Synthesis, Structure, and Characterization of a Novel Manganese(IV) Monomer, $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$ (Me_3TACN = *N,N′,N″*-Trimethyl-1,4,7-triazacyclononane), and Its Activity toward Olefin Oxidation with Hydrogen Peroxide

Vikki Chin Quee-Smith, Lisa DelPizzo, Sharon H. Jureller, and Judith L. Kerschner*

Unilever Research US, 45 River Road, Edgewater, New Jersey 07020

Ronald Hage

Unilever Research Laboratory, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands

Received November 30, 1995⊗

A novel manganese(IV) monomer, $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$, has been synthesized in methanol by the reaction of $MnCl_2$ with the ligand, *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (Me_3TACN), in the presence of Na_2O_2. The resulting product was isolated as the red/brown crystalline hexafluorophosphate salt. The compound crystallizes in the space group $P2/c$ with the cell dimensions $a = 15.652(2)$ Å, $b = 8.740(1)$ Å, $c = 15.208(2)$ Å, $\beta = 108.81(1)°$, $V = 1969.4(4)$ Å^3, and $Z = 4$. The structure was solved by the heavy-atom method and was refined by full-matrix least-squares techniques to a final value of $R = 0.067$ ($R_w = 0.097$) based upon 3087 observations. The manganese atom in the molecule is six-coordinate in an N_3O_3 ligand environment with the triazacyclononane facially coordinated. Pertinent average bond distances and angles are as follows: Mn−O, 1.797(5) Å; Mn−N, 2.116(5) Å; O−Mn−O, 97.8(2)°; N−Mn−N, 81.4(2)°; O−Mn−N, 167.8°(2); O−Mn−N, 86.8(2)°; O−Mn−N, 92.8(2)°. The complex was further characterized by UV−vis and EPR spectroscopies, solution magnetic susceptibility measurements, FAB-MS, and electrochemistry. $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$ was found to catalyze the oxidation of water-soluble olefins using hydrogen peroxide as the oxidant in an aqueous medium. The catalyzed rates of oxidation of these olefins indicate at least a 12-fold rate enhancement over oxidant alone. The unusual stability of the catalytic species was demonstrated by the repeated additions of substrate and oxidant while maintaining a constant catalytic rate of oxidation.

Introduction

Over the past decade, many systems using manganese porphyrin[1] or Schiff base[2] complexes as catalysts with various oxidants have been shown to oxidize unsaturated organic molecules effectively. More recently, a major focus of manganese-catalyzed oxidations has been to design catalysts which use hydrogen peroxide as the oxygen atom donor since this oxidant is readily available, inexpensive, and produces water as its only byproduct. However, several difficulties are encountered when manganese catalysts containing these ligand systems are used with hydrogen peroxide as the oxidant. A major limitation arises from the instability of these manganese complexes and their ligands to the oxidative conditions of the reaction, resulting in relatively short catalyst lifetimes.[1−3]

Herein is reported a new type of manganese complex which is capable of catalyzing the epoxidation of water-soluble olefins in an aqueous medium under very mild conditions using hydrogen peroxide as the oxidant. This complex is a manganese(IV) monomer containing *N,N′,N″*-trimethyl-1,4,7-triazacyclononane as the ligand. Substituted triazacyclononane ligands have been used to prepare several manganese complexes which have been studied as biomimics for the active site in photosystem II or catalase of *Thermus thermophilus*.[4] However, their capacity to act as catalysts for the oxidation of organic substrates has not been previously explored. Even though manganese(IV) complexes have been implicated as the active species in many olefin oxidation reactions, it is rare that manganese(IV) complexes are added directly as the catalyst or catalyst precursor.[5] This may be due to the fact that relatively few manganese(IV) monomers have actually been isolated and structurally characterized.[6−15]

⊗ Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) For reviews, see for example: (a) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411. (b) Stern, M. K.; Groves, J. T. In *Manganese Redox Enzymes*; Pecoraro, V., Ed.; VCH: New York, 1992; pp 233−259. (c) Mansuy, D. *Pure Appl. Chem.* **1987**, *59*, 759. (d) Traylor, T. G. *Pure Appl. Chem.* **1991**, *63*, 265. (e) Dolphin, D. H.; Nakano, T.; Kirk, T. K.; Wijesekera, T. P.; Farrell, R. L.; Maione, T. E. U.S. 4,892,941, 1990. (f) Ostovic, P.; Bruice, T. C. *Acc. Chem. Res.* **1992**, *25*, 314.

(2) (a) Srinirason, K.; Perier, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309. (b) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801. (c) Ire, R.; Ito, Y.; Katsuk, T. *Synlett* **1991**, 265. (d) Robert, A.; Tsapara, A.; Meunier, B. *J. Mol. Catal.* **1993**, *85*, 13.

