ORIGINAL ARTICLE

Molecular self-modification: homolog of a manganese laundry bleach catalyst oxidatively transforms its tetradentate ligand into a novel hexadentate derivative

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Abstract On the basis of mass spectral studies alone, the relatively new manganese complex, $Mn(Et_2EBC)Cl_2$ (Et_2EBC = 4,11-diethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane), a homolog of the well proven, peroxide-based laundry bleach, $Mn(Me_2EBC)Cl_2$, has been reported to undergo a sequence of 2-electron oxidation steps, ultimately converting its ethyl groups into chelated ethoxo and methylene carboxylato groups, $[Mn^{IV}\{(^-OCH_2CH_2)(^-O_2CCH_2)\}EBC)](PF_6)_2$. We report here the isolation and characterization of that unusual product, and provide insight into the remarkable catalytic pathway to its formation. At temperatures above 0 °C, oxidation by aqueous H_2O_2 reliably transforms $Mn(Et_2EBC)Cl_2$ into $[Mn^{IV}\{(^-OCH_2CH_2)(^-O_2CCH_2)\}EBC)]^{2+}$. The experimental data for this intramolecular ethyl group transformation is consistent with oxygen insertion into a methyl C–H moiety of the ethyl group, $–NCH_2C(–H)H_2$, by the $Mn^{IV}–OOH$ functional group.

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Introduction

The activated form of the first example of this family of complexes provided the first mononuclear manganese(IV) complex having two hydroxide ligands, $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$, and this relatively high valent species was isolated and characterized in these laboratories by X-ray, electrochemistry and chemical reactions [1]. The main ligand is a relatively rigid diagonally bridged tetradentate molecule, 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (Me_2EBC), in which the ethylene bridge links two *trans*-located amino groups. A significant structural feature of this Mn(IV) complex is the fact that the formation of μ-O bridges between pairs of these molecules is prevented by the bulky methyl substituents on the unbridged pair of *trans*-located amino functions. The resulting manganese(IV) complex, with its two hydroxide or oxide ligands (depending on pH), has provided insights into important fundamental issues, for example, the water oxidation events in PS II [2]. For the first time, a hydrogen peroxide adduct of a manganese(IV) ion was detected [3–5] by mass spectroscopy in the course of investigations of oxygen transfer from $[Mn^{IV}(Me_2EBC)(O)(OOH)]^+$ in olefin oxidation [6, 7]. Catalytic olefin epoxidations by $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$ and H_2O_2 are highly selective and this is attributable to the unusual Lewis acid pathway for the oxygen transfer process and the limited hydrogen abstracting ability of the moderate tetravalent

oxidation state, which also make it an excellent oxidation catalyst for certain applications [8–10]. The ligand's two methyl substituents were replaced with ethyl groups in (Et$_2$EBC) (Et$_2$EBC = 4,11-diethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane) as a first step in evaluating their effects on the catalytic actions of these molecules. Unlike the Me$_2$EBC derivative, attempts to synthesize the manganese(IV) reactive intermediate, [Mn(Et$_2$EBC)(OH)$_2$](PF$_6$)$_2$, were decidedly challenging. It soon became clear that the ethyl groups in Mn(Et$_2$EBC)Cl$_2$ are oxidized very easily and surprisingly completely. Precise molecular weight determinations in mass spectral studies of the oxidizing solutions indicated that each ethyl group proceeded from ethyl to hydroxyethyl, then to the corresponding aldehyde and, finally, for one group, to the carboxylate anion. The eventual product observed is a dipositive Mn(IV) complex with chelated oxymethylene and methylene carboxylato groups, [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)}EBC)]$^{2+}$. The studies reported here have produced good yields of the expected final product, bright red–violet [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)}EBC)]$^{2+}$, as its PF$_6^-$ salt, and identified it as a manganese(IV) complex. The mechanisms of the sequence of oxidation reactions leading to this product and the significance of the observations are discussed.

Experimental section

The Procter and Gamble Company provided the starting material, Mn^{II}(Et$_2$EBC)Cl$_2$ (+99.9%). X-ray study proceeded using a crystal of [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)}EBC)](PF$_6$)$_2$ obtained by diffusing ether into an acetone solution of the compound. Aldrich or Lancaster were the sources of other reagents. Quantitative Technologies, Inc. performed the elemental analyses. The University of Kansas' mass spectra laboratory provided the mass spectra on a VG ZAB HS spectrometer equipped with a xenon gun.

