitrogen using standard Schlenk glassware and/or in a Mbraun Unilab Glovebox. Solutions for spectroscopic studies were also prepared under a nitrogen atmosphere. Solvents were distilled from appropriate drying agents under nitrogen just prior to use: CH_2Cl_2 (CaH_2), hexane (CaH_2), and toluene (Na).

2.1. Chemicals and Instrumentation.

Acetamide ($\text{CH}_3\text{C}(=\text{O})\text{NH}_2$, 99%) was purchased from Acros. Acrylamide ($\text{CH}_2\text{CHC}(=\text{O})\text{NH}_2$, >98%) and silver perchlorate anhydrous (AgClO_4 , 99.5%), were purchased from Alfa Aesar Company. All chemicals were used as received. $[(\text{TPP})\text{Mn}(\text{THF})_2]\text{ClO}_4$, $[(\text{T}(p\text{-Cl})\text{PP})\text{Mn}(\text{THF})_2]\text{ClO}_4$, and $(\text{OEP})\text{Mn}(\text{ClO}_4)$ were prepared using the published procedures.[17] Infrared spectra were recorded on a Nicolet iS10 FTIR spectrometer. Cyclic voltammetry was performed at room temperature using a Pine wavenow potentiostat voltammetric analyzer. A three-electrode system was used and consisted of a Pt working electrode (1 mm disk), a Pt wire counter electrode, and a Ag/AgCl reference electrode.

2.2. Synthesis

[(TPP)Mn(O=C(NH₂)CH=CH₂)₂]ClO₄ (1): To a toluene solution (20 mL) of [(TPP)Mn(THF)₂]ClO₄ (25.1 mg, 0.028 mmol) was added CH₂=CHCONH₂ (6.1 mg, 0.086 mmol). The mixture was stirred for 45 min, during which time the color of the solution changed from brown-green to green. The solvent was reduced to ~5 mL and hexane (20 mL) was added. The black precipitate formed was collected by filtration, washed with hexane (2×15 mL), and dried in vacuo to give [(TPP)Mn(O=C(NH₂)CH=CH₂)₂]ClO₄ (16.5 mg, 0.0186 mmol, 66% isolated yield). Slow evaporation of a CH₂Cl₂/hexanes (1:1 ratio; 5 mL) solution of the product at room temperature gave suitable crystals for X-ray diffraction studies. Anal. Calcd for C₅₀H₃₈O₆N₆ClMn•0.025CH₂Cl₂•0.3C₆H₁₄: C, 66.34; H, 4.65; N, 8.96; Cl, 3.97. Found: C, 66.24; H, 4.41; N, 8.61; Cl, 4.08. IR (KBr, cm⁻¹): ν_{CO} 1655 m; also ν_{ClO₄} 1107 s, 1090 s, 1073 s, 625 m. UV–Vis spectrum (λ (ε, mM⁻¹ cm⁻¹), 3.9 × 10⁻⁶ M in CH₂Cl₂): 389 (71), 409 (53 sh), 482 (49), 571 (15), 604 (13) nm.

The other acetamide and acrylamide manganese porphyrin complexes were generated similarly using the respective porphyrin macrocycles and amides:

[(T(*p*-Cl)PP)Mn(O=C(NH₂)CH=CH₂)₂]ClO₄ (2). Yield: 74%. Anal. Calcd for C₅₀H₃₄O₆N₆Cl₅Mn•0.5C₃H₅NO: C, 57.14; H, 3.40; N, 8.41; Cl, 16.37. Found: C, 55.79; H, 3.43; N, 8.09; Cl, 16.00. IR (KBr, cm⁻¹): ν_{CO} 1657 s; also ν_{ClO₄} 1120 s, 1109 s, 1090 m, 1075 s, 623 m. UV–Vis spectrum (λ (ε, mM⁻¹ cm⁻¹), 3.4 × 10⁻⁶ M in CH₂Cl₂): 389 (57), 407 (44 sh), 482 (42), 569 (13), 603 (11) nm. Slow evaporation of a CH₂Cl₂/hexane (1:1 ratio; 4 mL) solution of the product at room temperature gave suitable crystals for X-ray diffraction studies.