(3) (a) Lee, W. A.; Bruice, T. *J. Am. Chem. Soc.* **1985**, *107*, 513. (b) Battioni, P.; Renaud, J.-P.; Bartoli, J. E.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462. (c) Anelli, P. L.; Banfi, S.; Lengramandi, F.; Montanari, F.; Pozzi, G.; Quici, S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1345. (d) Banfi, S.; Montanari, F.; Pozzi, G.; Quici, S. *Tetrahedron* **1994**, *50* (30), 9025.

(4) (a) Wieghardt, K.; Bossek, U.; Ventur, D.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1985**, 347. (b) Bossek, U.; Weyhermuller, T.; Wieghardt, K.; Nuber, B.; Weiss, J. *J. Am. Chem. Soc.* **1990**, *112*, 6387. (c) Belal, A. A.; Chaudhuri, P.; Fallis, I.; Farrugia, L. J.; Hartung, R.; Macdonald, N. M.; Nuber, B.; Peacock, R. D.; Weiss, J.; Wieghardt, K. *Inorg. Chem.* **1991**, *30*, 4397. (d) Wieghardt, K.; Bossek, U.; Nuber, B.; Weiss, J.; Bonvoisin, J.; Corbell, M.; Vitols, S. E.; Girerd, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 7398.

(5) Groves, J. T.; Stern, M. K. *J. Am. Chem Soc.* **1987**, *109*, 3812.

(6) Pecoraro, V. L. In *Manganese Redox Enzymes*; Pecoraro, V., Eds.; VCH: New York, 1992; pp 197−231.

(7) Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Inorg. Chem.* **1982**, *21*, 4301.

(8) Chin, D.; Sawyer, D. T.; Schaeffer, W. P.; Simmons, C. J. *Inorg. Chem.* **1983**, *22*, 752.

S0020-1669(95)01522-9 CCC: $12.00

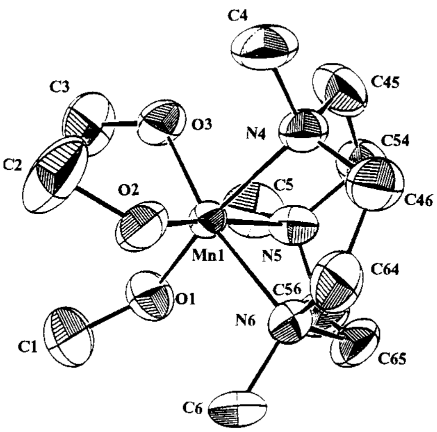


Figure 1. Molecular structure of $[Mn(Me_3TACN)(OMe)_3](PF_6)$ (**1**). ORTEP drawing shows 50% probability for thermal ellipsoids.

Results and Discussion

Synthesis and Characterization. The title compound, $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$ (**1**), is obtained by the reaction of $Mn^{II}Cl_2$ with *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (Me_3-TACN)[16] in methanol using Na_2O_2 as both a strong base and an oxidizing agent.[18] The resulting complex is crystallized from a methanol/water solution as the red/brown crystalline hexafluorophosphate salt, which is soluble in a number of polar organic solvents and is sparingly soluble in water. Recrystallization of the complex from cold methanol produced material suitable for single-crystal X-ray analysis.

The structure of **1** is shown in Figure 1, and the positional parameters and selected bond distances and bond angles are listed in Tables 1 and 2. The manganese(IV) atom in the complex is six-coordinate and possesses an N_3O_3 ligand environment with the Me_3TACN ligand facially coordinated. The average Mn−N and Mn−O bond lengths for **1** are 2.116(5) and 1.797(5) Å, respectively. The pseudooctahedral complex contains an average O−Mn−O angle of 97.8°, an average N−Mn−N angle of 81.5°, and average O−Mn−N angles of 167.5°, 86.8°, and 93.0°.

The average Mn−N and Mn−O bond distances can be compared directly to various reported Mn(IV) complexes containing similar ligation. The Mn(IV) complexes listed in Table 3 range from a MnO_6 core to a MnN_6 core with various combinations of oxygen and nitrogen ligation. When compared with several of these molecules as shown in Table 3, $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$ (**1**) has shorter Mn−O bond distances and longer Mn−N bond distances. Actually, **1** along with several oxo-bridged Mn(IV) dimers and tetramers with similar TACN ligation have some of the shortest Mn−O bond distances reported.[4d]

