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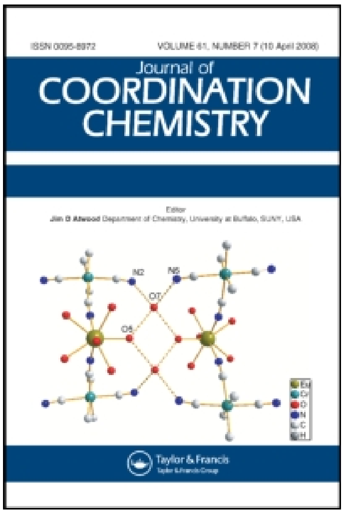

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Similarities and differences in properties and behavior of two H_2O_2-activated manganese catalysts having structures differing only by methyl and ethyl substituents

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Similarities and differences in properties and behavior of two H_2O_2-activated manganese catalysts having structures differing only by methyl and ethyl substituents

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The complex $[Mn(IV)(Me_2EBC)(OH)_2](PF_6)_2$, in which Me_2EBC is 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane, is a remarkably selective H_2O_2 oxidation catalyst that has been shown to be useful in removing stains from fabrics without affecting their colors. Mn(IV) is the highest oxidation state detected and the dihydroxo complex forms a peroxyhydroxy derivative that is responsible for catalytic oxidations. Study of the diethyl homolog of this catalyst has revealed surprising differences in chemical behavior. Oxidation of this new manganese complex, $Mn(Et_2EBC)Cl_2$, using aqueous H_2O_2, at $-30°C$ following removal of chloride ion, yields $[Mn(Et_2EBC)(OH)_2](PF_6)_2$. Above 0°C, H_2O_2 oxidation of $Mn(Et_2EBC)Cl_2$ oxidizes the ethyl substituents. X-ray structure determinations of Et_2EBC complexes with Mn(II), Mn(III), and Mn(IV) are reported. The complex $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ displays a surprisingly mild oxidizing potential of $+0.556$ V for the Mn^{4+}/Mn^{3+} couple; however, its hydrogen abstraction ability for selected substrates is limited by the BDE_{CH} value of $82\,kcal\,mol^{-1}$, the same as reported for $[Mn(Me_2EBC)(OH)_2](PF_6)_2$. However, unlike the methyl derivative, electrochemical results indicate a 5+/4+ couple, in addition to the expected 4+/3+ and 3+/2+ couples. The significance of these differences in behavior is discussed. Mass spectral studies have identified some products of ethyl group oxidations.

Keywords: Oxidation catalyst; Structure; Manganese catalysts

1. Introduction

New transition metal complexes continue to reveal new insights into the fundamental chemistry of metallic elements and their mechanistic capabilities, often increasing the understanding of biological systems [1]. Low oxidation state transition metal complexes have been well studied and their properties have been clearly elucidated. Exploring the corresponding high oxidation state complexes has not been so successful, especially for late transition metal ions, mainly because their high oxidizing power results in short lifetimes, even at low temperatures. Also, these high valence metal ions have strong

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tendencies to form dimers or oligomers through μ-oxo bridges by dehydration of M–OH groups, as exemplified by iron and manganese. Until now, there has been no reported characterization by X-ray structure determination of an iron(V) complex, although recent low temperature solution characterizations have been achieved [2]. For manganese catalysts, progress has been better. A few Mn(V)-oxo complexes with macrocyclic ligands have been characterized [3], and in these laboratories a first monomeric manganese(IV) complex having a *cis* pair of hydroxide ligands has been isolated and characterized by X-ray, electrochemistry, and chemical reactions [4]. For this first example, the complicating formation of μ-oxo bridges between metal ions is prevented by the bulky methyl substituents on the relatively rigid tetradentate ligand, 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (Me_2EBC), a so-called *cross-bridged* macrocycle. A first hydrogen peroxide adduct with a manganese(IV) ion, $Mn^{IV}(Et_2EBC)(OH)(OOH)^{2+}$, was detected by mass spectrometry during investigation of the olefin epoxidation [5] mechanism catalyzed by $[Mn^{IV}Et_2EBC)(OH)_2]^{2+}$. The unusual Lewis acid pathway for oxygen transfer of this manganese complex and the limited oxidizing power of its highest tetravalent oxidation state make it an excellent oxidation catalyst for the laundry products industry [6, 7].

This report extends the exciting chemistry of these manganese complexes of cross-bridged cyclam ligands, describing the chemistry of new manganese complexes of 4,11-diethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (Et_2EBC), the close homolog of Me_2EBC. Under similar conditions to those used for synthesis of $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$, even though its ligand is simply the diethyl sibling of Me_2EBC, attempts to generate $[Mn^{IV}Et_2EBC)(OH)_2]^{2+}$ were surprisingly unsuccessful, resulting in ligand alterations that are now the subject of a separate research program. The synthesis of the desired manganese(IV) compound having two hydroxide ligands, $[Mn(Et_2EBC)(OH)_2](PF_6)_2$, required an altered procedure involving temperatures as low as −30°C.

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2. Experimental

2.1. *Materials and methods*

$Mn^{II}(Et_2EBC)Cl_2$ (+99.9%) was generously supplied by the Procter and Gamble Company and X-ray quality crystals of the $Mn^{II}(Et_2EBC)Cl_2$ complex were obtained by diffusing ether into the acetone solution of $Mn^{II}(Et_2EBC)Cl_2$. The structure appears in figure 1. Other reagents were purchased from Aldrich or Lancaster. Elemental analysis was performed by Quantitative Technologies, Inc. Mass spectra were measured by the Analytical Service of the University of Kansas on a VG ZAB HS spectrometer equipped with a xenon gun.