[(OEP)Mn(O=C(NH₂)CH=CH₂)]ClO₄ (3). Yield: 72%. Anal. Calcd for C₃₉H₄₉O₅N₅ClMn•0.4C₃H₅NO: C, 61.38; H, 6.53; N, 9.61; Cl, 4.51. Found: C, 61.16; H, 6.51; N, 9.24; Cl, 4.50. IR (KBr, cm⁻¹): ν_{CO} 1655 m; also ν_{ClO_4} 1107 m, 1109 s, 1056 m, 624 m.

[(OEP)Mn(O=C(NH₂)CH₃)]ClO₄ (4). Yield: 80%. Anal. Calcd for C₃₈H₄₉O₅N₅ClMn: C, 61.16; H, 6.62; N, 9.39; Cl, 4.75. Found: C, 61.13; H, 6.78; N, 9.19; Cl, 4.95. IR (KBr, cm⁻¹): ν_{CO} 1649 m; also ν_{ClO_4} 1121 m, 1109 s, 1055 m, 624 m. Slow evaporation of a CH₂Cl₂/hexane (2:1 ratio; 4 mL) solution of the product at room temperature gave suitable crystals for X-ray diffraction studies.

2.3 Solid-State Structural Determinations.

Details of crystal data and refinement are given in Table 1. Single-crystal X-ray diffraction data were collected using an instrument with a Bruker APEX ccd area detector and a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 . [18, 19]

(i) [(TPP)Mn(O=C(NH₂)CH=CH₂)₂]ClO₄ (1). Cell parameters were determined from a non-linear least squares fit of 9746 peaks in the range $2.17 < \theta < 27.49^\circ$. A total of 96675 data were measured in the range $1.589 < \theta < 27.508^\circ$ using ϕ and ω oscillation frames. The data were merged to form a set of 10219 independent data with $R(\text{int}) = 0.0272$ 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. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms. A total of 713 parameters

were refined against 519 restraints and 10219 data to give $wR(F^2) = 0.1377$ and $S = 0.996$ for weights of $w = 1/[\sigma^2(F^2) + (0.0720 P)^2 + 6.7000 P]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final $R(F)$ was 0.0476 for the 8950 observed, $[F > 4\sigma(F)]$, data. The largest shift/s.u. was 0.025 in the final refinement cycle. In the structure, one phenyl group and one acrylamide group were disordered. The occupancies of the phenyl atoms C33-C38 refined to 0.57(3) and 0.43(3) for the unprimed and primed atoms. The occupancies of atoms N6 and C48-C50 refined to 0.473(5), 0.392(5), and 0.133(3) for the unprimed, primed, and double-primed atoms. Restraints to make similar bonds approximately equivalent and to make displacement parameters of bonded atoms similar along the bonds were required.

(ii) **[(T(*p*-Cl)PP)Mn(O=C(NH₂)CH=CH₂)₂]ClO₄ (2).** Cell parameters were determined from a non-linear least squares fit of 9866 peaks in the range $2.36 < \theta < 27.51^\circ$. A total of 50864 data were measured in the range $1.894 < \theta < 27.535^\circ$ using ϕ and ω oscillation frames. The data were merged to form a set of 5417 independent data with $R(\text{int}) = 0.0210$ and a coverage of 100.0 %. The monoclinic space group $C2/c$ was determined by systematic absences and statistical tests and verified by subsequent refinement. Non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms bonded to carbons were initially determined by geometry and were refined using a riding model. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms. A total of 337 parameters were refined against 21 restraints and 5417 data to give $wR(F^2) = 0.0934$ and $S = 0.855$ for weights of $w = 1/[\sigma^2(F^2) + (0.0800 P)^2 + 4.4000 P]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final $R(F)$ was 0.0268 for the 4999 observed, $[F > 4\sigma(F)]$, data. The largest shift/s.u. was 0.002 in the final

refinement cycle. The perchlorate anion was located near to a 2-fold rotation axis. Restraints on the positional parameters of the anion atoms were required.