Table 1. Positional Parameters and Their Estimated Standard Deviations for $[Mn(Me_3TACN)(OMe)_3](PF_6)$[a]

atom	*x*	*y*	*z*	B^b (Å^2)
Mn	0.75994(6)	0.4724(1)	0.13705(6)	3.14(2)
O(1)	0.7675(4)	0.6234(5)	0.2193(3)	5.6(1)
O(2)	0.8695(3)	0.4960(6)	0.1258(3)	4.9(1)
O(3)	0.6958(3)	0.5748(5)	0.0335(3)	5.0(1)
N(4)	0.7337(4)	0.2723(6)	0.0549(3)	4.2(1)
N(5)	0.6431(3)	0.3984(7)	0.1665(3)	4.3(1)
N(6)	0.8206(4)	0.3110(6)	0.2427(3)	3.9(1)
C(1)	0.8385(7)	0.737(1)	0.2483(6)	8.0(3)
C(2)	0.8940(6)	0.600(1)	0.0662(6)	8.2(2)
C(3)	0.6825(7)	0.7382(9)	0.0281(6)	7.2(2)
C(4)	0.7608(6)	0.290(1)	−0.0313(5)	6.4(2)
C(5)	0.5783(5)	0.527(1)	0.1531(6)	7.1(2)
C(6)	0.9002(5)	0.380(1)	0.3135(4)	5.4(2)
C(45)	0.6318(5)	0.258(1)	0.0206(6)	6.1(2)
C(46)	0.7807(6)	0.1364(9)	0.1106(5)	6.2(2)
C(54)	0.6003(5)	0.263(1)	0.1082(6)	6.2(2)
C(56)	0.6763(5)	0.357(1)	0.2675(5)	6.0(2)
C(64)	0.8554(5)	0.1870(8)	0.1953(5)	5.4(2)
C(65)	0.7530(5)	0.2498(9)	0.2855(5)	5.2(2)
P(1)	1.000	0.000	0.500	4.25(6)
P(2)	0.500	0.0602(3)	−0.250	5.62(7)
F(1)	0.8972(3)	0.0445(6)	0.4589(4)	7.8(1)
F(2)	0.9941(4)	0.0086(6)	0.6014(3)	8.0(1)
F(3)	1.0264(3)	0.1741(5)	0.5052(3)	6.7(1)
F(12)	0.500	0.213(1)	−0.250	36.4(5)
F(13)	0.5298(6)	0.062(1)	−0.3347(5)	17.4(3)
F(14)	0.544(1)	0.203(2)	−0.1938(7)	34.0(6)
F(15)	0.6018(5)	0.039(1)	−0.2312(9)	21.6(4)
F(16)	0.5327(8)	−0.086(1)	−0.2121(8)	32.4(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent temperature factor defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Mn(Me_3TACN)(OMe)_3](PF_6)$[a]

Mn−O(1)	1.796(5)	Mn−N(4)	2.112(5)
Mn−O(2)	1.789(5)	Mn−N(5)	2.120(6)
Mn−O(3)	1.807(4)	Mn−N(6)	2.118(5)
O(1)−Mn−O(2)	97.6(2)	O(3)−Mn−N(6)	167.8(2)
O(1)−Mn−O(3)	97.8(2)	N(4)−Mn−N(5)	81.7(2)
O(1)−Mn−N(4)	167.8(3)	N(4)−Mn−N(6)	81.5(2)
O(1)−Mn−N(5)	86.8(2)	N(5)−Mn−N(6)	81.0(2)
O(1)−Mn−N(6)	92.8(2)	Mn−O(1)−C(1)	126.0(6)
O(2)−Mn−O(3)	98.0(2)	Mn−O(2)−C(2)	126.7(4)
O(2)−Mn−N(4)	92.8(2)	Mn−O(3)−C(3)	124.7(4)
O(2)−Mn−N(5)	167.0(2)	Mn−N(4)−C(4)	111.9(4)
O(2)−Mn−N(6)	86.6(2)	Mn−N(4)−C(45)	104.9(4)
O(3)−Mn−N(4)	87.0(2)	Mn−N(4)−C(46)	110.7(4)
O(3)−Mn−N(5)	93.5(2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

$[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$ (**1**) was further characterized by a variety of techniques. Solution magnetic susceptibility studies[19] at room temperature in acetonitrile gave a magnetic moment measurement of 3.84 μ_B. This value is very close to the spin only value (3.87 μ_B) for a d^3 system. The X-band EPR spectrum performed on the solid crystalline complex at 77 and 300 K showed two broad resonances at $g = 2.0$ and $g = 3.6$ (Figure 2). Measurement of the spectrum in solution (methanol/acetonitrile) did not reveal any manganese hyperfine splitting. The absence of hyperfine coupling has been reported for other

---

(9) Pavacik, P. S.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1986**, 43.