2.2. *Synthesis of $[Mn^{III}(Et_2EBC)(OH)(Cl)]PF_6$*

After a 10 mL acetonitrile solution containing 0.41 g (0.001 mol) of $Mn^{II}(Et_2EBC)Cl_2$ and 0.815 g (0.005 mol) of NH_4PF_6 was cooled to −30°C with an acetone/dry ice bath, 2 mL of 30% H_2O_2 in 2 mL of acetonitrile, precooled to −30°C, was added stepwise, whereupon a dark green solution was generated immediately. The reaction mixture was continuously stirred until bubbling stopped; then, about 1 mL of the resulting dark

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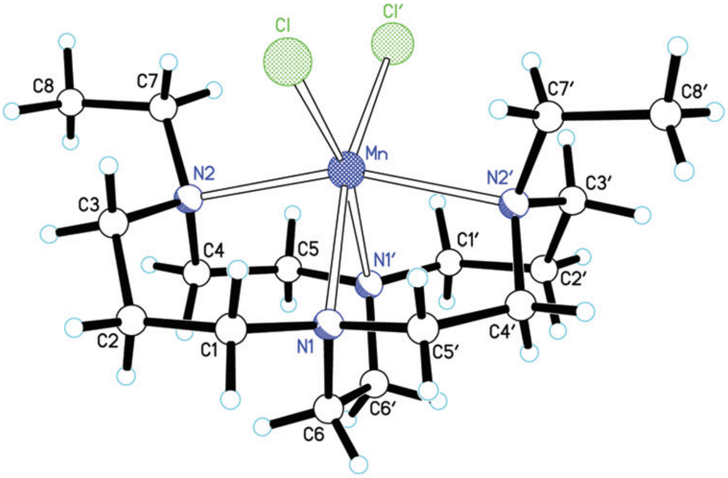

Figure 1. The structure of $Mn^{II}(Et_2EBC)Cl_2$.

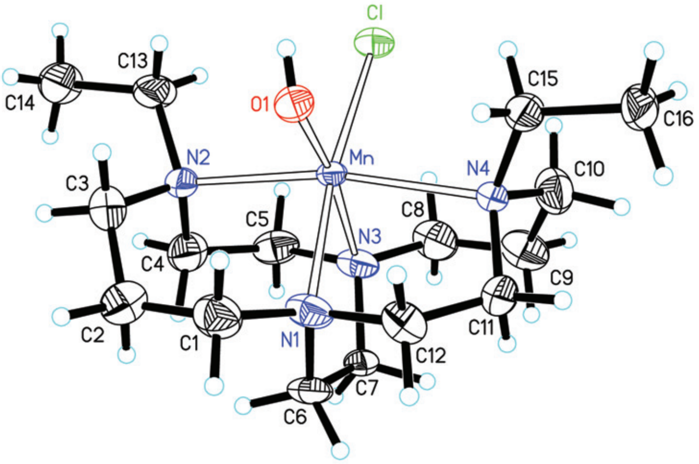

Figure 2. The structure of $Mn^{III}(Et_2EBC)(OH)Cl^+$ cation.

green solution was diffused with ether at a temperature below −20°C for days to grow green crystals for X-ray study. Those measurements verified the composition-based structure, $[Mn^{III}(Et_2EBC)(OH)(Cl)]PF_6$, with six-coordinate Mn(III) bound to Et_2EBC, one chloride, and one hydroxide ion, resulting in a net charge of +1, and neutralized by a single PF_6^- anion in the unit cell (figure 2).

2.3. *Synthesis of $[Mn^{IV}(Et_2EBC)(OH)_2](PF_6)_2$*

A 60 mL acetonitrile solution containing 0.82 g (0.002 mol) of $Mn^{II}(Et_2EBC)Cl_2$ was stirred at room temperature until dissolution was complete. Then, 3 mL of acetone solution containing 1.0 g (0.004 mol) of $AgPF_6$ was added, after which the AgCl

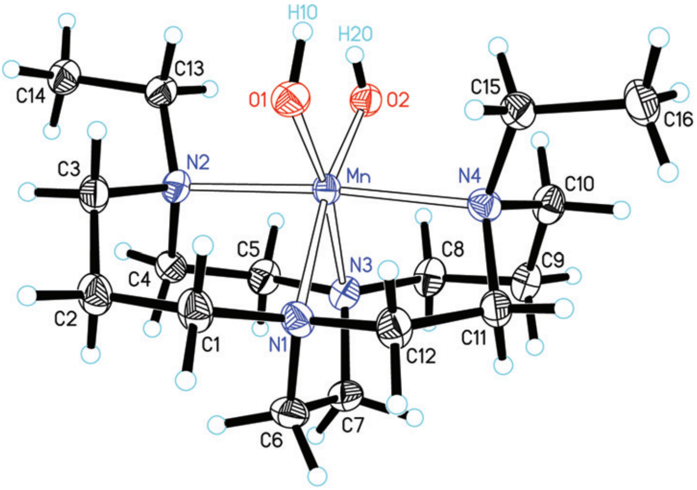

Figure 3. The structure of $Mn^{IV}(Et_2EBC)(OH)_2^{2+}$ cation.

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precipitate was removed by filtration to give the PF_6^- salt of the Mn^{II}/Et_2EBC complex in a colorless solution. The solution of $Mn^{II}(Et_2EBC)/(PF_6)_2$ was cooled to −30°C in an acetone/dry ice bath and 2 mL of 30% H_2O_2 in 2 mL of acetone, also precooled at −30°C, was added stepwise, resulting in a dark purple solution. This reaction mixture was stirred until bubbling stopped. Ether was diffused into the dark purple solution while maintaining the temperature below −20°C for weeks to grow dark macro-crystals which were suitable for X-ray structure determination (figure 3). Yield 45% (0.56 g). Anal. Calcd for $MnC_{16}H_{38}N_4O_2P_2F_{12}$: C 29.04%, H 5.49%, and N 8.47%. Found: C 29.10%, H 5.32%, and N 8.57%.

