(β-Octafluoro-*meso*-tetraarylporphyrin)manganese Complexes: Synthesis, Characterization and Catalytic Behaviour in Monooxygenation Reactions

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Keywords: Fluorinated porphyrins / Electrochemistry / Manganese / Oxidation catalysis

The synthesis and characterization of manganese complexes of β-octafluoro-*meso*-tetraarylporphyrins are reported. The presence of the electron-withdrawing β-fluorine atoms induces a very large shift of the redox potential for the oxidation of the manganese(II) derivatives. With the *meso*-aryl group bearing two *ortho*-chlorine atoms (2,6-dichlorophenyl) or five fluorine atoms (pentafluorophenyl), metal complexation leads to the isolation of pure manganese(II) compounds. The stability and catalytic activity of these new derivatives have been studied using hydrogen peroxide and iodosylbenzene as oxidants, and standard substrates for epoxidation and hydroxylation reactions. The results are compared to those obtained with the β-hydrogenated analogs under the same conditions. In the case of hydrogen peroxide, the high level of porphyrin degradation prevents efficient catalytic activity. With iodosylbenzene as oxidant, both stability and epoxidation are similar to those of the β-hydrogenated porphyrins, however, a substantial improvement in the efficiency of the hydroxylation of cyclohexane is observed with up to 33 turnovers with (perfluorotetraphenylporphyrin)manganese(II).

Introduction

Metalloporphyrins have long been known to catalyze the oxidation of various substrates. These catalytic reactions can be performed with a large variety of oxygen donors such as iodosylbenzene (PhIO), peroxides (hydrogen or alkyl), hypochlorites, potassium peroxysulfate, *N*-oxides or molecular oxygen.[1–4] Although various metalloporphyrins have been shown to be catalytically efficient,[5] the most studied ones are those containing iron and manganese. Despite substantial progress towards the use of metalloporphyrins as catalysts to perform cytochrome-P450-like oxidative reactions, especially in the hydroxylation of alkanes, synthesis of new porphyrins with electron-withdrawing substituents is still a challenge. The objective is to prepare porphyrins characterized by very high redox potentials which should resist oxidative decomposition and exhibit a very high efficiency in oxidation catalysis. Three generations of metalloporphyrins have been successively studied: i) the unsubstituted core-planar tetraphenylporphyrin (TPP),[6–9] ii) the porphyrins bearing substituents on the *meso*-aryl groups[10–13] and iii) the porphyrins β-octahalogenated or β-substituted with other electron-withdrawing groups.[14–18] In the latter group, the chloro and the bromo derivatives have been extensively studied whereas the fluorinated compounds have only recently been reported.[19,20]

In a misleading paper published in 1989, the ferric "Teflon" porphyrin [2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin] was reported to be very stable and very efficient for epoxidation and hydroxylation with hydrogen peroxide.[21] Not only was the characterization of the β-fluorinated porphyrins shown to be erroneous,[19,20] but the purported catalytic activities have been invalidated.[22] With the exception of the hydroxylation of aromatic compounds involving the use of a large excess of the substrate anisole[23] or toluene,[24] β-octahalogenation of metalloporphyrins leads to catalysts relatively unstable towards hydrogen peroxide[22,25,26] or hypochlorites.[27] Nevertheless, a great improvement in catalytic activity occurs through β-octahalogenation of *meso*-tetrakis(2,6-dichlorophenyl)porphyrin when using $KHSO_5$,[15] PhIO[22,28] or molecular oxygen[17] as oxidants. Surprisingly, the β-octahalogenation of the *meso*-tetrakis(pentafluorophenyl)porphyrin does not improve the efficiency of the epoxidation or hydroxylation with PhIO,[22,28] but does so for the hydroxylation of alkanes with molecular oxygen.[17]

The origin of the increased activity associated with the presence of electron-withdrawing substituents at the β-pyrrolic position is mainly related to a large anodic shift in the first oxidation potential[20,29–39] and to distortion of the macrocycle.[33,40–42]

Our previous work has shown that the β-fluorination of porphyriniron complexes leads to an increased catalytic activity with regard to the hydroxylation of alkanes.[22] However, with H_2O_2, the expected higher stability of the porphyriniron derivatives was not observed.[22] In the present study, we have prepared and characterized the manganese complexes of 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetraphenylporphyrin (β-F_8TPP), 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (β-F_8TDCPP) and 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (β-F_8TPFPP,

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  1434–1948/00/0505–1097 $ 17.50+.50/0

also called perfluorotetraphenylporphyrin). Their stability in the presence of PhIO and H_2O_2 has been measured, as well as their catalytic behaviour in the epoxidation of cyclooctene and the hydroxylation of cyclohexane.