Synthesis of [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)}EBC](PF$_6$)$_2$

Ten mL of an aqueous solution containing 0.41 g (0.001 mol) of Mn^{II}(Et$_2$EBC)Cl$_2$ and 0.815 g (0.005 mol) of NH$_4$PF$_6$ was prepared. With stirring, 2 mL of 30% H$_2$O$_2$ was added stepwise to the prepared solution over a period of 1 h and a deep red–purple solution formed rapidly. Stirring the reaction solution was continued until bubbles were no longer formed (about 1 h). During this time, a red purple precipitate gradually separated. The resulting reaction mixture was stored in a freezer overnight. The red purple precipitate was filtered with a glass frit, followed by washing with H$_2$O. The product was collected and dried overnight under reduced pressure at room temperature. The
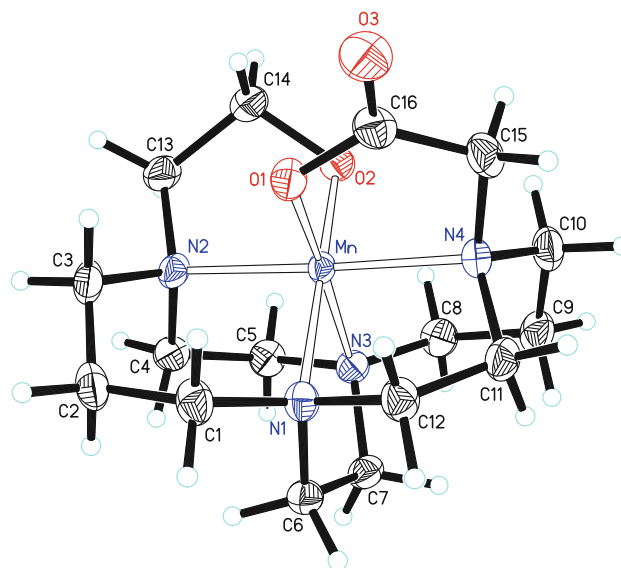
Fig. 1 Structure of [Mn^{IV}{(CH$_2$CH$_2$O)(CH$_2$CO$_2$)EBC}]$^{2+}$

yield of crude red purple powder was about 0.4 g. The crude product was recrystallized by complete dissolution in water followed by addition, with stirring, of a saturated aqueous solution containing 1 g of NH$_4$PF$_6$. A red purple precipitate gradually separated from solution. After filtration and drying under reduced pressure at room temperature, about 0.24 g of product was obtained. Yield: 36%. Anal. Calcd. for MnC$_{14}$H$_{30}$N$_4$O$_3$P$_2$F$_{12}$: C 28.61%, H 4.51%, N 8.35%, Found: C 28.47%, H 4.55%, N 8.37%. Crystals suitable for X-ray diffraction were obtained by diffusing ether into an acetonitrile solution containing [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)}EBC](PF$_6$)$_2$.

Physical methods

Electrochemical measurements were made under nitrogen with dry acetonitrile solutions using a CH Instruments Model 620A Cyclovoltameter with a homemade cell. The working electrode was a Pt button, used along with a Pt-wire counter electrode and an Ag/Ag$^+$ non-aqueous reference electrode. The supporting electrolyte was tetrabutyl ammonium hexafluorophosphate (0.1 M). The metal complex in the crystal structure is shown in Fig. 1. Crystal data and structure refinement details are listed in Table 1 and selected bond lengths and angles are summarized in Table 2. Additional information is contained in supporting information.

Results and discussion

Since the manganese(II) complex with Et$_2$EBC is almost identical to that of Mn(Me$_2$EBC)Cl$_2$ except for the two

Table 1 X-ray structure data

Empirical formula	$(Mn\ C_{16}\ H_{30}\ N_4\ O_3)^{2+}(PF_6^-)_2 \cdot (CH_3CN)$
	$Mn\ C_{18}\ H_{33}\ F_{12}\ N_5\ O_3\ P_2$
Formula weight	712.37
Crystal system	Triclinic
Space group	$P\ \bar{1}$
Unit cell dimensions	
$a = 10.288(3)$ Å	$\alpha = 78.868(5)°$
$b = 10.694(4)$ Å	$\beta = 82.599(5)°$
$c = 12.573(4)$ Å	$\gamma = 80.062(5)°$
Volume	1330.3(8) Å^3
Z, Z'	2, 1
Density (calculated)	1.778 Mg/m^3
Wavelength	0.71073 Å
Temperature	100(2) K
$F(000)$	726
Absorption coefficient	0.734 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9302 and 0.8552
Theta range for data collection	1.96–26.00°
Reflections collected	11658
Independent reflections	5221 [R(int) = 0.0220]
Data/restraints/parameters	5221/0/370
$wR(F^2$ all data)	$wR_2 = 0.1542$
$R(F$ obsd data)	$R_1 = 0.0574$
Goodness-of-fit on F^2	1.017
Observed data [$I > 2\sigma\ (I)$]	4642
Largest and mean shift/s.u.	0.001 and 0.000
Largest diff. peak and hole	1.024 and −0.516 e/Å^3