(10) (a) Kessissoglou, D. P.: Li, X.; Butler, W. M.; Pecoraro, V. L. *Inorg. Chem.* **1987**, *26*, 2487. (b) Saadeh, S; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1991**, *30*, 9.

(11) Chan, M. K.; Armstrong, W. H. *Inorg. Chem.* **1989**, *28*, 3777.

(12) (a) Hart, R. O. C.; Bott, S. G.; Atwood, J. L.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1992**, 894. (b) Hartman, J. R.; Fox, B. M.; Cooper, S. R. *Inorg. Chem.* **1983**, *23*, 1381.

(13) (a) Chandra, S. K.; Chakravorty, A. *Inorg. Chem.* **1992**, *31*, 760. (b) Dutta, S.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1991**, *30*, 4031. (c) Chandra, S. K.; Basu, P.; Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 2423. (d) Pal, S. *J. Chem. Res., Synop.* **1995**, 236.

(14) Mikuriya, M.; Jie, D.; Kakuta, Y.; Tokii, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1132.

(15) Fallis, I. A.; Farrugia, L. J.; Macdonald, N. M.; Peacock, R. D. *J. Chem. Soc., Dalton Trans.* **1993**, 2759.

(16) Wieghardt, K.; Chaudhuri, B.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982,** *21*, 3086.

(17) Koek, J. H.; Russell, S. W.; van der Wolf, L.; Hage, R.; Warnaar, J. B.; Spek, A. L.; Kerschner, J.; DelPizzo, L. *J. Chem. Soc., Dalton Trans.* **1996**, 353.

(18) Kerschner, J. L.; Chin Quee-Smith, V. U.S. Patent 5,280,117, 1994.

(19) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

Table 3. A Comparison of Average Mn−N and Mn−O Bond Distances of (**1**) with Those of Selected Mn(IV) Complexes Containing Metal Nitrogen and Oxygen Ligation[a]

complex	core	Mn−N (Å)	Mn−O (Å)	ref
1	N_3O_3	2.116	1.797	this work
$Mn_2(L)_2(\mu\text{-}O)_3^{2+}$	N_3O_3	2.108	1.821	4d
$Mn_4(L)_4(O)_6^{4+}$	N_3O_3	2.086	1.797	4d
$Mn(L^1)^+$	N_3O_3	2.048	1.825	15
$Mn(L^2)^+$	N_3O_3	2.044	1.836	4c
$Mn(L^3)(OMe)_2$	N_4O_2	1.933, 2.031	1.839	7
$Mn(L^4)\cdot 4H_2O$	N_4O_2	1.953, 2.038	1.847	13a
$Mn(L^5)\cdot MeOH$	N_4O_2	1.934, 2.084	1.858	13a
$Mn(L^6)_2\cdot 2THF$	N_2O_4	1.996	1.894	14
$K_2[Mn(L^7)_3]\cdot 6CH_3CN$	O_6		1.891, 1.922	12b
$[Mn(L^8)_3]^+$	N_6	1.932		12a

[a] L = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane; L^1 = *N,N′,N″*-tris[(2*R*)-2-hydroxy-3-methylbutyl]-1,4,7-triazacyclononane; L^2 = *N,N′,N″*-tris(hydroxyethyl)-1,4,7-triazacyclononane; L^3 = 5,10,15,20-tetraphenylporphyrin; L^4 = 1,8-bis(2-hydroxybenzamido)-3,6-diazaoctane; L^5 = 1,10−bis(2-hydroxybenzamido)-4,7-diazadecane; L^6 = *o*-[(salicylideneamino)methyl]-5-chlorophenol; L^7 = catecholate; L^8 = biguanide.

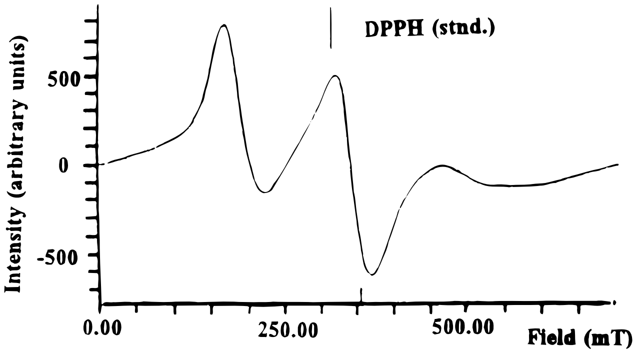


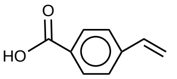
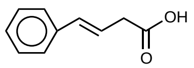
Figure 2. EPR spectrum of $[Mn(Me_3TACN)(OMe)_3](PF_6)$ (**1**) as a solid at 298 K.