Results

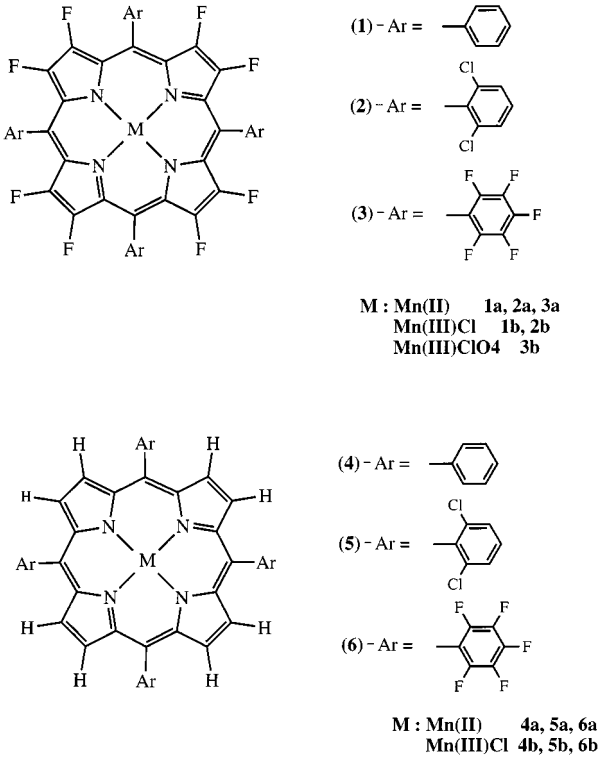
Synthesis of Metalloporphyrins

Preparation of the (β-octafluoro-*meso*-tetraarylporphyrin)manganese complexes (Scheme 1) was carried out under standard conditions,[43] from free-base porphyrins using a ten-fold excess of $Mn(OAc)_2{\cdot}4H_2O$ in DMF under an inert gas. Metallation was achieved after refluxing for a few minutes. Pure Mn^{II}(β-F_8TPP) complex (**1a**) could be obtained if the reaction was performed under anaerobic conditions, whereas pure manganese(II) complexes were always isolated, even after refluxing for several hours, under aerobic conditions, with the β-F_8TDCPP and β-F_8TPFPP porphyrins. These complexes, (β-F_8TDCPP)Mn^{II} (**2a**) and (β-F_8TPFPP)Mn^{II} (**3a**), obtained in high yield (>90%) after purification by column chromatography, are perfectly stable in air. In contrast, the complex (β-F_8TPP)Mn^{II} (**1a**) must be stored as an acetonitrile solution because slow oxidation occurs in air even in the solid state. A second step to prepare the manganese(III) derivatives is necessary, the protocol depending on the nature of the aryl groups. The complex (β-F_8TPP)Mn^{III}Cl (**1b**) was obtained from **1a** by autooxidation during column chromatography on silica gel. The compound (β-F_8TDCPP)Mn^{III}Cl (**2b**) can be prepared from **2a** by oxidation with iron perchlorate or ferricinium salt in dichloromethane solution. Attempts to isolate pure (β-F_8TPFPP)Mn^{III}Cl were unsuccessful because the manganese(III) complex is readily reduced to the Mn^{II} complex **3a**, but the perchloratomanganese(III) complex **3b** could be obtained in dichloromethane by addition of solid iron perchlorate.

Characterization of Metalloporphyrins

UV/Visible Spectroscopy

The electronic absorption spectra of the β-fluorinated manganese complexes in $CHCl_3$ are summarized in Table 1. The manganese(II) complexes display a hypsochromic shift of 13–16 nm compared to the β-hydrogenated analogs. The Soret bands of both (β-F_8TPP)Mn (**1a**) or (β-F_8TPFPP)Mn (**3a**) are found at 419 nm and that of the complex (β-F_8TDCPP)Mn (**2a**) at 422 nm. As for the β-hydrogenated analogs, two Q bands (551 and 588 nm) are observed for complex **1a** and only one near 550 nm for complexes **2a** and **3a**. The corresponding manganese(III) derivatives exhibit a Soret absorption at 474 nm for **1b** and **2b**, with a blue shift of only 3–4 nm as compared to **4b** and **5b**, respectively. However, the (perfluorotetraphenyl)porphyrin complex **3b** displays a shift of 14 nm (Soret band at 458 nm) relative to the hydrogenated complex **6b**.



Scheme 1. Structure and labels of porphyrinmanganese compounds

Table 1. UV/Vis data of various β-fluoroporphyrinmanganese complexes and other analogs [λ_{max} (nm)]

Compound	Soret band		Q bands			
(β-F_8TPP)Mn^{II} (**1a**)			419	549	586	
(β-F_8TDCPP)Mn^{II} (**2a**)			422	551	585	
(β-F_8TPFPP)Mn^{II} (**3a**)			546			
(TPP)Mn^{II} (**4a**)[a]			435	564	601	
(TDCPP)Mn^{II} (**5a**)[b]			435	567		
(TPFPP)Mn^{II} (**6a**)			432	561		
(β-F_8TPP)Mn^{III}Cl (**1b**)	365		474	519	572	607
(β-F_8TDCPP)Mn^{III}Cl (**2b**)	363		474		571	605
(β-F_8TPFPP)$Mn^{III}ClO_4$ (**3b**)	367		458		550	
(TPP)Mn^{III}Cl (**4b**)	375	401[c]	478	526	581	617
(TDCPP)Mn^{III}Cl (**5b**)	371	391[c]	477		579	606
(TPFPP)Mn^{III}Cl (**6b**)	365	395[c]	477		576	605

[a] From ref.[67]. – [b] From ref.[45]. – [c] Shoulder.

Electrochemistry

The redox potential data for the manganese compounds were obtained by cyclic voltammetry in dichloromethane containing 0.1 M Bu_4NPF_6 as supporting electrolyte. Results are referenced to the SCE and summarized in Table 2. All complexes undergo a reversible Mn^{II}/Mn^{III} process with $E^{1/2}$ ranging from –0.34 V for **4** to 0.70 V for **3**. Similar values have already been reported for the hydrogenated complexes **4**–**6**.[24,44,45] The potentials of the β-fluorinated porphyrinmanganese complexes are significantly higher than those of their hydrogenated analogs. The most important anodic shift is +0.82 V for (β-F_8TPFPP)Mn (**3**), compared to (TPFPP)Mn (**6**). Smaller shifts are observed be-

Table 2. Electrochemical data for porphyrinmanganese complexes (V vs. SCE)

Porphyrin complexes[a]	Ring oxidation		Mn^{II}/Mn^{III}	Ring reduction	
(β-F_8TPP)Mn (**1**)	n. o.[b]	1.51	0.16	–1.28	–1.53[c]
(β-F_8TDCPP)Mn (**2**)	n. o.	n. o.	0.30	–1.14	–1.40
(β-F_8TPFPP)Mn (**3**)	n. o.	n. o.	0.70	–0.64	–1.08
(TPP)Mn (**4**)[d]	1.53	1.09	–0.34	–1.58	n. o.
(TDCPP)Mn (**5**)[d]	n. o.	1.43	–0.28	–1.34	–1.50[c]
(TPFPP)Mn (**6**)[d]	n. o.	1.41[c]	–0.12	–1.26	–1.55