(iii) [(OEP)Mn(O=C(NH₂)CH₃)]ClO₄·CH₂Cl₂ (4·CH₂Cl₂). Cell parameters were determined from a non-linear least squares fit of 9975 peaks in the range $2.20 < \theta < 30.96^\circ$. A total of 58290 data were measured in the range $1.525 < \theta < 31.542^\circ$ using φ and ω oscillation frames. The data were merged to form a set of 13512 independent data with $R(\text{int}) = 0.0291$ and a coverage of 100.0 %. The triclinic space group $P\bar{1}$ was determined by statistical tests and verified by subsequent refinement. Non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogens bonded to carbons were initially determined by geometry and were refined using a riding model. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. A total of 484 parameters were refined against 13512 data to give $wR(F^2) = 0.1219$ and $S = 0.992$ for weights of $w = 1/[\sigma^2(F^2) + (0.0600 P)^2 + 1.5100 P]$, where $P = [F_O^2 + 2F_C^2] / 3$. The final $R(F)$ was 0.0434 for the 11012 observed, $[F > 4\sigma(F)]$, data. The largest shift/s.u. was 0.002 in the final refinement cycle. An additional dichloromethane was observed that was severely disordered and best modeled using the Squeeze method.[20]

The crystallographic data for the complexes are summarized in Table 1.

Table 1. Crystal Data and Structure Refinement

Compound	[(TPP)Mn(OC(NH ₂)CH=CH ₂) ₂]ClO ₄ (1)	[(T(<i>p</i> -Cl)PP)Mn(OC(NH ₂)CH=CH ₂) ₂]ClO ₄ (2)	[(OEP)Mn(OC(NH ₂)CH ₃)]ClO ₄ ·CH ₂ Cl ₂ (4 ·CH ₂ Cl ₂)
Empirical Formula (FW)	(C ₅₀ H ₃₈ ClMnN ₅ O ₆)	C ₅₀ H ₃₄ Cl ₅ MnN ₅ O ₆	(C ₃₈ H ₄₉ ClMnN ₅ O ₅)·(CH ₂ Cl ₂)
Formula weight	909.25	1047.02	831.13
<i>T</i> (K)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
Cell Parameters			
<i>a</i> (Å), α(°)	17.400(2), 90	24.342(2), 90	12.115(1), 106.066(1)
<i>b</i> (Å), β(°)	13.572(2), 90.381(2)	9.4077(8), 117.951(1)	13.460(1), 100.322(1)
<i>c</i> (Å), γ(°)	18.801(2), 90	23.250(2), 90	14.194(1), 93.366(1)
<i>V</i> , <i>Z</i> / <i>Z'</i>	4439.9(9) Å ³ , 4/1	4703.2(7) Å ³ , 4/0.5	2173.8(3) Å ³ , 2/1
<i>D</i> (calcd), g/cm ³	1.360	1.479	1.270
Abs coeff, mm ⁻¹	0.415	0.622	0.533
<i>F</i> (000)	1880	2136	872
Crystal size (mm)	0.52 x 0.20 x 0.16	0.42 x 0.31 x 0.14	0.34 x 0.26 x 0.16
θ range for data collection	1.589–27.508°	1.894–27.535°	1.53–31.54°
Reflections collected	96675	50864	58290
Independent reflns	10219 [<i>R</i> _{int} = 0.0272]	5417 [<i>R</i> _{int} = 0.0210]	13512 [<i>R</i> _{int} = 0.0291]
Max. and min. transmission	0.937 and 0.813	0.918 and 0.780	0.920 and 0.840
Data / restraints / parameters	10219 / 519 / 713	5417 / 21 / 337	13512 / 0 / 484
Goodness-of-fit on <i>F</i> ²	0.996	0.855	0.992
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0476	<i>R</i> 1 = 0.0268	<i>R</i> 1 = 0.0434
<i>R</i> indices (all data)	w <i>R</i> 2 = 0.1377	w <i>R</i> 2 = 0.0934	w <i>R</i> 2 = 0.1219
Largest diff. peak and hole, e.Å ⁻³	1.077 and –1.240	0.429 and –0.360	1.102 and –0.897

3. Results and discussion

3.1. Synthesis and characterization

The acrylamide manganese porphyrin complexes were prepared by displacing coordinated solvent or perchlorate from the precursors [(por)Mn(THF)₂]ClO₄ (por = TPP, T(*p*-Cl)PP) and (OEP)Mn(ClO₄). The reactions of the tetraphenylporphyrin [(por)Mn(THF)₂]ClO₄ compounds with excess acrylamide in toluene generated, after workup, the six-coordinate acrylamide derivatives, [(por)Mn(O=C(NH₂)CH=CH₂)₂]ClO₄ in 66% (TPP) and 74% (T(*p*-Cl)PP) isolated yields. The five-coordinate acrylamide and acetamide manganese octaethylporphyrin complexes, [(OEP)Mn(O=C(NH₂)R)]ClO₄ (R = CH₃, CH=CH₂), were prepared in a similar manner, using CH₂Cl₂ as the solvent instead of toluene. We find that the primary amide ligands are only **weakly bound**, as they dissociate readily from the manganese center at low concentration. Thus, the use of excess amides in the reactions and recrystallizations is required to assure the binding of the amides to the manganese centers. These products are moderately air-stable in the solid state. No decomposition was observed in the solid state in air for one week based on IR spectroscopy. The extended exposure to halogenated solvents such as dichloromethane leads to the formation of five-coordinate (por)MnCl due to the great affinity of Mn to halogens.[16]