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

$R_1 = \Sigma\ ||F_o|-|F_c||/\Sigma\ |F_o|$

methyl substituents which are replaced by two ethyl groups [11], the first studies involved an attempt to synthesize the dihydroxo manganese(IV) complex of the Et$_2$EBC ligand, [Mn(Et$_2$EBC)(OH)$_2$](PF$_6$)$_2$, following the procedure used to make [Mn(Me$_2$EBC)(OH)$_2$](PF$_6$)$_2$. A red–purple solution was generated upon adding oxidant, suggesting the formation of the desired manganese(IV) species. However, the X-ray structure of this product and the elemental analysis showed that the two ethyl groups had been drastically altered. In fact, the compound isolated is [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)EBC}](PF$_6$)$_2$, in which one ethyl group was oxidized into a carboxyl group and the other into an ethoxy group and both functional groups had given up their protons and bonded to the central manganese(IV) atom. (see Fig. 1). The crystal data and structure refinement for [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)}EBC](PF$_6$)$_2$ are reported in Table 1 and selected bond distances and angles are summarized in Table 2.

Table 2 Selected bond lengths (Å) and angles (°) for [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)EBC}](PF$_6$)$_2$

Bond length(Å)	
Mn–O(2)	1.812(2)
Mn–O(1)	1.871(2)
Mn–N(3)	2.029(3)
Mn–N(4)	2.043(3)
Mn–N(2)	2.049(3)
Mn–N(1)	2.068(3)
Bond angle(°)	
O(2)-Mn–O(1)	94.64(11)
O(2)-Mn–N(3)	92.09(11)
O(1)-Mn–N(3)	173.26(11)
O(2)-Mn–N(4)	92.61(11)
O(1)-Mn–N(4)	85.26(11)
N(3)-Mn–N(4)	94.01(11)
O(2)-Mn–N(2)	85.68(11)
O(1)-Mn–N(2)	93.56(11)
N(3)-Mn–N(2)	87.37(11)
N(4)-Mn–N(2)	177.84(11)
O(2)-Mn–N(1)	177.93(11)
O(1)-Mn–N(1)	87.31(11)
N(3)-Mn–N(1)	85.97(11)
N(4)-Mn–N(1)	88.25(11)
N(2)-Mn–N(1)	93.50(11)

Because both of the substituents, –CH$_2$CH$_2$O$^-$ and –CH$_2$CO$_2^-$ are ligated to the Mn^{IV} ion in [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)}EBC](PF$_6$)$_2$, this central metal ion is deeply engulfed within the ligand cavity compared with the Mn^{IV} ion in [Mn(Et$_2$EBC)(OH)$_2$](PF$_6$)$_2$, as shown by the N–Mn bond lengths (2.068(3), 2.049(3), 2.043(3) and 2.029(3) Å) and the N–Mn–N bond angles of 177.84(11)° and 85.97°. For comparison, the corresponding values for [Mn(Et$_2$EBC)(OH)$_2$](PF$_6$)$_2$[11] are Mn–N bond lengths of 2.143(2), 2.141(2), 2.091(2) and 2.075(2) Å and N–Mn–N bond angles of 175.42(7)° and 84.17(9)°. The Mn-OH bonds in the manganese(IV) complex, [Mn(Et$_2$EBC)(OH)$_2$](PF$_6$)$_2$, whose values are 1.803(2) and 1.810(2) Å, are in contrast with the Mn–O bond lengths found for [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)}EBC](PF$_6$)$_2$. Whereas the Mn–O bond length in the Mn–OCH$_2$CH$_2$ group (1.812(2) Å) is similar to the Mn^{IV}–OH bond, indicating that swapping a proton for a CH$_2$CH$_2$ group does not greatly change the properties of the Mn^{IV}–O bond, the Mn^{IV}–O bond to the carboxylato function (1.871(2) Å) is much longer than that of Mn^{IV}–OH bond, showing the electron withdrawing influence of the C=O group, which results in the lengthening of the corresponding Mn^{IV}–O bond and indicating a decrease in Mn–O bond order.