[a] Cyclic voltammetry conditions: in CH_2Cl_2 containing 1 mM porphyrinmanganese complexes and 0.1 M Bu_4NPF_6; scan rate, 50 $mV \cdot s^{-1}$. – [b] Not observed. – [c] Irreversible process, E^{ox}_p or E^{red}_p. – [d] These metalloporphyrins have been previously studied with different solvents: **4**,[44] **5**[45] and **6**.[24]

tween **2** and **5** (+0.58 V) and between **1** and **4** (+0.5 V). Furthermore, the amplitude of the redox potential values, which follows the order **1** < **2** < **3**, is larger than that of the hydrogenated complexes, which follows the order **4** < **5** < **6**. With the exception of the complex **1**, which shows a second oxidation wave at 1.51 V, there are no accessible oxidation waves, up to 1.8 V, for the complexes **2** and **3**. Two reversible reductions are often observed with manganese complexes.[46] The presence of the eight fluorine atoms induces small shifts at lower potentials for the complexes **1** and **2**, whereas a much larger influence is observed in the case of **3** with differences of 0.62 V and 0.47 V for the first and the second reduction waves, respectively.

Nuclear Magnetic Resonance

The fluorine chemical shifts of the new β-fluorinated porphyrinmanganese complexes are reported in the Experimental Section. To the best of our knowledge, only one report has been dedicated to fluorine-NMR study of (pentafluorophenyl)porphyrin derivatives complexed by zinc, iron or ruthenium.[47] With the paramagnetic manganese complexes, the resonances of the β-fluorine atoms are broadened beyond detection in the case of manganese(II) derivatives, whereas for the manganese(III) complexes broad signals are detected at δ = –4.9, –4.2 and –2.8 for complexes **1b**, **2b** and **3b**, respectively. The chemical shifts seem to correlate with the redox potential for the reduction of the manganese complexes [δ (ppm) = –5.44 + 3.8 $E^{1/2}$ (V); correlation coefficient: 0.993], but additional compounds would be needed to confirm this relationship.

Oxidation with Iodosylbenzene

Stability in the Absence of Substrate

The robustness of porphyrinmanganese complexes towards PhIO as oxidant has been studied at room temperature under aerobic conditions, both in the absence and presence of a co-catalyst such as 1-methylimidazole or ammonium acetate, and in the absence of substrate. The ratio catalyst/oxidant/co-catalyst employed was 1:100:10. An excess of cyclooctene was added to the cuvette prior to measurement to convert high-valent manganese species into Mn^{III} derivatives, allowing us to estimate the decrease of the Soret band of the Mn^{III} complexes (Table 3). Addition of cyclooctene was necessary since manganese complexes react with iodosylbenzene to generate, in the absence of substrate, (porphyrin)Mn^{IV} complexes.[48,49] A dimeric complex [(PhIO)TPPMn^{IV}Cl]$_2$O has been characterized by a broad Soret band at 421 nm in chlorobenzene.[48] Under similar conditions, but in dichloromethane, a Soret band was observed at 426 nm for the new complexes obtained from **4b** and **5b**, and at 417 nm from **6b**. With the β-fluorinated porphyrinmanganese complexes, the addition of PhIO to **1**(**a** or **b**), **2**(**a** or **b**) and **3a** produces new intermediates, characterized by Soret bands at 412, 410 and 404 nm, respectively, irrespective of the oxidation state of the starting complexes Mn^{II} or Mn^{III} (Table 4). Once again, β-fluorination leads to a blue-shift of 13–16 nm when compared with the β-hydrogenated analogs.

The results obtained show that with 1-methylimidazole or without co-catalyst, the β-fluorinated porphyrinmanganese(II) or -manganese(III) complexes show a similar robustness comparable with the β-hydrogenated analogs. It must be emphasized that the sterically protected porphyrins **2a**, **2b** and **5b** are very stable (loss <5%) even under the drastic conditions employed. On the other hand, the decomposition of complexes **3a** and **6b** is around 50%. In the absence of co-catalyst, complexes **1a**, **1b** and **4b** are quite stable, exhibiting only a 15 to 19% decrease in the intensity of Soret band. With a co-catalyst this decrease is ca. 55%. The stability depends on the nature of the aryl groups and increases in the order $C_6H_5 < C_6F_5 < C_6H_3Cl_2$, which applies both for the β-hydrogenated and the β-fluorinated porphyrins. With ammonium acetate as co-catalyst the stabilities of the catalysts were close to those observed with imidazole. However, with this co-catalyst, the reaction of PhIO with **2a**,**b** and **3a** leads to new complexes characterized by Soret peaks at 407 and 401 nm, respectively. These species still remain after addition of cyclooctene and have not been further characterized.

Epoxidation

The catalytic activity of the porphyrinmanganese complexes in cyclooctene epoxidation has been evaluated using unusually drastic catalytic conditions with a cyclooctene/PhIO/co-catalyst/catalyst ratio of 100:100:10:1 (Table 5). Thus, the epoxide yields, calculated relative to the substrate and the oxidant, which are in equal amounts, correspond directly to the turnover numbers.

Table 3. Stability of various porphyrinmanganese complexes towards PhIO

Catalyst	Decrease in Soret absorbance (%)[a]		Catalyst
(β-F_8TPP)Mn (**1a** or **1b**)[b]	55 (15)[c]	56 (19)[c]	(TPP)Mn^{III}Cl (**4b**)
(β-F_8TDCPP)Mn (**2a** or **2b**)[b]	5 (0)[c]	3 (0)[c]	(TDCPP)Mn^{III}Cl (**5b**)
(β-F_8TPFPP)Mn^{II} (**3a**)	48 (47)[c]	53 (51)[c]	(TPFPP)Mn^{III}Cl (**6b**)

[a] Porphyrin complexes were dissolved in dichloromethane (2 mM) with 1-methylimidazole (10 equiv.) and PhIO (100 equiv.) was added at 25 °C. After 15 min, 20 μL of cyclooctene was added in the cuvette and UV/Vis measurement was performed. – [b] Reduced and oxidized manganese complexes give identical values. – [c] In parentheses, same experiment without co-catalyst.