The IR spectra of the six-coordinate acrylamide [(TPP)Mn(O=C(NH₂)CH=CH₂)₂]ClO₄ and [(T(*p*-Cl)PP)Mn(O=C(NH₂)CH=CH₂)₂]ClO₄ complexes as KBr pellets show intense bands at 1655 cm⁻¹ and 1657 cm⁻¹, respectively, that we assign to the ν_{CO} s for the coordinated-acrylamide. The five-coordinate [(OEP)Mn(O=C(NH₂)CH=CH₂)]ClO₄ and [(OEP)Mn(O=C(NH₂)CH₃)]ClO₄ complexes show the ν_{CO} bands at 1655 cm⁻¹ and 1649 cm⁻¹, respectively. The ν_{CO} s of the bound acetamide and acrylamide ligands are lower than those of

free acetamide (1695 cm^{-1})[21] and acrylamide (1681 cm^{-1})[21] which suggests an (C=)O-binding mode. We note that lowered ν_{COs} of the O-bound acetamides and acrylamides have been reported for their metal complexes.[22-24] In addition, the IR absorption bands centered at ~ 1100 (br) and $\sim 622\text{ cm}^{-1}$ indicate the presence of uncoordinated perchlorate anion in the complexes.[25] The UV-vis spectra of the two tetraphenyl-based porphyrins were obtained in the presence of $\sim 50\times$ excess of acrylamide in CH_2Cl_2 . The resulting spectra resemble the characteristic absorption bands of high-spin six-coordinate Mn(III) porphyrin complexes.[16, 26]

3.2. Crystallography

The six-coordinate bis-acrylamide complexes: We were successful in obtaining X-ray diffraction quality crystals of two bis-acrylamide complexes from their CH_2Cl_2 /hexane solutions. The corresponding crystal structures of these two compounds $[(\text{TPP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}=\text{CH}_2)_2]\text{ClO}_4$ (**1**), and $[(\text{T}(p\text{-Cl})\text{PP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}=\text{CH}_2)_2]\text{ClO}_4$ (**2**) are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are listed in Table 2.

Figure 1. Structure of the bis-acrylamide complex $[(\text{TPP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}=\text{CH}_2)_2]\text{ClO}_4$ (**1**). Hydrogen atoms on carbon atoms have been omitted for clarity.

Figure 2. Structure of the bis-acrylamide complex $[(T(p\text{-Cl})PP)Mn(O=C(NH_2)CH=CH_2)_2]ClO_4$ (**2**). Hydrogen atoms on carbon atoms have been omitted for clarity.

As shown in Figs. 1 and 2, each of the molecular structures contains only one porphyrin cation and one associated perchlorate anion, that is weakly H-bonded to the NH_2 group of the acrylamide ligands with the $O\cdots N$ distances of 2.949 Å (O2A) and 3.177 Å (O1A) in **1** and Å in **2**, respectively. The acrylamide ligands are O-bound to the manganese centers in the two complexes, which is consistent with the lower ν_{CO} of the bound acrylamide. The equatorial Mn–N(por) lengths in the two complexes are in the 2.013(2) Å - 2.018(1) Å range. The axial Mn–O bonds are 2.184(1) Å and 2.280(2) Å for **1**, and 2.212(1) Å for **2**. The similar bond lengths and resulting tetragonal elongation geometry around the Mn center have been observed in other high-spin d^4 six-coordinate Mn(III) porphyrin complexes.[16, 26, 27] It is worth noting that most of the d^4 Mn(III) porphyrin complexes reported have a high-spin Mn(III) ion, with only a couple of exceptions.[28, 29]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Primary Amide Manganese Porphyrin Compounds and Free Acetamide and Acrylamide.