2.4. *Hydrogen abstraction experiment*

In a typical reaction, 0.1 mmol of $[Mn^{IV}(Et_2EBC)(OH)_2](PF_6)_2$ was dissolved with stirring at room temperature in 5 mL of acetone containing 2.5 mmol of 1,4-cyclohexadiene. The resulting reaction mixtures were stirred overnight and the original Mn(IV) purple color changed to the brown of the Mn(III) derivative. Product analysis was performed by gas chromatography (GC) using the internal standard method and the products were identified by GC/MS (MS, mass spectroscopy).

2.5. *Physical methods*

Electrochemical experiments were performed in dry acetonitrile under nitrogen on a Model 620A CH Instrument using a homemade cell. A Pt button was used as the working electrode in conjunction with a Pt-wire counter electrode and a Ag/Ag^+ non-aqueous reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) was the supporting electrolyte in all cases.

The three crystal structures are illustrated in figures 1–3; the crystal data and structure refinement details are listed in table 1; the selected bond lengths and angles are summarized in table 2; further details are provided in supporting information.

3. Results and discussion

3.1. *Synthesis*

As reported [4], the manganese(IV) complex having two monodentate hydroxide ligands and the cross-bridged macrocycle (Me_2EBC), $[Mn(Me_2EBC)(OH)_2](PF_6)_2$, was synthesized by simple oxidation of $Mn(Me_2EBC)Cl_2$ with H_2O_2 in the presence of NH_4PF_6 in aqueous solution at room temperature. Since the Mn(II) complex with Et_2EBC is almost identical to $Mn(Me_2EBC)Cl_2$ except for two ethyl instead of two methyl groups, the first attempt to synthesize the corresponding Mn(IV) complex with Et_2EBC ligand, $[Mn(Et_2EBC)(OH)_2]^{2+}$, was conducted under conditions identical to those for $[Mn(Me_2EBC)(OH)_2]^{2+}$. The reaction soon revealed attack on the ligand and mass spectral studies indicated that the ethyl groups were undergoing a series of oxidations. Based on this unexpected result, the redox potential of the targeted Mn(IV) complex, $[Mn(Et_2EBC)(OH)_2]^{2+}$, was assumed to be more positive than that of $[Mn(Me_2EBC)(OH)_2](PF_6)_2$.

To avoid the previously observed over oxidation, the second attempt was carried out using an ice water bath. However, the identical damaging of ethyl groups was again observed. In the third attempt, the procedure was further modified by oxidizing $Mn(Et_2EBC)Cl_2$ in acetonitrile at $-30^\circ C$ using 30% aqueous H_2O_2 in acetonitrile, precooled at $-30^\circ C$ with an acetone/dry ice bath. The resulting dark green solution was diffused with ether at $-20^\circ C$, resulting in a green crystalline product which was identified by X-ray structure determination as the Mn(III) complex having hydroxide and chloride ligands, $[Mn^{III}(Et_2EBC)(OH)(Cl)]PF_6$ (figure 2); the ethyl substituents remained undamaged, but the product had one chloride ion and only one hydroxide bound to the manganese. The final modification of the oxidation procedure was the simple removal of chloride from $Mn(Et_2EBC)Cl_2$ with two equivalents of $AgPF_6$, prior to oxidizing the resulting $Mn^{II}(Et_2EBC)$ complex with H_2O_2 in acetonitrile at $-30^\circ C$ in an acetone/dry ice bath. Upon adding the oxidant, the colorless solution immediately turned purple, indicating the successful oxidation of the Mn(II) species to the Mn(IV) product. The purple manganese(IV) solution was diffused with ether at $-20^\circ C$ for weeks, finally generating the dark macro-crystals which were characterized by elemental analysis and X-ray structure determination, confirming the successful synthesis of the targeted manganese(IV) complex $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ (figure 3).

3.2. *Crystal structures*

The crystal data and structural details for the three crystal structures, $Mn^{II}(Et_2EBC)Cl_2$, $[Mn^{III}(Et_2EBC)(OH)(Cl)]PF_6$, and $[Mn(Et_2EBC)(OH)_2](PF_6)_2$, are listed in table 1. The corresponding selected bond distances and angles are summarized in table 2, and the X-ray structures are displayed in figures 1–3.

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Table 1. Crystal data and structure refinement details.