Table 4. UV/Vis data of the porphyrinmanganese complexes obtained after addition of iodosylbenzene [λ_{max} (nm), at 25 °C in CH_2Cl_2]

Intermediate	From	Soret band		Intermediate	From
"(β-F_8TPP)Mn^{IV}"	**1a** or **1b**	412	426 (421)[a]	"(TPP)Mn^{IV}"	**4b**
"(β-F_8TDCPP)Mn^{IV}"	**2a** or **2b**	410	426	"(TDCPP)Mn^{IV}"	**5b**
"(β-F_8TPFPP)Mn^{IV}"	**3a**	404	417	"(TPFPP)Mn^{IV}"	**6b**

[a] From ref.[48] in chlorobenzene.

Table 5. Cyclooctene epoxidation by PhIO catalyzed by porphyrinmanganese complexes

Catalyst	Epoxide yield (%)[a] Cyclooctene/PhIO		Catalyst
(β-F_8TPP)Mn (**1a** or **1b**)[b]	43 (42)[c]	42 (43)[c]	(TPP)Mn^{III}Cl (**4b**)
(β-F_8TDCPP)Mn (**2a** or **2b**)[b]	73 (71)[c]	73 (74)[c]	(TDCPP)Mn^{III}Cl (**5b**)
(β-F_8TPFPP)Mn^{II} (**3a**)	63 (60)[c]	59 (60)[c]	(TPFPP)Mn^{III}Cl (**6b**)

[a] Cyclooctene/PhIO/1-MeIm/catalyst = 100:100:10:1 in CH_2Cl_2 (catalyst at 2 mM), at room temperature. Yields were determined by GC after 1 h and based on starting cyclooctene. – [b] Reduced and oxidized manganese complexes give identical values. – [c] In parentheses, $CH_3CO_2NH_4$ used as co-catalyst with same ratio.

With 1-methylimidazole or ammonium acetate as co-catalyst, the activities of β-fluorinated (porphyrin)Mn^{II} or -Mn^{III} catalysts are very similar. Surprisingly, the results are also comparable to those obtained with the β-hydrogenated analogs. The epoxide yield was found to be about 43% for catalysts **1a**,**b** or **4b** and 60% for **3a** or **6b**. The best yields, of ca. 73%, were observed with the protected manganese complexes **2a**,**b** and **5b**. Therefore the activity is dependant on the nature of the aryl groups and increases in the order $C_6H_5 < C_6F_5 < C_6H_3Cl_2$.

Hydroxylation

The hydroxylation of cyclohexane was chosen to evaluate the catalytic activity of the porphyrinmanganese complexes. We used the same ratio as for epoxidation, namely a cyclohexane/PhIO/co-catalyst/catalyst ratio equal to 100:100:10:1, and the results are reported in Table 6. Again, we noticed similar activities for both β-fluorinated Mn^{II} and Mn^{III} catalysts. However, in this case, the presence of β-fluorine atoms improves the cyclohexane hydroxylation. In particular, with 1-methylimidazole, a two-fold increase in yield was observed with the catalyst **2**, as compared with **5b**. The best hydroxylation yield is obtained with the (perfluorotetraphenyl)porphyrin complex **3a**, with a 33% yield of cyclohexanol in the presence of 1-methylimidazole as co-catalyst. The activity depends also on the nature of the aryl groups, increasing in the order: $C_6H_5 < C_6H_3Cl_2 < C_6F_5$, in contrast to that observed for epoxidation. Finally, the co-catalyst clearly has an effect on the yields, 1-methylimidazole being more effective than ammonium acetate.

Oxidation with Hydrogen Peroxide

Stability in the Absence of Substrate

The stability of the manganese porphyrins was studied with a H_2O_2/co-catalyst/porphyrin ratio of 100:10:1, under aerobic conditions at room temperature (Table 7). Usually, acetonitrile is used for diluting hydrogen peroxide, but in this solvent complexes **2a** and **3a** remain in the reduced state, even in the presence of H_2O_2. Coordination of acetonitrile prevents reaction with H_2O_2. Moreover, the addition of acetonitrile to a dichloromethane solution of complex **2b** induces its reduction to the Mn^{II} complex **2a**. Therefore, we used methanol as co-solvent to assess the stability and catalytic activities of complexes **2a** and **2b**. However, the most electron-deficient catalyst **3a** was found to be unreactive towards H_2O_2 in methanol.

The effect of the co-solvent on the reactivity of the porphyrin complexes **2a** and **2b** was shown to be crucial, but the nature of the co-solvent is also important when measuring the stability of the β-hydrogenated complexes **4–6**. The complex **6b** is stable with acetonitrile as co-solvent and partially decomposed in the presence of methanol, whereas complex **5b** shows the opposite behaviour. The introduction of fluorine at the β-position of (TPP)Mn seems to stabilize the complex in acetonitrile but not in methanol. Degrada-

Table 6. Cyclohexane hydroxylation by PhIO, catalyzed by porphyrinmanganese complexes

Catalyst	Cyclohexane/PhIO with $CH_3CO_2NH_4$	Product yield (%)[a] Cyclohexanol + -one	Cyclohexane/PhIO with 1-MeIm
(β-F_8TPP)Mn (**1a** or **1b**)[b]	–		8
(β-F_8TDCPP)Mn (**2a** or **2b**)[b]	8		20
(β-F_8TPFPP)Mn^{II} (**3a**)	12		33
(TPP)Mn^{III}Cl (**4b**)	–		4
(TDCPP)Mn^{III}Cl (**5b**)	5		9
(TPFPP)Mn^{III}Cl (**6b**)	9		26

[a] Cyclohexane/PhIO/co-catalyst/catalyst = 100:100:10:1 in CH_2Cl_2 (catalyst at 2 mM), at room temp. Yields were determinated by GC after 1 h and based on starting cyclohexane. – [b] Reduced and oxidized manganese complexes give identical values.