manganese compounds,[11,13b,d] and this spectrum is essentially identical to the EPR reported by Fallis et al. for a manganese complex containing a similar N_3O_3 ligand donor.[15] The EPR spectrum is typical for a d^3 ion with axial symmetry in a strong ligand field and along with the magnetic moment measurements confirms the Mn(IV) oxidation state.[10,11,13,15]

The nature of the EPR spectrum of such a species is dependant on the axial (*D*) and rhombic (*E*) zero-field splitting parameters. In an axial field ($E/D = 0$), when *D* is very large ($2D \gg h\nu$), a strong signal around $g = 4$ and a weaker one at $g = 2$ is expected. The other limiting case is when *D* is small ($2D \ll h\nu$), and in that case a strong signal at $g = 2$ and a weaker one at $g = 4$ is predicted. The EPR spectrum of the intermediate case is expected to be complicated.[20] Two independently synthesized samples of **1** were measured, and both samples gave similar spectra in which the $g = 3.6$ and $g = 2.0$ signals were of relatively the same intensity. Since the EPR spectrum of the molecule was not complex, as expected for a molecule where *D* is intermediate, it is likely that a minute impurity having a $g = 2$ signal is present, adding to the overall intensity of this signal.[11] Therefore compound **1** most likely belongs to the first class where *D* is large ($2D \gg h\nu$).

The absorption spectra of **1** was measured in acetonitrile solutions. There are three prominent electronic transitions for the complex at λ_{max}/nm (ϵ M^{-1} cm^{-1}): 228 (11 600), 287 (12 900), and 326 (13 300). The intensities of the three high-energy absorption bands ($\epsilon > 10\,000$ M^{-1} cm^{-1}) in the spectra for both compounds indicate that they can be assigned as charge-transfer transitions. These intense high-energy absorption bands have also been reported for other manganese(IV) complexes including $[Mn^{IV}_2(Me_3TACN)_2(\mu\text{-}O)_3](PF_6)_2$,[4d] $[Mn^{III}Mn^{IV}(Me_3TACN)_2(\mu\text{-}O)(\mu\text{-}OCH_3CO_2)_2](ClO_4)_3$[4d] and $[Mn^{IV}(biguanide)_3](OAc)$.[12]

Table 4. Oxidation of Various Water-Soluble Olefins with H_2O_2 Catalyzed by $[Mn(Me_3TACN)(OMe)_3](PF_6)$[a]

substrate	structure	% conversion	time (h)
4-vinylbenzoic acid		82[b]	1.0
		98[b]	1.5
styrylacetic acid		69[c]	1.5
		98[c]	3.0

[a] Reaction conditions: 0.01 mmol of $[Mn(Me_3TACN)(OMe)_3](PF_6)$; 1.0 mmol of substrate, 0.1 mol of H_2O_2 in 100 mL of 0.1 M $NaHCO_3$ aqueous solution at pH = 9; *T* = 25 °C. Percent conversion was calculated as conversion of olefin and quantified by HPLC. [b] The only product observed during the oxidation reaction was the corresponding epoxide as confirmed by ^1H NMR and quantified by HPLC. [c] A product mixture of the corresponding epoxide, diol, and a ring-closed lactone was observed during the reaction as confirmed by ^1H NMR and quantified by HPLC. The amount of diol and lactone increased with increasing reaction time.

The cyclic voltammogram of **1** in 0.1 M $TBAPF_6/CH_3CN$ shows only an irreversible reduction at −0.54 V (vs SCE) [Mn(IV)-Mn(III)] over the potential range from +1.5 to −1.5 V (vs SCE). This indicates a relatively stable Mn(IV) complex which upon reduction to Mn(III) results in a chemically labile species prohibiting the reversible oxidation from occurring. The reduction wave at −0.54 V is rather negative compared to other manganese monomers containing the triazacyclononane ligand system. $Mn(Me_3TACN)(N_3)_3$ and $Mn(Me_3TACN)(Cl)_3$ exhibit pseudoreversible reduction waves at −0.27 and 0.10 V (vs Fc^+/Fc), respectively. It has been suggested that the presence of alkoxide ligands should stabilize the high-valent Mn(IV) complex and therefore result in a negative reduction potential for the Mn(IV)−Mn(III) couple.[6,10] The stability of the 4+ oxidation state of manganese with alkoxide ligands has been reported in complexes such as $Mn^{IV}(SALADHP)_2$ and $Mn^{IV}(SALAHP)_2$, which display quasi-reversible metal-centered reductions at −0.32 and −0.46 V (vs SCE), respectively ($H_2SALADHP$ = 2-(salicylideneamino)-2-methyl-1,3-dihydroxypropane and $H_2SALAHP$ = 3-(salicylideneamino)-1-hydroxypropane).[10] However, other systems are also known that exhibit similar or even more negative reduction waves and do not contain alkoxide ligands.[12,14]