Electrochemically, the newly synthesized complex [Mn(Et$_2$EBC)(OH)$_2$](PF$_6$)$_2$ demonstrated a gentle oxidizing power with redox potential of +0.556 V (vs SHE) for the Mn^{4+}/Mn^{3+} couple This redox potential appears at a lower voltage than that of the Mn^{4+}/Mn^{3+} couple in [Mn(Me$_2$EBC)(OH)$_2$](PF$_6$)$_2$ (+0.756 V), suggesting that the oxidation of the ethyl group may not be caused by the supposed high oxidizing power of the manganese(IV) ion [1]. On the other hand, this manganese(IV) complex of Et$_2$EBC displayed a reversible Mn^{5+}/Mn^{4+} couple having relatively low redox potential (+0.868 V) which, however, is more positive than the Mn^{4+}/Mn^{3+} couple of [Mn(Me$_2$EBC)(OH)$_2$](PF$_6$)$_2$. Further, the Mn^{5+}/Mn^{4+} couple of [Mn(Me$_2$EBC)(OH)$_2$](PF$_6$)$_2$, with a redox potential of +1.013 V[11], gave a weak signal and was obviously irreversible. These numbers reveal the possibility that disproportionation of [Mn(Et$_2$EBC)(OH)$_2$]$^{2+}$ might facilitate the ethyl group oxidation via the familiar rebound mechanism often invoked for Mn(V) and high valent iron complexes. Interestingly, although the redox potentials for both of the Mn^{4+}/Mn^{3+} couple and Mn^{5+}/Mn^{4+} couple in [Mn(Et$_2$EBC)(OH)$_2$]$^{2+}$ are lower than those of [Mn(Me$_2$EBC)(OH)$_2$]$^{2+}$, its redox potential for the Mn^{3+}/Mn^{2+} couple (−0.201 V) was much higher than that of [Mn(Me$_2$EBC)(OH)$_2$]$^{2+}$ (−0.696 V) (Figs. 2, 3).

Because [Mn(Et$_2$EBC)(OH)$_2$]$^{2+}$ and [Mn(Me$_2$EBC)(OH)$_2$]$^{2+}$ have very similar structures and, the redox potential of the Mn^{4+}/Mn^{3+} couple is lower for [Mn(Et$_2$EBC)(OH)$_2$]$^{2+}$ than for [Mn(Me$_2$EBC)(OH)$_2$]$^{2+}$ (+0.556 V vs. +0.756 V), one might expect [Mn(Me$_2$EBC)(OH)$_2$]$^{2+}$ to be more reactive than [Mn(Et$_2$EBC)(OH)$_2$]$^{2+}$. It follows that the 'ethyl complex' would seem less likely to undergo self destruction. However, under identically conditions at room temperature, the reaction of Mn^{II}(Me$_2$EBC)Cl$_2$ with aqueous H$_2$O$_2$ generates [Mn(Me$_2$EBC)(OH)$_2$](PF$_6$)$_2$ quantitatively, whereas the corresponding reaction with Mn^{II}(Et$_2$EBC)Cl$_2$ produces high yields of [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)EBC}](PF$_6$)$_2$ with profoundly transformed ethyl groups. The chemical reactions responsible for conversion of the ethyl groups can not be attributed to a radical process, such as attack by ·OH or ·OOH, because such reagents should attack the
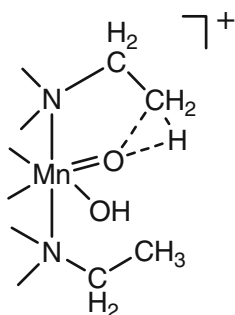
Fig. 3 The assumed 6-membered cyclic transition state for oxygen insertion to C–H bond by Mn^{IV}–OOH moiety
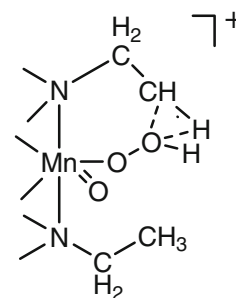
methyl groups on the Me$_2$EBC ligand, as well as other structural components of both complexes. Such random attacks do not occur in these R$_2$EBC systems.

Thus, a different kind of mechanism must facilitate the process by which hydrogen peroxide converts the ethyl substituents of the Mn/Et$_2$EBC complex into chelated ethoxo and methylene carboxylato functions and, based on mass spectral results, even into another intermediate product, the corresponding aldehyde. Further, if there is not something special about the role of the ethyl group in promoting this reaction, then coordinated hydrogen peroxide molecules should be activated equally by the methyl and ethyl derivatives to perform oxidations by the usual catalytic mechanisms. This latter consideration is especially true if a second order reaction were involved between two molecules of the activated complex, one molecule activating the oxidant (H$_2$O$_2$) and the second molecule serving as the substrate. The much studied *rebound mechanism* is an obvious pathway for such a process. As was the case for a radical process, a second order rebound mechanism involving activation by electron extraction or hydrogen abstraction from a C–H bond is equally unlikely for both the dimethyl complex and the diethyl derivatives, since neither compound abstracts hydrogen atoms from substrates with BDEs greater than 80 kcal/mol.