Table 7. Stability of various porphyrinmanganese complexes towards H_2O_2

Catalyst	Decrease in Soret absorbance (%)[a]				Catalyst
	CH_2Cl_2/CH_3CN	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3CN	CH_2Cl_2/CH_3OH	
(β-F_8TPP)Mn^{II} (**1a**)	100	100			
(β-F_8TPP)Mn^{III}Cl (**1b**)	36	79	65	61	(TPP)Mn^{III}Cl (**4b**)
(β-F_8TDCPP)Mn^{II} (**2a**)	< 5[b]	52			
(β-F_8TDCPP)Mn^{III}Cl (**2b**)	< 5[c]	54	27	9	(TDCPP)Mn^{III}Cl (**5b**)
(β-F_8TPFPP)Mn^{II} (**3a**)	< 5[b]	< 5[b]			
			3	37	(TPFPP)Mn^{III}Cl (**6b**)

[a] H_2O_2 was added at once (100 equiv., 3% in CH_3CN or CH_3OH) to the porphyrinmanganese complex (2 mM) in CH_2Cl_2/CH_3CN (1:1) or CH_2Cl_2/CH_3OH (1:1) and the decrease was measured after 15 min at 25 °C. – [b] The complex remains as Mn^{II}. – [c] The complex is reduced to Mn^{II}.

tion of ca. 53% was measured for both Mn^{II} and Mn^{III} complexes **2a**, **2b**, much more important than that observed for the hydrogenated analog. Finally, the oxidized and reduced complexes **2a**, **2b** show the same decrease in intensity of the Soret band whereas the stability of complex **1** depends on the oxidation state. Bleaching of the reduced form **1a** is very rapid with both co-solvents even though the oxidized form **1b** decays more slowly and is sensitive to the nature of the co-solvent.9

Epoxidation and Hydroxylation

The olefin epoxidation activity of the porphyrinmanganese complexes was investigated by epoxidation of cyclooctene, with a cyclooctene/H_2O_2/$CH_3CO_2NH_4$/catalyst ratio of 100:200:10:1, in CH_2Cl_2/CH_3CN and CH_2Cl_2/CH_3OH mixtures (Table 8). As suggested by the stability test, the complex **3a** is inactive in these solvent mixtures. Both oxidation states of (β-F_8TDCPP)manganese complexes **2a** and **2b** are also inactive in acetonitrile. However, in methanol, a similar efficiency was observed for the two complexes. With a 15% yield of cyclooctene epoxide, these

Table 9. Oxidation in acetone by H_2O_2, catalyzed by (β-F_8TPFPP)Mn^{II} and (TPFPP)Mn^{III}Cl

Catalyst	Product yield (%)[a] Cyclooctene + H_2O_2 8 equiv. Epoxide	Cyclohexane + H_2O_2 8 equiv. ol + -one
(β-F_8TPFPP)Mn^{II} (**3a**)	32	9
(TPFPP)Mn^{III}Cl (**6b**)	44	4

[a] Substrate/H_2O_2/$CH_3CO_2NH_4$/catalyst = 100:800:10:1 (catalyst at 2 mM), at room temperature. H_2O_2 35% was added (2 molar equivalent relative to substrate) at 0, 10, 20 and 30 min. Mn(P), substrate and co-catalyst were dissolved in CH_2Cl_2/CH_3COCH_3 (80:20).

Table 8. Cyclooctene epoxidation by H_2O_2, catalyzed by porphyrinmanganese complexes

Catalyst	Epoxide yield (%)[a]				Catalyst
	CH_2Cl_2/CH_3CN	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3CN	CH_2Cl_2/CH_3OH	
(β-F_8TPP)Mn^{II} (**1a**)	1	–			
(β-F_8TPP)Mn^{III}Cl (**1b**)	1	1	4	5	(TPP)Mn^{III}Cl (**4b**)
(β-F_8TDCPP)Mn^{II} (**2a**)	n. d.[b]	16			
(β-F_8TDCPP)Mn^{III}Cl (**2b**)	n. d.[b]	14	> 98	48	(TDCPP)Mn^{III}Cl (**5b**)
(β-F_8TPFPP)Mn^{II} (**3a**)	n. d.[b]	n. d.[b]	69	41	(TPFPP)Mn^{III}Cl (**6b**)

[a] Cyclooctene/H_2O_2/$CH_3CO_2NH_4$/catalyst = 100:200:10:1 (catalyst at 2 mM), at room temperature. Yields were determined by GC after 1 h and based on starting cyclooctene. Mn(P), substrate and co-catalyst were dissolved in CH_2Cl_2/CH_3CN or CH_3OH (1:1); concentrated aqueous H_2O_2 diluted to 3% in the indicated solvent, was added by 2 additions of 1 molar equivalent relative to cyclooctene, at 0 and 20 min. – [b] Not detected.

β-fluorinated porphyrinmanganese complexes were less efficient than the analog (TDCPP)MnCl (**5b**). The same applies for the complexes of β-F_8TPP, **1a** and **1b**, which exhibit poor activities that are even inferior to the hydrogen equivalent **4b**.

In order to gain some insight into the catalytic activities of (perfluorotetraphenylporphyrin)manganese, a co-solvent which permits oxidations with H_2O_2 was required. With acetone as co-solvent instead of acetonitrile or methanol, we found that the perfluorotetraphenylporphyrin complex **3a** reacts with hydrogen peroxide.[50] A decrease in the Soret absorption of the (β-F_8TPFPP)Mn band was observed by UV/Vis spectroscopy, but without appearance of the Mn^{III} band, presumably due to a rapid return to the reduced form. In this system, even in the presence of the substrate, part of the hydrogen peroxide was consumed and reduced to water by the continual oxidation of Mn^{II} to Mn^{III}, to the detriment of substrate oxidation. Consequently, the use of a larger amount of H_2O_2 (8 equivalents relative to the substrate) led to a yield of epoxide of 32% (Table 9).

Hydroxylation reactions were only performed with the perfluorotetraphenylporphyrin complex **3a** and its β-hydrogenated analog **6b** (Table 9) based on their reasonable yields obtained for epoxidation. The yields of hydroxylation with these two porphyrinmanganese complexes are low although a slight increase is observed through β-fluorination.