	$Mn^{II}(Et_2EBC)Cl_2$	$[Mn^{III}(Et_2EBC)(OH)(Cl)]PF_6CH_3CN$	$[Mn^{IV}(Et_2EBC)(OH)_2](PF_6)_2 \cdot H_2O$
Empirical formula	$C_{16}H_{34}Cl_2MnN_4$	$C_{18}H_{38}ClF_6MnN_5OP$	$C_{16}H_{38}F_{12}MnN_4O_3P_2$
Formula weight	408.31	575.89	679.38
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$Fdd2 - C_{2v}^{19}$ (No. 43)	$P\bar{1}(C_i^1$ – No. 2)	$Cc\ (C_s^4$ – No. 9)
Unit cell dimensions (Å, °)			
a	29.336(4)	7.7645(6)	11.4741(9)
b	10.1652(13)	12.074(1)	11.2920(9)
c	12.7898(16)	14.887(1)	20.0738(15)
α	90	68.475(2)	90
β	90	80.817(2)	97.769(1)
γ	90	72.044(2)	90
Volume (Å^3), Z	3813.9(8), 8	1233.4(2), 2	2577.0(3), 4
Calculated density (Mg m^{-3})	1.422	1.551	1.751
Absorption coefficient (mm^{-1})	0.977	0.775	0.752
$F(000)$	1736	600	1396
Crystal size (mm^3)	0.30 × 0.19 × 0.07	0.14 × 0.10 × 0.03	0.38 × 0.30 × 0.04
θ range for data collection (°)	2.65–30.00	2.76–30.06	2.54–30.01
Limiting Indices	$-41 \le h \le 41$; $-13 \le k \le 14$; $-18 \le l \le 17$	$-10 \le h \le 10$; $-16 \le k \le 16$; $-20 \le l \le 20$	$-16 \le h \le 16$; $-15 \le k \le 15$; $-28 \le l \le 28$
Reflections collected	10,908	14,750	14,946
Independent reflections	2770 [$R_{int} = 0.049$]	7101 [$R_{int} = 0.052$]	7255 [$R_{int} = 0.0652$]
Completeness to $\theta = 30.00$ (%)	99.9	98.4	99.8
Absorption correction	Empirical	Empirical	Empirical
Max. and min. transmission	0.598 and 0.511	0.649 and 0.615	0.503 and 0.366
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2770/1/173	7101/0/315	7255/38/413
Goodness-of-fit on F^2	1.017	0.889	0.997
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.031$, $wR_2 = 0.066$	$R_1 = 0.060$, $wR_2 = 0.136$	$R_1 = 0.045$, $wR_2 = 0.110$
R indices (all data)	$R_1 = 0.032$, $wR_2 = 0.066$	$R_1 = 0.103$, $wR_2 = 0.149$	$R_1 = 0.048$, $wR_2 = 0.112$
Largest difference peak and hole (e Å^{-3})	0.51 and −0.25	1.16 and −0.52	0.814 and −0.366

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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Table 2. Selected bond lengths (Å) and angles (°).

$[Mn^{II}(Et_2EBC)(Cl)_2]$			
Mn–N(1)	2.3303(16)	N(2)#1–Mn–N(2)	159.00(8)
Mn–N(1)#1	2.3303(16)	N(1)–Mn–Cl	92.82(4)
Mn–N(2)#1	2.3415(16)	N(1)#1–Mn–Cl	166.21(4)
Mn–N(2)	2.3415(16)	N(2)#1–Mn–Cl	101.33(4)
Mn–Cl	2.4701(5)	N(2)–Mn–Cl	92.26(4)
Mn–Cl#1	2.4701(5)	N(1)–Mn–Cl#1	166.21(4)
N(1)–Mn–N(1)#1	75.93(8)	N(1)#1–Mn–Cl#1	92.82(4)
N(1)–Mn–N(2)#1	78.93(6)	N(2)#1–Mn–Cl#1	92.26(4)
N(1)#1–Mn–N(2)#1	84.53(6)	N(2)–Mn–Cl#1	101.33(4)
N(1)–Mn–N(2)	84.53(6)	Cl–Mn–Cl#1	99.36(3)
N(1)#1–Mn–N(2)	78.93(6)		
$[Mn^{III}(Et_2EBC)(OH)(Cl)]PF_6$			
Mn–O(1)	1.822(2)	N(1)–Mn–N(2)	89.01(11)
Mn–N(3)	2.094(3)	N(3)–Mn–N(4)	87.96(11)
Mn–N(1)	2.166(3)	N(1)–Mn–N(4)	82.25(11)
Mn–N(2)	2.272(3)	N(2)–Mn–N(4)	168.98(10)
Mn–N(4)	2.303(3)	O(1)–Mn–Cl	94.40(8)
Mn–Cl	2.3412(9)	N(3)–Mn–Cl	94.92(8)
O(1)–Mn–N(3)	170.23(11)	N(1)–Mn–Cl	172.59(9)
O(1)–Mn–N(1)	88.79(11)	N(2)–Mn–Cl	97.57(8)
N(3)–Mn–N(1)	82.31(11)	N(4)–Mn–Cl	90.80(7)
O(1)–Mn–N(2)	91.67(11)	Mn–O(1)–H(1O)	110(3)
N(3)–Mn–N(2)	84.20(12)	O(1)–Mn–N(4)	94.83(11)
$[Mn^{IV}(N_4C_{16}H_{34})(OH)_2](PF_6)_2 \cdot H_2O$			
Mn–O(2)	1.803(2)	N(3)–Mn–N(1)	84.17(9)
Mn–O(1)	1.810(2)	O(2)–Mn–N(4)	89.10(9)
Mn–N(3)	2.075(2)	O(1)–Mn–N(4)	93.98(9)
Mn–N(1)	2.091(2)	N(3)–Mn–N(4)	91.90(9)
Mn–N(4)	2.141(2)	N(1)–Mn–N(4)	84.69(9)
Mn–N(2)	2.143(2)	O(2)–Mn–N(2)	94.10(9)
O(2)–Mn–O(1)	98.12(9)	O(1)–Mn–N(2)	88.81(9)
O(2)–Mn–N(3)	88.56(10)	N(3)–Mn–N(2)	84.91(9)
O(1)–Mn–N(3)	171.15(10)	N(1)–Mn–N(2)	91.70(9)
O(2)–Mn–N(1)	170.27(10)	Mn–O(2)–H(2O)	102(3)
O(1)–Mn–N(1)	89.79(9)	Mn–O(1)–H(1O)	112(2)
N(4)–Mn–N(2)	175.42(7)		

As the oxidation state of the corresponding manganese increases from +2 to +4, the manganese ion gradually decreases in size and is more engulfed in the ligand cavity, as reported for the manganese complexes with Me_2EBC [4]. These changes are displayed in the Mn–N bond lengths and N–Mn–N angles of the corresponding manganese complexes. The four Mn–N bond lengths in $Mn^{II}(Et_2EBC)Cl_2$ are 2.330(2), 2.330(2), 2.342(2), and 2.342(2) Å with N-Mn-N angles of 158.99(8)° and 84.53(6)°. In $[Mn^{III}(Et_2EBC)(OH)(Cl)]PF_6$, they are 2.303(3), 2.272(3), 2.166(3), and 2.094(3) Å for the Mn–N bond lengths, having N–Mn–N angles of 168.98(10)° and 82.31(11)°. The complex $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ provides Mn–N bond lengths of 2.143(2), 2.141(2), 2.091(2), and 2.075(2) Å with the N–Mn–N angles of 175.42(7)° and 84.17(9)°, respectively. This is consistent with the decrease of cation sizes in the series $Mn^{2+} > Mn^{3+} > Mn^{4+}$. The Mn–OH bond in the Mn(IV) complex is slightly shorter than that in the Mn(III) complex, that is, 1.803(2) and 1.810(2) Å in $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ *versus* 1.822 Å in $[Mn^{III}(Et_2EBC)(OH)(Cl)]PF_6$.