Compounds	Mn–O	C–O	C–N(H ₂)	Mn–N(por)	C=C	∠Mn–O–C
[(TPP)Mn(O=C(NH ₂)CH=CH ₂) ₂]ClO ₄ (1)	2.1841(14)	1.253(2)	1.328(3)	2.013(2)	1.317(3)	131.08(13)
	2.280(2)	1.239(3)	1.321(3)	2.013(2)	1.313(4)	132.1(2)
		1.240(4)*	1.327(4)*	2.014(2)	1.315(4)*	135.0(2)*
		1.254(3)*	1.321(4)*	2.016(2)	1.316(5)*	120.9(5)*
[(T(<i>p</i> -Cl)PP)Mn(O=C(NH ₂)CH=CH ₂) ₂]ClO ₄ (2)	2.2115(9)	1.244(2)	1.327(2)	2.0178(10)	1.320(2)	139.60(9)
				2.0180(10)		
[(OEP)Mn(O=C(NH ₂)CH ₃)]ClO ₄ (4)	2.0925(11)	1.249(2)	1.322(2)	2.0085(13)		142.07(11)
				2.0079(13)		
				2.0099(13)		
				2.0104(13)		
CH ₃ C(=O)NH ₂ [30]		1.242(2)	1.326(2)			
CH=CH ₂ C(=O)NH ₂ [31]		1.2413(14)	1.3275(14)		1.3106(18)	

* The disordered components

The bound acrylamide ligands in **1** and **2** show nearly planar geometry. Comparing to the C–O bond length of 1.241(1) Å in free acrylamide[31], one of the acrylamide ligands in **1** shows a longer C–O bond at 1.253(2) Å. The other acrylamide ligand displays a three-fold disorder with the major component having a C–O bond length of 1.239(3) Å, and the two minor components having the C–O bond lengths of 1.240(4) Å and 1.254(3) Å. The C–NH₂ and C–C bonds are in the 1.321(4) Å to 1.328(3) Å, and 1.313 (4) Å to 1.320(2) Å ranges, respectively, which are comparable to those of free acrylamide. The molecular structure of complex **2** shows similar bond lengths of C–O (1.244(2) Å) and C–NH₂ (1.327(2) Å) with those of free acrylamide, and a slightly longer C–C bond (1.320(2) Å).

The five-coordinate complex: A five-coordinate ionic iron porphyrin complex, [(OEP)Fe(ONNMe₂)]ClO₄, has been crystallized by taking advantage of the π - π porphyrin stacking in OEP-type compounds, where a 5-coordinate monomer essentially blocks the 6th

coordination site.[32] We adopted the same strategy to obtain the five-coordinate manganese acrylamide complex. However, attempts to obtain single crystals of the $[(\text{OEP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}=\text{CH}_2)]^+$ product were not successful. We then employed another primary amide, acetamide, and we were able to obtain single crystals of the five-coordinate acetamide manganese porphyrin complex, namely $[(\text{OEP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}_3)]\text{ClO}_4$ from its CH_2Cl_2 /hexane solution. As shown in Figure 3, the structure contains a single acetamide ligand bound to manganese porphyrin cation. The perchlorate anion is H-bounded to the acetamide NH_2 group through its oxygen atoms with the $\text{O1A}\cdots\text{N5}$ distance of 2.933 Å.

Figure 3. Structure of the acetamide complex $[(\text{OEP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}_3)]\text{ClO}_4$ (**4**). Hydrogen atoms on carbon atoms have been omitted for clarity.

For the acetamide complex $[(\text{OEP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}_3)]\text{ClO}_4$ (**4**), the equatorial Mn–N(por) and axial Mn–O bond lengths are 2.008(1)–2.010(1) Å and 2.093(1) Å, respectively. The manganese is displaced 0.19 Å out of the 24-atom plane towards the acetamide ligand in this five-coordinated complex. The C–O bond and C–N bond of the bound acetamide are 1.249(2) Å and 1.322(2) Å, respectively, which are comparable to those of other O-bound acetamide Ni[33], Pt[34] complexes and free acetamide[30].

The π - π interactions between the two adjacent OEP macrocycles is most likely responsible for the formation of stable five-coordinate complexes during the crystallization.[32] As shown in Figure 4, for $[(\text{OEP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}_3)]\text{ClO}_4$, the mean plane separation (M.P.S.) between the 24-atom porphyrin planes is 3.37 Å, the Mn – Mn distance is 4.752 Å, and the lateral shift is ~2.91 Å. These structural parameters suggest that this compound is in between Class S and Class I with real π - π interactions between the two neighbor macrocycles, according to the nomenclature of Scheidt and Lee[35].