Discussion

In some cases, β-octachlorinated or β-octabrominated porphyrins display higher activities, especially in hydroxylation catalysis. However, due to the strong electron-withdrawing character of the fluorine atoms, recent calculations have predicted that β-octafluorination should exert an electronic effect significantly larger than that of β-octachlorination or β-octabromination.[51] Furthermore, the effect on the energy level of the HOMO should be even more pronounced because the core distortion induced by steric hindrance between the aryl groups and the β-chlorine or -bromine is absent with the smaller fluorine atoms. This saddle distortion is responsible for some destabilization of the HOMO, resulting in a decrease in the first oxidation potential.[33,39,52] In a sense, the erroneous paper by Tsuchiya and Seno[21] corresponded to the expected improvement in stability and efficiency in hydroxylation catalysis. We recently unambiguously demonstrated the erroneous character of these results using authentic iron complexes of β-octafluorinated porphyrins. On the other hand, an increase in the efficiency of the catalyst for alkane hydroxylation is associated with β-octafluorination.[22]

Synthesis and Characterization

Manganese complexation results in the formation of stable Mn^{II} derivatives. Oxidation of manganese is not observed for complexes **2** and **3**, even during prolonged reflux in air, in contrast with β-octachlorinated or β-octabrominated porphyrins,[15] but in agreement with electrochemical data. The presence of the β-fluorine atoms induces a blue-shift in the Mn^{II} and Mn^{III} UV/Vis spectra as compared to the hydrogenated compounds. The amplitude of these blue-shifts varies in the range 5–20 nm depending on the oxidation state of the metal and the aryl substituents. This range is very close to the observed variation for the free-base porphyrins[19,20] or iron complexes.[53] This result, consistent with the planar structure of the β-octafluorinated porphyrins,[20,54] contrasts with the strong red-shifts observed for other β-octahalogenated derivatives which are associated with a large macrocycle distortion. However, the crystallographic structure of the pentacoordinated (H_2O)β-F_8TPPZn complex shows a pronounced saddle shape,[19] which is more likely attributable to crystal packing. Also surprising, but possibly related to the same variations between the solution and the solid state, is the near-planar structure of the hexacoordinated zinc complex of the β-heptanitrotetraphenylporphyrin,[18] whereas strong red-shifts of the Soret band are observed for the β-(nitro)$_{1-7}$porphyrins.[18,28,30,38]

The data for one-electron redox potentials are also in agreement with the strong electron-withdrawing character of the fluorine atoms. β-Octafluorinated porphyrinmanganese(III) complexes are more easily reduced to manganese(II) complexes than the hydrogenated analogs. Redox potentials of 0.16 V and 0.30 V are found for the derivatives **1** and **2**, respectively, whereas complex **3** exhibits a value of 0.70 V which corresponds to the highest redox potential for a halogenated porphyrin. Only the (β-heptanitrotetraphenylporphyrin)manganese complex was reported to have a higher potential (0.94 V).[38] Similarly, positive shifts of the potentials are observed, but to a lesser extent, for the first and the second ring reduction. These data explain why the complexes are isolated as reduced manganese derivatives as well as their extreme stability of the reduced state. For example, the complexes **2** and **3** remain as Mn^{II} under reflux in air, whereas the (β-octabromotetramesitylporphyrin)Mn^{II} is converted into the Mn^{III} complex.[15]

Oxidation Reactions

Over the last few years, the main objective in the search for new metalloporphyrins as oxidation catalysts has been the preparation of very stable and efficient molecules. In accordance with this aim, we have performed all tests of stability and catalytic activity under severe conditions, with equimolar proportions of oxidant and substrate. The catalyst was used at 1% relative to the oxidant, even for the measures of stability. These conditions allowed us to obtain directly the turnover number without any protection by excess substrate. Consequently, most of our results correspond to relatively modest yields. Furthermore, analysis of the influence of the β-octafluorination required us to carry out the experiments on the nonfluorinated porphyrinmanganese complexes under the same conditions.

Iodosylbenzene

This oxidant is not a good one in terms of the environment, but has been extensively used in order to assess the

catalytic properties of metalloporphyrins. It has been used as oxygen donor with porphyrinmanganese complexes for some time.[8,9] Beside porphyrin modifications, an improvement is associated with the use of imidazole as co-catalyst, corresponding to an enhancement of the reaction rate.[55] In this study, we used 1-methylimidazole or ammonium acetate as co-catalysts, the latter known to be a good co-catalyst in oxidation reactions with hydrogen peroxide.[56]

The study of the stability of the new β-octafluorinated porphyrinmanganese derivatives towards iodosylbenzene, in the absence of substrate, gave unexpected results. The decrease in the intensity of the Soret band is the same for both the β-octafluorinated complexes **1–3** and the β-octahydrogenated analogs **4–6**. The amount of decomposition is also independent of the manganese oxidation state in the starting compounds, the reduced state being available in the complexes **1–3**. The addition of 1-methylimidazole as co-catalyst induces a difference in the case of the tetraphenyl derivatives **1** and **4** only, with a larger (or at least faster) decomposition of these catalysts. The extent of the decrease in intensity of the Soret band was measured after addition of cyclooctene because an intermediate was formed during the reaction of the manganese complexes with iodosylbenzene. These intermediates are converted into Mn^{III} by adding the substrate with concomitant formation of epoxide, characteristic of a higher oxidation state of manganese. Mn^{IV} complexes have been extensively studied,[1,48,49,57–60] and the formation of a dimeric (μ-oxo)porphyrinmanganese complex that contains one iodosylbenzene per manganese has been reported.[48] This product was characterized by a Soret band at 421 nm. Compared to the non-β-halogenated derivatives **4–6**, a blue-shift of the Soret bands of 13–16 nm is also observed for the β-fluorinated complexes **1–3**. This analogous result suggests the formation of Mn^{IV} derivatives.