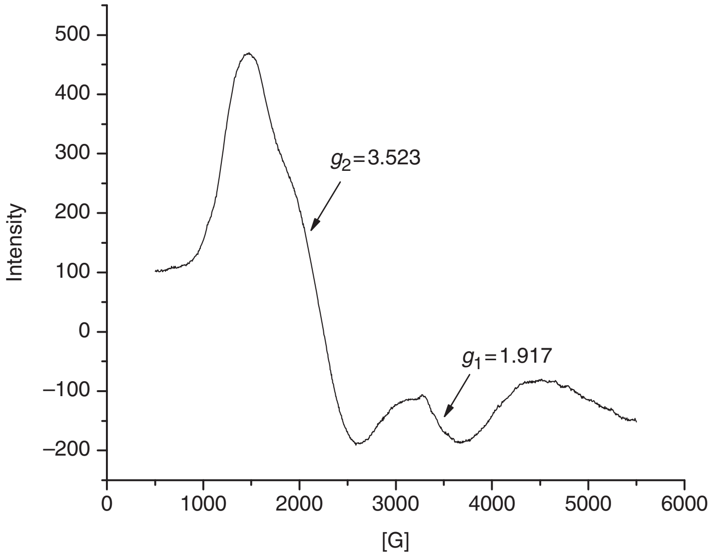

Figure 4. EPR spectrum of $[Mn^{IV}(Et_2EBC)(OH)_2](PF_6)_2$ in dry acetonitrile at 70 K.

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Table 3. Redox potentials and peak separations for $[Mn^{IV}(Et_2EBC)(OH)_2](PF_6)_2$ (*vs*. SHE) under nitrogen at 298 K.

Redox couple	$E_{1/2}$ (V)	$E_a - E_c$ (mV)
Mn^{5+}/Mn^{4+}	+0.868	84
Mn^{4+}/Mn^{3+}	+0.556	99
Mn^{3+}/Mn^{2+}	−0.201	106

3.3. *EPR, electrochemistry, and reactivity*

The electron paramagnetic resonance (EPR) spectrum of $[Mn^{IV}(Et_2EBC)(OH)_2](PF_6)_2$ in dry acetonitrile at 70 K showed two broad resonances at $g = 1.917$ and $g = 3.523$ (figure 4). This spectrum is essentially identical to the EPR reported earlier for its sibling, $[Mn(Me_2EBC)(OH)_2](PF_6)_2$ [4], and very similar to that reported by Kerschner for the Mn(IV) complex containing a N,N′,N″-trimethyl-1,4,7-triazacyclononane [8]. It is typical of a high spin d^3-ion with axial symmetry in a strong ligand field and confirms the Mn(IV)oxidation state in $[Mn^{IV}(Et_2EBC)(OH)_2]^{2+}$ [9].

Electrochemically, newly synthesized $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ displayed a gentle oxidizing power with a redox potential of +0.556 V (*vs*. SHE) for the Mn^{4+}/Mn^{3+} couple (table 3). This redox potential is distinctly lower than that of the Mn^{4+}/Mn^{3+} couple in $[Mn(Me_2EBC)(OH)_2](PF_6)_2$ (+0.756 V), suggesting that the destruction of the ethyl group may not be caused by the assumed high oxidizing power of the Mn(IV) ion in the Et_2EBC complex [4]. In support of this view, the manganese(IV) complex displayed a strong signal for the reversible Mn^{5+}/Mn^{4+} couple, also having a relatively low redox potential (+0.868 V) (figure 5), whereas the weak signal that might be attributed to a Mn^{5+}/Mn^{4+} couple for $[Mn(Me_2EBC)(OH)_2](PF_6)_2$ was obviously

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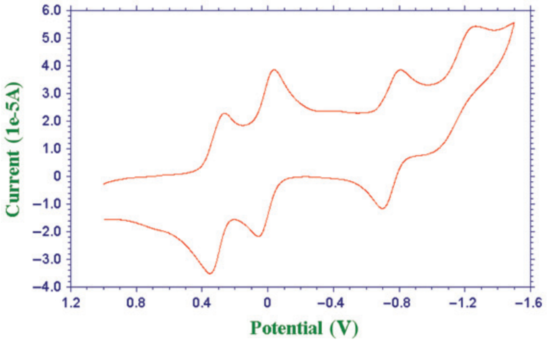

Figure 5. Cyclic voltammogram for $[Mn^{IV}(Et_2EBC)(OH)_2](PF_6)_2$ in dry acetonitrile at 298 K.

Table 4. Hydrogen abstraction from selected substrates by manganese(IV) complex.