The mechanism operating in this system displays an interesting selectivity; the usual reactivities are reversed. Consider the C–H bonds of the ethyl group. Those of its methyl group are substantially stronger, by 5 or 6 kcal/mol, than those of its methylene group [12]. An obvious possibility is that a regioselective attack is involved and the reaction occurs because of orientation relationships.

On that basis, there remain at least two possibilities for the selective reactions of the ethyl groups in the Et$_2$EBC ligand. One is the reaction of the ethyl group with its own Mn^{IV}–OH moiety after the formation of [Mn(Et$_2$EBC)(OH)$_2$]$^{2+}$. As stated earlier, in the most stable state, the two ethyl substituents would orientate their methyl groups far away from the two Mn^{IV}–OH functions as is true in the crystal structure, but the free rotation of the N–C bond in –NCH$_2$CH$_3$ group, allows the methyl part of the

Fig. 2 Possible 5-membered cyclic transition state for oxygen insertion into C–H bond by Mn^{IV}=O

ethyl group to approach close to the Mn^{IV}–OH moiety, and such an orientation could generate a 5-membered ring at the transition state. This makes oxygen insertion into a C–H bond of $NCH_2C(–H)H_2$ by an Mn^{IV}–OH or Mn^V–OH moiety appear reasonable, at least in simple terms. Such an alternative is arguably more likely than a process confronting the high BDE_{CH} value of the methyl group in $NCH_2C(–H)H_2$ (above 100 kcal/mol). The relatively low oxidizing power of $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ (+0.556 V) argues against hydrogen abstraction from the $NCH_2C(–H)H_2$ substituent. On the other hand, since the ethyl group is bound to the nitrogen atom in the ligand, it has been highly organized and oriented in a way similar to that of substrates in the case of some enzymatic reactions [13]. The very weak driving force for hydrogen abstraction may be amplified by the precisely oriented ethyl group in the Et_2EBC ligand. Such highly favorable orientation between potential reactants is equivalent to very high concentrations of those reactants; the oxygen of the Mn^{IV}–OH moiety and the C–H of the methyl group. Would this facilitate the familiar rebound mechanism of Mn=O groups? Possibly, but a serious argument against such a rebound mechanism can be based on the spontaneous stoichiometric degradation of both of these complexes in base.

When $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ undergoes self-degradation in strong base, it reproducibly generates ∼88% yield of the corresponding $Mn^{III}(Me_2EBC)$ complex and a little damaged ligand is observed by mass spectrometry (the mass spectrum below m/z = 300 showed damaged free ligand and that above m/z = 600, traces of a dimer) [1]. In contrast, when $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ is treated with strong base, its mass spectrum shows neither obvious *trash peaks* attributable to damaged ligand below m/z = 300 nor dimer *trash peaks* above m/z = 400 (m/z = 282 for free Et_2EBC). The dominant mass peak appears at m/z = 371.2, corresponding to the reduced complex $Mn^{III}(Et_2EBC)(OH)_2^+$, containing unaltered ligand. If an ethyl group in the coordinated Et_2EBC ligand had been converted to a chelated ethoxide group, the dominant mass peak would have appeared at m/z = 369.2, corresponding to $[Mn^{III}\{(^-OCH_2CH_2)(CH_3CH_2)EBC\}(OH)]^+$. In fact the mass peak observed at 369.2 was very weak, supporting the conclusion that the self-destruction of the ethyl groups by Mn^{IV}–OH or Mn^{IV}=O does not occur upon exposure of $Mn^{IV}(Et_2EBC)(OH)_2^{2+}$, to strong base. That is $[Mn(Et_2EBC)(OH)_2](PF_6)_2$ alone is incapable of attacking the methyl group on its own ligand, even under its most reactive conditions. Further, these observations support the conclusion that the disproportionation of the Mn(IV) complex into its trivalent and pentavalent counterparts followed by oxidation of an ethyl group by the rebound mechanism is unlikely.