As far as the epoxidation catalysis is concerned, the absence of any significant difference in the yields of epoxidation between the β-fluorinated and the β-hydrogenated complexes is surprising. The best systems contain *meso*-2,6-dichlorophenyl as the aryl group, independent of the substitution at the β-positions. According to the results of the stability study, the use of catalysts with reduced or oxidized manganese leads to a very similar outcome suggesting the same reactive intermediates. Finally, the use of co-catalysts increases the rate of the reactions as previously observed,[55] without any difference in the turnover numbers obtained with 1-methylimidazole or ammonium acetate.

In contrast to epoxidation, large variations in the yields of hydroxylation of cyclohexane are observed, depending on: i) the presence of β-fluorine atoms, ii) the absence or the nature of co-catalyst and iii) the nature of the aryl group of the tetraarylporphyrins. 1-Methylimidazole has been shown to be an efficient co-catalyst favoring a high-valent (oxo)Mn intermediate.[61] With this co-catalyst, conversion of cyclohexane lies in the range 5–25% for the β-hydrogenated complexes **4–6** and 8–33% for the β-fluorinated porphyrinmanganese complexes **1–3**. The increase in the turnover number is close to 100% for Ar = phenyl (**1** and **4**) and dichlorophenyl (**2** and **5**) and 30% for Ar = pentafluorophenyl (**3** and **6**), with up to 33 turnovers for the perfluorotetraphenylporphyrin catalyst. It should also be emphasized that, in contrast with the epoxidation reaction, the best yields are obtained with Ar = pentafluorophenyl (**3** and **6**) rather than Ar = dichlorophenyl (**2** and **5**). Similarly, the efficiency for the hydroxylation of linear alkane by PhIO by tetraarylporphyriniron complexes is larger for Ar = pentafluorophenyl than for Ar = dichlorophenyl.[62]

Hydrogen Peroxide

The conditions employed correspond to two bulk additions of equimolar hydrogen peroxide (relative to the substrate) rather than dropwise addition. We used ammonium acetate as co-catalyst which has been shown to be more efficient than imidazole and carboxylic acids.[56] However, the studies have been complicated by the high metal oxidation potentials of the β-fluoroporphyrin complexes, corresponding to a very easy reduction of the manganese. Acetonitrile, the most common solvent for homogeneous reaction with H_2O_2, binds and stabilizes Mn^{II} complexes. Even methanol is able to prevent the reaction of hydrogen peroxide with (perfluorotetraphenylporphyrin)manganese. For this last porphyrin derivative, we have found a way to perform catalytic studies using acetone as solvent.

Under the conditions employed, the main finding is the instability of the β-fluoroporphyrinmanganese complexes towards hydrogen peroxide. Similar results have already been reported for β-chloro- or β-bromoporphyrinmanganese complexes.[25,26] However, good yields of hydroxylation have been reported, but in the presence of very large excess of substrate and very small oxidant/catalyst ratios.[23,24] The large amount of decomposition of the β-fluoroporphyrins, previously encountered with the iron complexes, has been associated with the high reactivity of the β-fluorinated positions towards homolytic cleavage, or nucleophilic attack of H_2O_2.[22] We have observed that β-fluoroporphyrinzinc complexes exhibit good stability towards H_2O_2, while extensive protection of β-halogenated porphyrins can be achieved with the use of radical scavengers.[26] Overall, these data are more in favor of the homolytic cleavage of hydrogen peroxide.

Conclusion

Many factors are involved in the catalytic activity of metalloporphyrins. Among these are the reactivity of the oxometal intermediate, the steric protection due to the substituents on the aryl groups, the distortion of the macrocycle, the resistance towards oxidation of the porphyrin and also the nature of the co-catalyst, the oxidant and the effect of solvent. It is still difficult to rationalize why the *meso*-tetraarylmetalloporphyrins are so efficient when the aryl groups are 2,6-dichlorophenyl or pentafluorophenyl. However, the olefin requires a less reactive oxometal intermediate for epoxidation than alkane hydroxylation. In the for-

mer reaction, steric protection due to the chlorine atoms of the dichlorophenyl group could be considered an important factor in efficient epoxidation. With alkane hydroxylation, more electron-deficient metalloporphyrins are responsible for an increase in the reactivity of the oxometal species, which favors a higher yield in hydroxylation. This view is consistent with the very small differences in the results obtained with iodosylbenzene, associated with the β-fluorination of the porphyrin in epoxidation, whereas larger effects are observed in the hydroxylation of cyclohexane. With hydrogen peroxide, the high level of decomposition prevents any improvement in epoxidation from being detected, as was previously observed with iron β-chloro- or -bromoporphyrins[26] and β-fluoroporphyrins.[22] However, a small increase in hydroxylation is observed with the (perfluorotetraphenylporphyrin)manganese as compared to the β-hydrogenated analog.

In conclusion, these results, as well as those obtained with β-fluoroporphyriniron complexes,[22] show an improvement in the reactivity of the oxometal intermediate leading to better yields in reactions of hydroxylation.

Experimental Section

General: All solvents were distilled prior to use. Chemical reagents were obtained from commercial sources. PhIO was prepared according to a literature procedure.[63] – UV/Vis spectra were recorded with a Uvikon 941 spectrometer. – NMR spectra were recorded with a Bruker 200 DPX spectrometer in $CDCl_3$ (^1H: 200 MHz, ^{19}F: 188 MHz). – Cyclic voltammograms were measured with a PAR M 263, the $E^{1/2}$ values (V) are reported versus SCE. – FAB mass spectrometry was performed, at the CRMPO, with a ZabSepc TOF Micromass. – Gas chromatography analyses were performed with a GC 121 DFL Delsi instrument. – Analytical thin layer chromatography was performed on commercial aluminium sheets coated with silica gel 60 F_{254} (Merck).

General Complexation Procedure for β-Octafluoroporphyrins: The porphyrins were prepared as previously reported using the Lindsey procedure[64] by condensation of the desired aldehyde and 3,4-difluoropyrrole.[19,65,66] To a suspension of the porphyrin (10 mmol) in DMF (5 mL), under argon, $Mn(OAc)_2{\cdot}4H_2O$ (10 equiv.) was added, and then the mixture was heated to reflux.[43] The complexation was completed within 5 min and after cooling the solvent was removed under vacuum. The complexes **2a** and **3a** were dissolved in dichloromethane and the solutions were filtered through a short silica gel column and concentrated. The complex **1a** was dissolved in dichloromethane/*n*-hexane (1:1 in volume) and the solution filtered and concentrated. **1a** was stored in acetonitrile to prevent oxidation.