Substrate	BDE_{CH} ($kcal\,mol^{-1}$)	Reaction time	Product	Yield (%)[c]
1,4-Cyclohexadiene[a]	73	Overnight	Benzene	86
9,10-Dihydroanthracene[b]	78	1 day	Anthracene	70
Fluorene[b]	80	6 days	9-Fluorenone	36
Diphenyl methane[b]	82	No reaction	–	
Toluene[b]	90	No reaction	–	
Cyclohexane[b]	99	No reaction	–	

Reactions were run at room temperature in 5 mL of acetonitrile.
Using [a]0.1 mmol of Mn^{IV} complex and 2.5 mmol of 1,4-cyclohexadiene; [b]0.04 mmol of Mn^{IV} complex and 0.16 mmol of substrate were used, solvent: acetone 5 mL; and [c]Yield was based on the Mn(IV) complex.

irreversible and showed a redox potential of +1.013 V. Interestingly, although the redox potentials for both the Mn^{4+}/Mn^{3+} couple and Mn^{5+}/Mn^{4+} couple in $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ were lower than those of $[Mn(Me_2EBC)(OH)_2](PF_6)_2$, the redox potential of the Mn^{3+}/Mn^{2+} couple (−0.201 V) for the ethyl-substituted complex is much higher than that of the methyl derivative, $[Mn(Me_2EBC)(OH)_2](PF_6)_2$ (−0.696 V).

The oxidizing power of this freshly synthesized complex, $[Mn(Et_2EBC)(OH)_2](PF_6)_2$, was tested by hydrogen abstraction from selected substrates with known C–H bond dissociation energies (BDE_{CH}) and compared with the results of similar experiments with $[Mn(Me_2EBC)(OH)_2](PF_6)_2$ [6]. The reactions were performed in acetone at room temperature and the results appear in table 4. As the hydrogen abstraction reaction proceeds, the purple color of the Mn(IV) species gradually turns to the brown of the Mn(III) derivative. Quantitative oxidation of 1,4-cyclohexadiene provided 86% yield of benzene based on added Mn(IV) complex; with 9,10-dihydroanthracene, the yield of anthracene was 70% and no anthraquinone was detected in the products. Fluorene gave 36% fluorenone product. With the BDE_{CH} values of the selected substrates increasing from 73 $kcal\,mol^{-1}$ for 1,4-cyclohexadiene to 80 $kcal\,mol^{-1}$ for fluorene, the required reaction time increased dramatically from overnight to 6 days. No product was detected when using substrates having the BDE_{CH} values greater than 80 $kcal\,mol^{-1}$, including diphenylmethane ($BDE_{CH} = 82\,kcal\,mol^{-1}$), toluene ($BDE_{CH} = 90\,kcal\,mol^{-1}$), and cyclohexane ($BDE_{CH} = 99\,kcal\,mol^{-1}$). These data recall the hydrogen abstraction results with $[Mn(Me_2EBC)(OH)_2](PF_6)_2$, where hydrogen abstraction also terminated at diphenylmethane, despite the fact that the redox potential of the Mn^{4+}/Mn^{3+} couple in $[Mn(Me_2EBC)(OH)_2](PF_6)_2$ is greater than that of $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ (+0.756 V *vs.* +0.556 V) [4]. Since the deprotonation constant (pKa) of this new manganese(IV) complex was not available, the independent calculation of the oxidizing power in $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ cannot be performed to indicate the theoretical hydrogen abstraction ability of this Mn(IV) complex.

3.4. *Self-destruction of $Mn^{II}(Me_2EBC)Cl_2$*

Structurally, $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ and $[Mn(Me_2EBC)(OH)_2](PF_6)_2$ are very similar as are $Mn^{II}(Et_2EBC)Cl_2$ and $Mn^{II}(Me_2EBC)Cl_2$, except that the methyl substituents were replaced by the ethyl groups; however, the redox potential of the Mn^{4+}/Mn^{3+} couple in $[Mn(Et_2EBC)(OH)_2]^{2+}$ is significantly lower than that of $[Mn(Me_2EBC)(OH)_2]^{2+}$ (+0.556 V *vs.* +0.756 V). On this basis, it could be inferred that the stability of $[Mn(Et_2EBC)(OH)_2]^{2+}$ would be better than that of $[Mn(Me_2EBC)(OH)_2]^{2+}$.

To the contrary, under identical oxidative conditions at room temperature, oxidation of $Mn^{II}(Me_2EBC)Cl_2$ using aqueous H_2O_2 generated $[Mn(Me_2EBC)(OH)_2](PF_6)_2$ quantitatively, whereas $Mn^{II}(Et_2EBC)Cl_2$ underwent a series of destructive reactions at the ethyl groups. This destruction of the ethyl groups cannot be attributed to a radical attack on ethyl groups by $\cdots$OH or $\cdots$OOH radicals, because such an attack should occur on the methyl of Me_2EBC as well and that does not happen. It follows that the events destroying the ethyl substituents in $Mn(Et_2EBC)$ complex are not likely to be radical processes. This mechanism is the subject of on-going investigations.

Preliminary investigation of the destruction of the ethyl substituents on Et_2EBC by mass spectrometry was conducted using H_2O_2 to oxidize the $Mn^{II}(Et_2EBC)(PF_6)_2$ in aqueous solution at room temperature. First of all, the chloride ion was removed by adding $AgPF_6$ in acetone before adding aqueous H_2O_2. Some intermediate products that are formed during the destruction of the ethyl group were detected in the mass spectra and confirmed by accurate mass measurements. Figure 6 shows the concept and structures and figure 7 is an example of the spectra. These early determinations indicated that $Mn^{II}(Et_2EBC)^{2+}$ was first oxidized to $Mn^{IV}(Et_2EBC)(OH)(O)^+$ ($m/z = 370.2$), then to $Mn^{IV}(CH_2CH_2O, CH_3CH_2EBC)(OH)(O)^+$ ($m/z = 368.2$) in which a coordinated alcoholate function is detected, then to $Mn^{IV}(CH_2CHO, CH_3CH_2EBC)(O)^+$ ($m/z = 384.2$) where the aldehyde group is produced by a second two-electron oxidation step. The aldehyde does not coordinate to the Mn^{IV} ion. In the next step, the compound is converted to $Mn^{IV}(CH_2CO_2, CH_3CH_2EBC)(O)^+$ ($m/z = 382.2$) in which a carboxylate anion is formed and that functional group bonds to the Mn^{IV}. In the final step revealed in this study, the second ethyl group is transformed into a coordinated ethoxy group. That is, $Mn^{IV}(CH_3CH_2O, CH_2CO_2 EBC)^{2+}$ ($m/z = 190.6$) is formed and both a carboxylate and an alcoholate are ligated to Mn^{IV}. A parallel pathway was also observed for the corresponding Mn(III) species, including $Mn^{III}(CH_2CH_2O, CH_3CH_2EBC)(OH)^+$ ($m/z = 369.2$) and $Mn^{III}(CH_2CO_2, CH_3CH_2EBC)(OH)^+$ ($m/z = 383.2$), and finally $Mn^{III}(CH_2CH_2O, CH_3CO_2EBC)$ ($m/z = 381.2$) is produced. These observations provide the rationale for an on-going