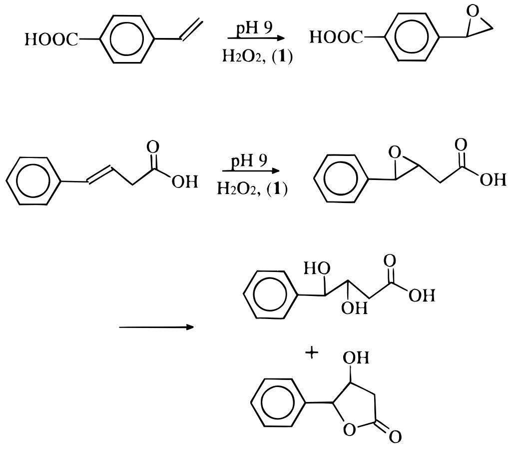
Olefin Oxidation Studies. To determine the catalytic activity of this monomeric manganese(IV) complex, a series of olefin oxidation reactions was examined in aqueous solutions using hydrogen peroxide as the oxidant. In these solution oxidation studies, $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$ (**1**) was found to activate the hydrogen peroxide effectively at room temperature to oxidize a number of water-soluble olefins.[20] These oxidation reactions were monitored by HPLC, and the results are listed in Table 4. The data are represented as the percent conversion of starting olefin to products. For both 4-vinylbenzoic acid and styrylacetic acid, the products were isolated and characterized by NMR spectroscopy, and then these fully characterized molecules were used as standards in the HPLC analysis of the reaction mixtures to quantify conversion of olefin and yields of reaction products.

The only oxidation product of the reaction with 4-vinylbenzoic acid was the corresponding epoxide, 4-epoxybenzoic acid, whereas several products were identified during the oxidation of styrylacetic acid (Scheme 1). Unlike the stable 4-epoxybenzoic acid, the epoxide of styrylacetic acid is much more labile

---

(20) Pederson, E.; Toftlund, H. *Inorg. Chem.* **1974**, *13*, 1603.

Scheme 1. Reaction Products of the Oxidation of Vinylbenzoic Acid and Styrylacetic Acid with **1** and Hydrogen Peroxide



under the reaction conditions and either hydrolyzes to the diol, 3,4-dihydroxy-4-phenylbutyric acid, or undergoes an intramolecular ring opening of the epoxide by the carboxylic acid anion to form the five-membered lactone, 3-hydroxy-4-phenylbutyrolactone. The lactone can also be formed via dehydration of the diol. As the reaction progresses, less of the epoxide is present and more of the lactone and diol are formed which suggests that the major oxidation product of the reaction is the epoxide which then further reacts to form the final product mixture. When comparing the rates of both the catalyzed versus the noncatalyzed oxidations with hydrogen peroxide, at least a 12-fold rate enhancement was found upon addition of 1 mol % catalyst.

Since the persistent problem of catalyst stability has plagued manganese-catalyzed hydrogen peroxide reactions, experiments were performed to investigate the integrity of this manganese catalyst. The stability of the catalytic species was demonstrated by the repeated additions of substrate and oxidant. A second 100 equiv of 4-vinylbenzoic acid can be added to the original oxidation solution, and the rate of conversion of the olefin to the epoxide remains constant. This oxidation of additional substrate can continue as long as there are sufficient quantities of hydrogen peroxide remaining in solution, since the reactive catalyst in this system competitively decomposes hydrogen peroxide during the olefin oxidation process. The catalytic species has been shown to experience more than 400 turnovers without any noticeable catalyst degradation. While the exact lifetime of the catalyst is yet to be determined, the data represent an increase in catalyst stability when compared to data published for some early manganese systems which reported complete catalyst decomposition after fewer than 30 turnovers.[3b]

Concluding Remarks

A novel manganese(IV) monomer, $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$, has been synthesized and characterized by X-ray crystallography and a number of analytical techniques. The characterization confirms the presence of a d^3 manganese complex with an N_3O_3 ligand environment. $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$ was found to be a catalyst for the hydrogen peroxide oxidation of water-soluble olefins in an aqueous medium under very mild conditions. The oxidation of the olefins formed the corresponding epoxides as the major products, and in the case of styrylacetic acid, this epoxide further reacted to form the corresponding diol, 3,4-dihydroxy-4-phenylbutyric acid, and lactone, 3-hydroxy-4-phenylbutyrolactone. At least a 12-fold increase in the rate of oxidation was obtained with the addition of 1 mol % catalyst, and the stability of the complex was verified by repeated additions of both olefin and oxidant. Although the rate enhancement with this complex is less than that observed for some other compounds, the fact that this system is active in a totally aqueous medium and is very robust makes it an interesting system for the catalysis of epoxidation reactions under mild conditions.