The second possible mechanism for the destruction of ethyl substituents in manganese coordinated Et_2EBC assumes that the catalytically active intermediate is the hydrogen peroxide adduct of the manganese(IV)/Et_2EBC complex, $Mn^{IV}(Et_2EBC)(O)(OOH)^+$. The insertion of oxygen into a C–H bond of the $NCH_2C(–H)H_2$ group by Mn^{IV}–OOH is easily justified via formation of a 6-membered ring intermediate. Such an oxygen insertion process has been well documented in hydroxylation of substrates by the Fe^{III}–OOH group in P450 enzymes and their models [13–23]. The self-destruction of the porphyrin ligand to form *meso*-hydroxyheme through oxygen insertion by Fe^{III}–OOH in P450 enzymes has also been widely accepted for the heme hydroxylation process [24–26]. Although the presence of $Mn^{IV}(Et_2EBC)(O)(OOH)^+$ cannot be verified by mass spectral detection due to its high reactivity, its sibling H_2O_2 complex, $Mn^{IV}(Me_2EBC)(O)(OOH)^+$, has been detected in these laboratories when investigating the olefin epoxidation mechanism catalyzed by $Mn^{II}(Me_2EBC)Cl_2$ [7]. The fortuitous locations of substrate, an ethyl group, and oxidant, ligated H_2O_2, so that the configuration of an appropriate transition state is highly favored appears to be responsible for the oxygen insertion into a C–H bond of an otherwise relatively unreactive methyl component of an ethyl substituent, all of this built into the structure of $Mn^{IV}(Et_2EBC)(OH)(OOH)^{2+}$. These considerations led us to the conclusion that insertion, not hydrogen atom abstraction must be involved.

Detailed investigations of the destruction of ethyl substituents in the Et_2EBC ligand by mass spectral determinations was conducted using H_2O_2 to oxidize $Mn^{II}(Et_2EBC)(PF_6)_2$ in aqueous solution at room temperature. Before oxidation, the original chloride counter ion was removed by reaction with $AgPF_6$ in acetone. A series of the intermediate products during the oxidative attack on the ethyl groups was detected by mass spectroscopy, and confirmed by accurate mass measurements [11]. The $Mn^{II}(Et_2EBC)^{2+}$ was first oxidized to $Mn^{IV}(Et_2EBC)(OH)(O)^+$ (m/z = 370.2), then to $[Mn^{IV}\{(^-OCH_2CH_2)(CH_3CH_2)EBC\}(O)]^+$ (m/z = 368.2) in which an alcoholate group is coordinated to the Mn^{IV} ion. This is followed by formation of $[Mn^{IV}\{(OHCCH_2)(CH_3CH_2)EBC\}(OH)(O)]^+$ (m/z = 384.2), where the aldehyde group is not coordinated to the Mn^{IV} ion. The last step in the ethyl group conversion produces a carboxylate methylene functional group, $[Mn^{IV}\{(^-O_2CCH_2)(CH3CH_2)EBC\}(O)]^+$ (m/z = 382.2) with the carboxylate anion ligating to the Mn^{IV} ion. This sequence of 2-electron processes provides strong support for the conclusion that the hydrogen peroxide inserts an oxygen atom into a C–H linkage in these reactions. In these studies, the oxidation process then moves to the second ethyl group, converting it into a coordinated ethanolato