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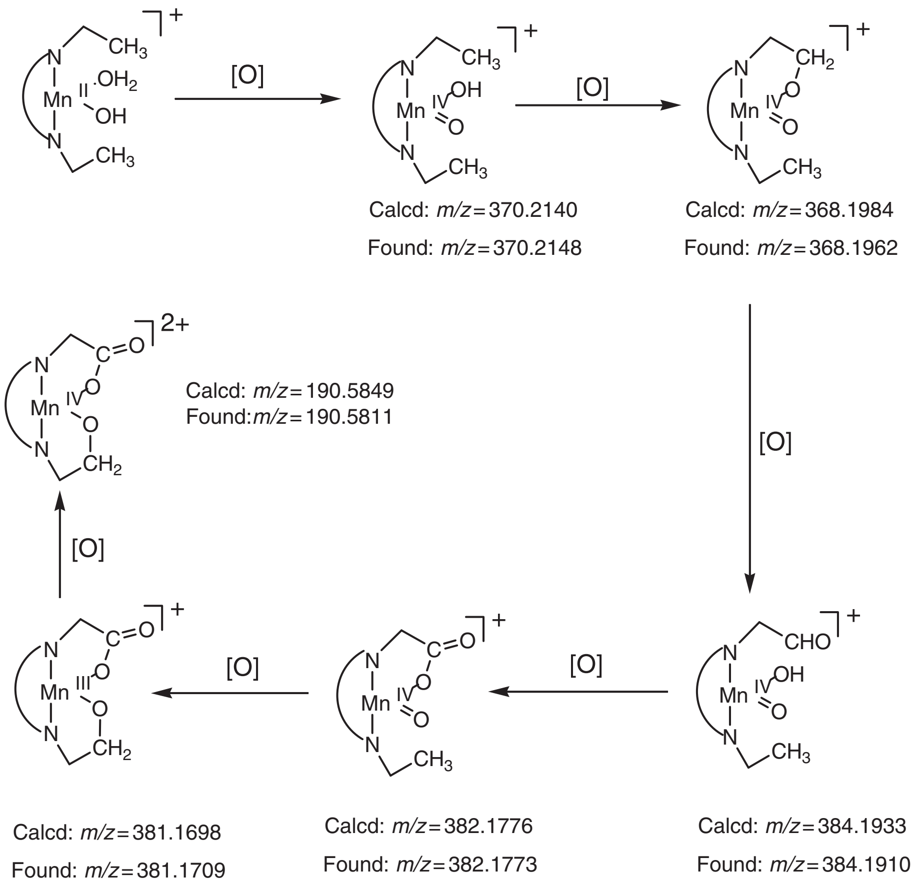

Figure 6. The possible destruction process of ethyl group in Mn(Et_2EBC) complex by oxidation.

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program to isolate and characterize the products of self oxidation of $Mn^{II}(Et_2EBC)^{2+}$ using H_2O_2.

3.5. *Oxidative reactivity of* $Mn^{IV}(Et_2EBC)(OH)_2^{2+}$

The properties and capabilities of the activated catalyst, $Mn^{IV}(Et_2EBC)(OH)_2^{2+}$, are the present focus and the redox properties of this complex are interesting, even surprising. Whereas the only well-defined redox couples for the Me_2EBC complex were Mn^{4+}/Mn^{3+} and Mn^{3+}/Mn^{2+}; $Mn^{IV}(Et_2EBC)(OH)_2^{2+}$ also displayed a strong reversible couple for the Mn^{5+}/Mn^{4+} reaction at a halfwave potential of $+0.868$ V. Consequently, the ethyl derivative has the potential to perform substantially more powerful oxidations than the long known $Mn(Me_2EBC)Cl_2$ catalyst. Further the ethyl complex may be capable of oxidizing substrates *via* the *rebound mechanism*, a long recognized mechanism for oxidation by pentavalent manganese. It is, in fact, possible that the hydrogen abstraction reactions described here for $Mn(Et_2EBC)Cl_2$ and H_2O_2 might occur by that mechanism since the Mn^{5+}/Mn^{4+} couple is certainly strong enough.