Figure 4. (a) View of the π - π stacking involving the cation of $[(\text{OEP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}_3)]\text{ClO}_4$ (**4**), showing (top) the 3.37 Å separation of the porphyrin planes, and (b) Sketch of the geometric parameters for the OEP-OEP π stacking in $[(\text{OEP})\text{Mn}(\text{O}=\text{C}(\text{NH}_2)\text{CH}_3)]\text{ClO}_4$. Perchlorate anions and hydrogen atoms have been omitted for clarity.

3.3. Electro-reduction

The electrochemistry studies of many synthetic manganese porphyrins have been reported.[11, 36-38] In this work, the reductions of the $[(T(p\text{-Cl})PP)Mn(O=C(NH_2)CH=CH_3)_2]^+$ and $[(TPP)Mn(O=C(NH_2)CH=CH_3)_2]^+$ cations were examined in the presence of $\sim 50\times$ excess of acrylamide in CH_2Cl_2 at room temperature. The excess acrylamide was added to ensure the formation of the six-coordination acrylamide Mn^{III} porphyrin complexes. The resulting cyclic voltammograms are shown in Figure 5.

Figure 5. Cyclic voltammograms showing the first reductions of $[(T(p\text{-Cl})PP)Mn(O=C(NH_2)CH=CH_2)_2]^+$ (a) and $[(TPP)Mn(O=C(NH_2)CH=CH_2)_2]^+$ (b) in the presence of $\sim 50\times$ excess acrylamide, in CH_2Cl_2 containing 0.1 M NBu_4PF_6 and at a scan rate of 200 mV/s.

Both cations show well-defined reversible reduction couples. The TPP derivative is reduced at an $E_{1/2}$ of -0.68 V versus Fc/Fc^+ within the solvent potential limit, which is more negative than the reduction potential of -0.63 V for $T(p\text{-Cl})PP$ derivative. The potential difference between the two cations is consistent with the electron-withdrawing ability of the

corresponding porphyrin macrocycles. The reduction potentials of a series of similar six-coordinate Mn(III) perchlorate complexes were reported, ranging from -0.09 V to -0.25 V versus SCE in various solvents.[37] A similar bis-DMF manganese porphyrin complex, [(TPP)Mn(DMF)₂](ClO₄), showed the first reduction potential at -0.19 V versus SCE in DMF, which is -0.65 V using Fc/Fc⁺ as the reference ($E^{\circ}_{\text{Fc/Fc}^+} = +0.47$ V versus SCE[39]). The first reduction of these Mn(III) porphyrin complexes is metal centered, reducing Mn(III) to Mn(II). Upon the reduction, one axial ligand would dissociate from the manganese center to form a five coordinate manganese porphyrin complex.[37, 40, 41] Based on the similar reduction behavior observed in our work, it is most likely that the Mn(III) centers of both TPP and T(*p*-Cl)PP derivatives are reduced to Mn(II) and one of the two axial acrylamide ligands dissociates from the metal center to form a five-coordinate Mn(II) complex upon the first reduction as shown in eq. 1.

The dissociate acrylamide molecule can reversibly bind back to the manganese center while it is oxidized back to Mn(III).

4. Conclusions

We have prepared a number of primary amide manganese porphyrins from the reactions of the cationic [(OEP)Mn]ClO₄ and [(por)Mn(THF)₂](ClO₄) precursors with acrylamide or acetamide. We have structurally characterized, by single-crystal X-ray crystallography, two six-coordinate [(por)Mn(O=C(NH₂)CH=CH₂)₂](ClO₄) (por = TPP, T(*p*-Cl)PP) compounds and one five-coordinate [(OEP)Mn(O=C(NH₂)CH₃)]ClO₄ derivative. We have shown that the C=O vibrations of the amides shift negatively upon the coordination. Importantly, a sole O binding

mode of the amide ligands has been shown in the crystal structures. Furthermore, the electro-reductions of the two six-coordinate acrylamide complexes have been studied. The redox behavior is consistent with those for other manganese porphyrins that show metal-centered reduction. This class of compounds represents the first reported molecular structure of primary amide metalloporphyrin complexes.

Appendix A. Supplementary data: CCDC 1504199-1504201 contains the supplementary crystallographic data for **1**, **2** and **4**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: ([+44](tel:+441223336033)) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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