Oxidation of Mn^{II} Complexes to $Mn^{III}Cl$: The complex **1a** obtained after evaporation of DMF, was chromatographed on a silica gel column (CH_2Cl_2/CH_3OH, 90:10). The solvents were removed and the residue was dissolved in CH_2Cl_2, washed with 3 M HCl, dried with NaCl and concentrated to give the complex **1b**. An excess of solid $FeClO_4$ was added to the complex **2a** in dichloromethane, and the oxidation monitored by UV/Vis spectroscopy. After filtration, the solution was washed with 3 M HCl, dried with NaCl and concentrated to give the complex **2b**.

The complex **3b** was prepared in situ by addition of a small excess of iron perchlorate to **3a** in dichloromethane.

[2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetraphenylporphyrin]-manganese(II) (1a): MS (FAB HRMS); *m/z* (%): 811.0923 (100) [M^+]; calcd. for $C_{44}H_{20}F_8MnN_4$: 811.0941. – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 419 (5.08), 549 (3.95), 586 nm (3.87). – CV (CH_2Cl_2/Bu_4NPF_6): E = 1.51 V, 0.16 V, –1.28 V, –1.53 V.

[5,10,15,20-Tetrakis(2,6-dichlorophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin]manganese(II) (2a): R_f: 0.78 (silica gel, dichloromethane, room temperature) – MS (FAB HRMS); *m/z* (%): 1082.7796 (100) [M^+]; calcd. for $C_{44}H_{12}{}^{35}Cl_8F_8MnN_4$: 1082.7823. – UV/Vis ($CHCl_3$): λ_{max} nm (log ε) = 422 (5.13), 551 (4.11), 585 (3.79). – CV (CH_2Cl_2/Bu_4NPF_6): E = 0.30 V, –1.14 V, –1.40 V.

[2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin]manganese(II) (3a): R_f: 0.61 (silica gel, dichloromethane, room temperature). – MS (FAB HRMS); *m/z* (%): 1170.9057 (100) [M^+]; calcd. for $C_{44}F_{28}MnN_4$: 1170.9056. – UV/Vis ($CHCl_3$): λ_{max} (log ε) = 419 (5.24), 546 nm (4.28). – ^{19}F NMR ($CDCl_3/CD_3OD$, 80:20; δ in ppm referenced to $CFCl_3$): δ = –131.93 (br., 8 F, *o*-F), –148.38 (s, 4 F, *p*-F), –157.57 (s, 8 F, *m*-F). – CV (CH_2Cl_2/Bu_4NPF_6): E = 0.70 V, –0.64 V, –1.08 V.

[2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetraphenylporphyrin]-manganese(III) Chloride (1b): R_f: 0.25 (silica gel, dichloromethane/methanol 95:5, room temperature). – UV/Vis ($CHCl_3$): λ_{max} (log ε) = 365 (4.73), 474 (4.62), 572 (3.89), 607 nm (3.95). – ^{19}F NMR ($CDCl_3$): δ = –4.9 (br., 8 F, β-F).

[5,10,15,20-Tetrakis(2,6-dichlorophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin]manganese(III) Chloride (2b): UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 363 (4.89), 474 (4.72), 571 (4.03), 605 nm (3.89). – ^{19}F NMR ($CDCl_3$): δ = –4.2 (br., 8 F, β-F).

[2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin]manganese(III) Perchlorate (3b): UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 367 (4.83), 458 (4.82), 547 nm (4.05). – ^{19}F NMR ($CDCl_3/CD_3OD$, 80:20): δ = 2.8 (br., 8 F, β-F), –141.60 (br., 8 F, *o*-F), –149.73 (s, 4 F, *p*-F), –160.57 (s, 8 F, *m*-F).

Oxidation Procedure: All reactions were carried out, in duplicate, at room temperature, under aerobic conditions in a tube stirred by a Vortex.

Oxidation with Iodosylbenzene: To the desired porphyrinmanganese complex (0.4 μmol), substrate (cyclooctene or cyclohexane, 40 μmol), and co-catalyst (4 μmol when present), in 200 μL of CH_2Cl_2, PhIO (40 μmol, 8.8 mg) was added in a single aliquot. The reaction mixtures were analyzed by gas chromatography and UV/Vis at 20 min and 60 min by taking 10-μL aliquots.

Oxidation with Hydrogen Peroxide: To the desired porphyrinmanganese complex (0.4 μmol), substrate (cyclooctene or cyclohexane, 40 μmol), and $AcONH_4$ as co-catalyst (4 μmol) in 200 μL of CH_2Cl_2/CH_3OH or CH_2Cl_2/CH_3CN (1:1 in volume), two additions of 50 μL (one molar equivalent, relative to the substrate) of H_2O_2, diluted to 3% in CH_3OH or CH_3CN, were performed at 0 min and 20 min. The reaction mixtures were analyzed by gas chromatography at 20 min and 60 min by taking 10-μL aliquots.

Oxidation in Acetone with Hydrogen Peroxide: To the desired manganese porphyrin (0.4 μmol), substrate (cyclooctene or cyclohexane, 40 μmol), and $AcONH_4$ as co-catalyst (4 μmol) in 200 μL of CH_2Cl_2/CH_3COCH_3 (80:20), concentrated (35%) aqueous solution of H_2O_2 (5 μL, two equivalents relative to the substrate) was added

at 0, 10, 20 and 30 min. The reaction mixtures were analyzed by gas chromatography at 20 min and 60 min by taking 10-μL aliquots.

Acknowledgments

We thank Dr. B. Meunier for fruitful comments and Dr. P. de Oliveira for a careful reading of the manuscript and gratefully acknowledge the financial support of the Brittany Region as a grant to E. P.

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Received November 12, 1999
[I99417]