Fig. 4 The possible destruction process of ethyl group in Mn(Et$_2$EBC) complex by oxidation
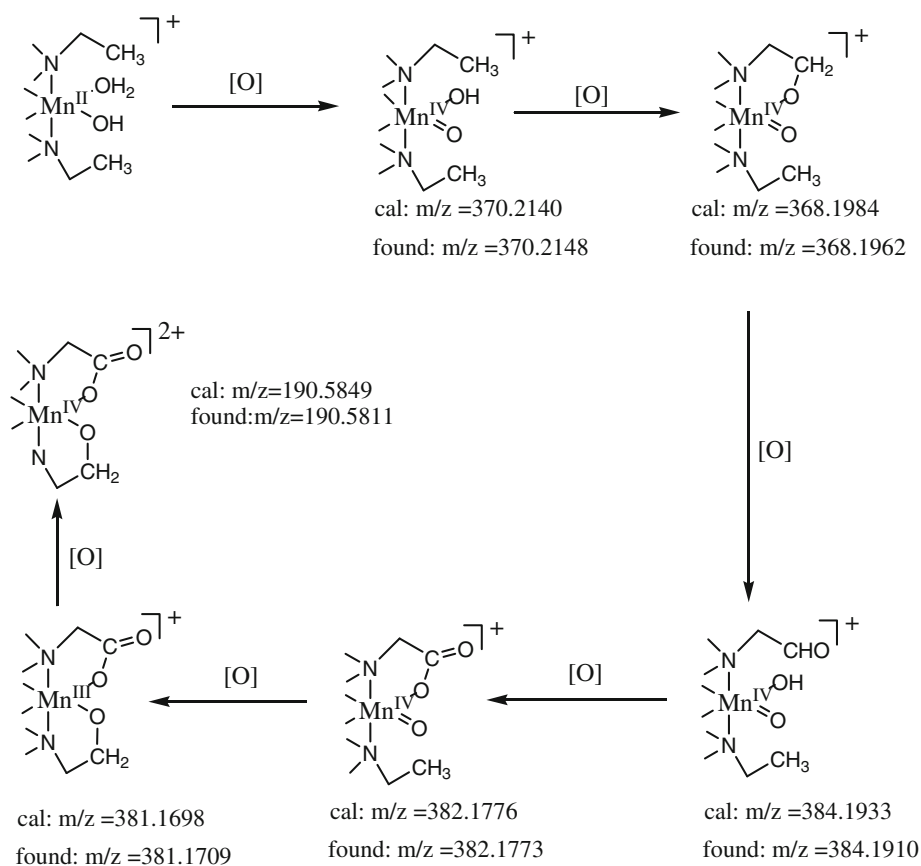
function, [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)EBC}]$^{2+}$ (m/z = 381.2) in which both of the carboxylate and alcoholate are bound to the Mn^{IV} ion. At this point the central metal ion is coordinatively saturated by the newly formed hexadentate ligand, apparently terminating the process by inhibiting formation of the hydrogen peroxide complex. Also, it should be pointed out that some of the corresponding manganese(III) species have been detected, including [Mn^{III}{($^-$OCH$_2$CH$_2$)(CH$_3$CH$_2$)EBC}(OH)]$^+$ (m/z = 369.2) and [Mn^{III}{($^-$O$_2$CCH$_2$)(CH$_3$CH$_2$)EBC}OH)]$^+$ (m/z = 383.2).

In order to confirm the assumption that Mn^{IV}–OOH is involved in oxygen insertion into the C–H bonds of ethyl groups, [18] O isotope labeling experiments were applied to the oxidation of Mn^{II}(Et$_2$EBC)$^{2+}$ using aqueous 2% H$_2^{18}$O$_2$ (90% atom enrichment). The mass peak patterns for the corresponding well defined oxidation intermediates apparently shifted two mass units when using the H$_2^{18}$O$_2$ oxidant, however, the accurate mass did not provide the desired precise support for the ^{18}O insertion into the C–H bond of the Et$_2$EBC ligand by the Mn^{IV}–^{18}O^{18}OH moiety,. The key intermediate to establish oxygen insertion by Mn^{IV}–OOH is the first oxygen atom insertion product, [Mn^{IV}{($^-$OCH$_2$CH$_2$)(CH$_3$CH$_2$)EBC}(O)]$^+$ (m/z = 368.2), because the water solvent cannot exchange oxygen rapidly

with the chelated ethoxy group, –OCH$_2$CH$_2$– If the Mn^{IV}–^{18}O^{18}OH group inserts a peroxide oxygen atom into a C–H bond, the product would be [Mn^{IV}{(^{18}OCH$_2$CH$_2$)(CH$_3$CH$_2$)EBC}(^{16}O)]$^+$ having an accurate mass of m/z = 370.2027. The experimental result is 370.1285. Thus, although the isotope labeling experiment may qualitatively support oxygen insertion by Mn^{IV}–OOH, the result is not conclusive Fig. 4.

Conclusions

The oxidation chemistry of a new family of manganese complexes with the cross-bridged cyclam ligand, Et$_2$EBC, has been investigated using aqueous H$_2$O$_2$ as oxidant. Unlike its relatively unreactive methyl substituted sibling, Mn^{II}(Me$_2$EBC)Cl$_2$, the ethyl derivative, Mn^{II}(Et$_2$EBC)Cl$_2$, is easily oxidized by aqueous H$_2$O$_2$ at temperatures above 0 °C, forming the colorful manganese(IV) complex of a new hexadentate ligand, [Mn^{IV}{($^-$OCH$_2$CH$_2$)($^-$O$_2$CCH$_2$)EBC}](PF$_6$)$_2$. Mn^{II}(Et$_2$EBC)Cl$_2$ can also be oxidized to [Mn^{III}(Et$_2$EBC)(OH)(Cl)]PF$_6$ at −30 °C. In order to make [Mn(Et$_2$EBC)(OH)$_2$](PF$_6$)$_2$, it is essential to remove the chloride by AgPF$_6$ prior to oxidation by H$_2$O$_2$ at −30 °C.