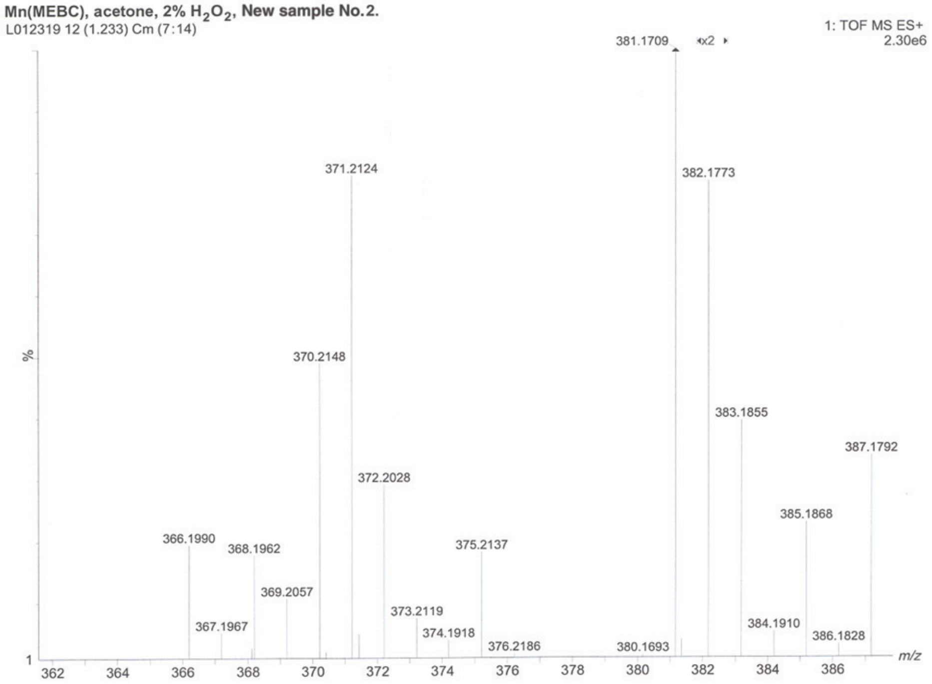

Figure 7. Mass spectrum showing products of H_2O_2 oxidation of $Mn^{II}(Et_2EBC)(PF_6)_2$.

The distinctly different redox behavior of $Mn(Et_2EBC)Cl_2$ compared to its ethyl substituted sibling continues to the Mn^{3+}/Mn^{2+} couple, which has a potential of −0.201 V versus a potential of −0.696 V for $Mn(Me_2EBC)Cl_2$. Remarkably, the +3 state for the Et_2EBC complex is stable only over a range of 0.757 V while that of Me_2EBC is almost twice as great, 1.425 V. These striking differences between compounds of very similar structures may derive from the effect of the pair of much larger ethyl substituents in the region flanking the reaction site. Perhaps the large freely rotating ethyl group interferes with solvation of substrate in the reaction zone. For certain, these two very similar ligands produce substantially different catalysts. This matter is the subject of on-going research. The crystal structures of the activated form, $Mn^{IV}(R_2EBC)(OH)_2^{2+}$, are very similar, except for the presence of the different substituents, and their EPR spectra are very similar indicating essentially identical electronic structures on the parts of the central metal ions. The differences in the redox reactions of these two catalysts are traceable only to the pair of substituents on the unbridged nitrogens of the main ligand and the effects of this difference on any factors determining the mechanistic behavior. These matters are the subject of continuing studies.

4. Conclusions

The oxidation chemistry of the second example of a family of manganese complexes with the cross-bridged cyclam ligand, Et_2EBC, has been investigated using aqueous

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H_2O_2 as oxidant. The well studied first example, $Mn^{II}(Me_2EBC)Cl_2$, is a successful catalyst for the use of H_2O_2 in laundry detergents. It is highly selective, abstracting hydrogens only from substrates having BDEs less than 82 kcal mol^{-1}, and only performing epoxidations of olefins in the form of its hydrogen peroxide complex, $Mn^{IV}(Me_2EBC)(OH)(OOH)^{2+}$. The activated form of the complex (prior to binding H_2O_2), $Mn(Me_2EBC)(OH)_2^{2+}$, is stable in the solid state and in aqueous solution at pH values less than ~10. In contrast, in the presence of hydrogen peroxide the complex of the new ligand, $Mn^{II}(Et_2EBC)Cl_2$, undergoes a self-oxidation process that proceeds through a series of oxygen atom additions and, under ambient reaction conditions, terminates in a compound whose ligand contains ethoxo and methylene carboxalato groups, both bound to the metal ion, $[Mn^{IV}(CH_3CH_2O, CH_2CO_2EBC)](PF_6)_2$. The study of the product of self oxidation of its ligand by $Mn^{II}(Et_2EBC)Cl_2$ and H_2O_2 is on-going.

The targeted complex in this study is the active form of the oxidation catalyst, $[Mn(Et_2EBC)(OH)_2](PF_6)_2$. In order to obtain this product, it is essential to remove the chloride using $AgPF_6$ prior to oxidation by H_2O_2; otherwise $Mn^{III}(Et_2EBC)(OH)(Cl)]PF_6$ is the product at −30°C. The complex $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ was also successfully synthesized at −30°C. The newly synthesized compound, $[Mn(Et_2EBC)(OH)_2](PF_6)_2$, demonstrated a gentle oxidizing power with the redox potential of +0.556 V for the Mn^{4+}/Mn^{3+} couple (*vs*. SHE), substantially different from the value reported for the methyl substituted catalyst, +0.756 V. This result is not totally consistent with the hydrogen abstraction results reported here; these results are closely parallel for the two catalysts. Most obvious, both activated catalysts stop abstracting hydrogen from substrates when the BDE reaches 82 kcal mol^{-1}. It is possible that the oxidation processes derive from different oxidation states of the manganese for these two closely related catalysts. All attempts to observe a +5/+4 couple for the Me_2EBC catalyst have failed and cyclic voltammetry reveals only a weak irreversible signal that might be assigned to such a process. In contrast, the Et_2EBC complex shows a strong reversible 5+/4+ couple at +0.868 V. The complexes are similar in additional very basic ways. The two manganese(IV) complexes are of the same color, a deep violet, with similar electronic spectra, and their EPR spectra also suggest essentially the same high spin d^3 electronic structures for manganese.

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Acknowledgments

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