An investigation to identify the breadth of the catalytic oxidation activity of this complex with various organic substrates and the mechanism of the catalytic cycle continues.[21] Several other manganese dimers and monomers containing this ligand system are also under examination for their ability to catalyze the oxidation of organic molecules.[22–24]

Experimental Section

All chemical reagents except *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane were purchased and used as received. *N*,*N*′,*N*″-Trimethyl-1,4,7-triazacyclononane[16] was synthesized using literature methods. UV−vis spectra were recorded on a Varian Cary 1 spectrophotometer using acetonitrile as the solvent. Microanalyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY. The FAB mass spectrum was recorded on a Finnigan TSQ-70 mass spectrometer. Fast atom bombardment was accomplished using xenon atoms at 8 kV with a current of 1 mA. The EPR spectra were obtained on a JEOL JCS-RE2X spectrometer equipped with a JEOL Esprit 330 data system. The electrochemistry measurements were performed with a BioAnalytical Systems Inc. (Model CV-27) instrument. The cyclic voltammograms were obtained in a 0.1 M $TBAPF_6/CH_3CN$ solution with a glassy carbon working electrode, a calomel reference electrode, and a copper auxiliary electrode.

HPLC data were recorded on a Hewlett Packard 1050 instrument equipped with a 1040A diode array detector and a Regis ODS II 15 cm reverse phase column. Mobile phases were combinations of acetonitrile and triethylamine/phosphoric acid buffers at pH 3 and 6, depending on the pK_a of the acid being oxidized. The polarity of the system was altered by changing the ratio of buffer to acetonitrile in the mobile phase from 75:25 to 83:17.

Synthesis of $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$. To a solution of *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (1.0 g, 5.78 mmol) in 80 mL of methanol was added $MnCl_2$ (0.74g, 5.78 mmol) predissolved in 20 mL of methanol. This mixture was stirred and cooled to 0−10 °C, and Na_2O_2 (0.46 g, 5.78 mmol) was slowly added to the mixture. After 1 h of stirring, the reaction mixture was warmed to room temperature and mixed for an additional 1−2 h. Finally, $NaPF_6$ (1.0 g, 5.90 mmol) was added to the solution. The mixture was filtered through a porous

---

(21) In response to a reviewer's comment on the possibility of the formation of and subsequent oxidation by superoxide in the catalyzed epoxidation reactions, experiments were designed to determine if superoxide was the oxygen transfer reagent in this reaction. First, superoxide dismutase (SOD from bovine liver—3000 units) was added to the reaction mixture under the conditions described in the Experimental Section on the premise that if superoxide were the oxygen transfer reagent, the rate of the epoxidation reaction should be inhibited in the presense of SOD. The rate of epoxidation formation with and without SOD was identical, which indicates that the enzyme had little to no effect on the olefin oxidation reaction, therefore implying that superoxide itself was not the oxidizing species. Also, the addition of a 10-fold excess of potassium superoxide as the oxidant for the oxidation of 4-vinylbenzoic acid showed that very little epoxide (10%) was formed under the reaction conditions within 2 h, whereas the combination of H_2O_2 and **1** produced complete conversion of the olefin to the epoxide in 1 h. The small conversion observed upon addition of superoxide to the olefin is most likely due to hydrogen peroxide that is formed by disproportionation of superoxide. These results indicate that while superoxide may be formed in these reactions, it is not the oxygen transfer reagent.

(22) Jureller, S. H.; Kerschner, J. L.; Humphreys, R. U.S. Patent 5,329,024, 1994.

(23) Hage, R.; Iburg, J. E.; Kerschner, J.; Koek, J. H.; Lempers, E. L. M.; Martens, R. J.; Racherla, U. S.; Russell, S. W.; Swarthoff, T.; van Vliet, M. R. P.; Warnaar, J. B.; van der Wolf, L.; Krijnen, B. *Nature* **1994,** *369*, 637.

(24) De Vos, D; Bein, T. *Chem. Commun.* **1996**, 917.

glass frit and neutralized with dilute sulfuric acid. Then 50 mL of water was added to the neutralized solution, and it was filtered again. This filtrate was concentrated to one-third the original volume in vacuo and chilled at 0−10 °C. Brown crystals were obtained and isolated by filtration. Yield: 1.38 g (51%). Anal. Calcd for $C_{12}H_{30}F_6MnN_3O_3P$: C, 31.03; H, 6.47; Mn, 11.85; N, 9.05; P, 6.68. Found: C, 29.28; H, 5.68; Mn, 10.60; N, 9.20; P, 6.86. UV−vis (CH_3CN): λ_{max} nm (ϵ, L mol^{-1} cm^{-1}) 326 (13 300), 287 (12 900), 228 (11 600). Mp: 160−165 °C. FAB-MS (positive ion): 319. Magnetic moment (Evan's method[19]): 3.84 μ_B (CH_3CN). Cyclic voltammetry (0.1 M TBAPF$_6$/CH$_3$CN): −0.54 V (vs SCE)—irreversible reduction.

Catalytic Oxidation of Olefins. The olefin to be oxidized (0.001 mol) was added to 90 mL of a 0.1 M $NaHCO_3$ aqueous buffer solution in an open vessel, and the pH was adjusted to 9.0 with 1.0 M NaOH. The temperature of the reaction was maintained at 25 °C with a water bath. Then 10 mL of 30% hydrogen peroxide (10 M) was added to the olefin solution, followed by removal of a 1.0 mL sample for analysis by HPLC which represented time zero. Then a 1.25 mL aliquot of a 0.008 M solution of **1** was added to start the oxidation. Samples were taken at the desired intervals and analyzed by HPLC.

For the reactions with potassium superoxide as the oxidant, the reaction was performed as stated previously with the addition of KO_2 (0.01 mol) instead of H_2O_2 and **1**. Samples of the reaction mixture were taken at the desired intervals for 120 min. Superoxide dismutase (SOD, 3000 units) was also added to the olefin oxidation reaction with H_2O_2 and **1** to determine if SOD would inhibit the reaction rate. The reaction with SOD was compared directly to the same reaction without the SOD by following the rate of both reactions at the desired time intervals over 90 min by HPLC.

Crystallographic Studies. X-ray Structure Determination. The X-ray diffraction study was completed at the Enraf Nonius Co., Bohemia, NY. Some selected crystallographic data are collected in Table 5. A suitable dark red faceted crystal having the approximate dimensions of 1.20 × 0.80 × 0.40 mm was mounted on a glass fiber in a random orientation. A total of 3518 reflections were collected from which 3087 were unique. The crystal quality was checked every 3 h by scanning three representative reflections. The intensities of these reflections dropped by 169% during the data collection. Lorentz and polarization corrections were applied to the data. Cell constants were obtained from a least-squares fit of 25 reflections.

Structure Solution and Refinement. Reduced cell constants and an orientation matrix for data collection were obtained from INDEX, a least-squares refinement and autoindexing routine of the CAD4v5.1 diffractometer control software. The structure was solved using the Patterson heavy-atom method and was refined with full-matrix least-squares procedures. The hydrogen atoms were included in the refinement. A final data set of 2259 reflections ($I > 3\sigma(I)$) was used. The atomic scattering factors and anomalous dispersion terms were taken from standard compilations,[25] and all calculations were performed on a VAX computer using molEN.[26]

Table 5. Crystallographic Data

	$MnN_3O_3C_{12}H_{30}PF_6$
fw	464.28
space group	$P2/c$
a, Å	15.652(2)
b, Å	8.740(1)
c, Å	15.208(2)
α, deg	90
β, deg	108.81(1)
γ, deg	90
Z	4
V, Å^3	1969.4(4)
ρ_{calcd}, g cm^{-3}	1.566
T, °C	23(1)
radiation λ, Å	Mo Kα (0.710 73)
$R(F_o)^a$	0.067
$R_w(F_o)^a$	0.097

[a] $R(F_o) = \sum|F_o - F_c|/\sum F_o$ and $R_w(F_o) = (\sum w(F_o - F_c)^2/\sum wF_o^2)^{1/2}$.

A manganese environment with three methoxy groups and three nitrogens bridged in pairs by two carbons appeared readily from all structure solution techniques. One PF$_6^-$ ion also was readily identified. The other PF$_6^-$ ion is extremely disordered. The central P atom refines well, and the other P atoms are found at distances that are approximately equal to P−F distances but in high numbers and with high thermal values. This disorder limited the analysis of the structure with regard to refining H-atom positions. More details for the data collection and refinement, atomic coordinates, bond distances, and bond angles are available in the supporting information.

Acknowledgment. The authors acknowledge H. Kalinoski, Unilever Research US, for performing the FAB-MS analysis and J. Phillips, Enraf Nonius Co., for performing the X-ray crystal structure analysis.

Supporting Information Available: Complete details for data collection and refinement, a listing of fractional coordinates, anisotropic thermal parameters, and complete bond distances and angles for [Mn^{IV}(Me$_3$TACN)(OMe)$_3$](PF$_6$) (8 pages). Ordering information is given on any current masthead page.

IC951522W

---

(25) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(26) *MolEN, An Interactive Structure Solution Procedure*; Enraf Nonius: Delft, The Netherlands, 1990.