Otherwise the ethyl groups of the ligand also undergo oxidation. The results of detailed study of the oxidation by H_2O_2 of the ethyl groups of the Et_2EBC ligand in its manganese complex attribute the self-oxidation to oxygen insertion into a C–H bond of the CH_3 group in the ethyl substituent. The active intermediate is believed to proceed via a 6-membered ring involving the Mn^{IV}–OO oxidizing group and an NCH_2CH_3 atomic group belonging to the Et_2EBC ligand of the same manganese atom. The unique chemistry occurs because of the facilitative orientation of the two reacting components of the complex ion. Isotopic labeling experiments using $H_2^{18}O_2$ as the oxidant provides only limited support of this assumption because, while the mass peak patterns of the related oxidation intermediates did shift by ~ 2 mass units, the accurate mass determinations did not match the expected value with the required precision.

Supporting information available

Detailed crystal structure data and the infrared and UV–Vis spectra for the carboxy ethoxy complex, $[Mn^{IV}\{(^-OCH_2CH_2)(^-O_2CCH_2)EBC\}](PF_6)_2$.

References

1. Yin, G., McCormick, J.M., Buchalova, M., Danby, A.M., Rodgers, K., Smith, K., Perkins, C., Kitko, D., Carter, J., Scheper, W.M., Busch, D.H.: Synthesis, characterization, and solution properties of a novel cross-bridged cyclam manganese(IV) complex having two terminal hydroxo ligands. Inorg Chem **45**, 8052–8061 (2006)
2. Ferreira, K.N., Iverson, T.M., Maghlaoui, K., Barber, J., Iwata, S.: Architecture of the photosynthetic oxygen-evolving center. Science **303**, 1831–1838 (2004)
3. Tommos, C., Babcock, G.T.: Oxygen production in nature: a light-driven metalloradical enzyme process. Acc. Chem. Res. **31**, 18–25 (1998)
4. Vrettos, J.S., Brudvig, G.W.: Oxygen evolution. In: Comprehensive coordination chemistry II. **8**, 507–547 (2004)
5. Pecoraro, V.L., Baldwin, M.J., Caudle, M.T., Hsieh, W., Law, N.A.: A proposal for water oxidation in photosystem II. Pure Appl. Chem. **70**, 925–929 (1998)
6. Yin, G., Buchalova, M., Danby, A.M., Perkins, C.M., David Kitko, D., Carter, J., Scheper, W.M., Busch, D.H.: Olefin oxygenation by the hydroperoxide adduct of a nonheme manganese(IV) complex: epoxidations by a metallo-peracid produces gentle selective oxidations. J. Am. Chem. Soc. **127**, 17170–17171 (2005)
7. Yin, G., Buchalova, M., Danby, A.M., Perkins, C.M., David Kitko, D., Carter, J., Scheper, W.M., Busch, D.H.: Olefin epoxidation by the hydrogen peroxide adduct of a novel non-heme mangangesi(IV) complex: demonstration of oxygen transfer by multiple mechanisms. Inorg. Chem **45**, 3467–3474 (2006)
8. Yin, G., Danby, A.M., Kitko, D., Carter, J.D., Scheper, W.M., Busch, D.H.: Understanding the selectivity of a moderate oxidation catalyst: hydrogen abstraction by a fully characterized, activated catalyst, the robust dihydroxo manganese(IV) complex of a bridged cyclam. J. Am. Chem. Soc. **129**, 1512–1513 (2007)
9. Busch, D.H.; Collinson, S.R.; Hubin, T.J.; Labeque, R.; Williams, B.K.; Johnston, J.P.; Kitko, D.J.; St. Laurent, J.C.T.R.B.; Perkins, C.M. Bleach compositions containing metal bleach catalyst for detergents. WO 98/39406
10. Busch, D.H.; Collinson, S.R.; Hubin, T.J. Catalysts and methods for catalytic oxidation. WO98/39098, 1998
11. Yin, G.; Danby, A.M.; Day, V.R; Roy, S.B.; Carter, J.; Scheper, W.M.; Busch, D.H.: Similarities and differences in properties and behavior of two H2O2-activated manganese catalysts having structures differing only by methyl and ethyl substituents. J. Coordinat. Chem. **2011**, 64(1), 4-17, 40th Anniversary Issue
12. Yu-LRan, Liu.: Bond dissociation energies in organic compounds. CRC Press, Boca Raton, FL (2003)
13. Frey, P.A., Hegeman, A.D.: Enzymatic reaction mechanisms. Oxford University Press, New York (2007)
14. Vaz, D.N., McGinnity, D.F., Coon, M.J.: Epoxidation of olefins by cytochrome P450: evidence from site-specific mutagenesis for hydroperoxo-iron as an electrophilic oxidant. Proc. Natl. Acad. Sci. USA **95**, 3555–3560 (1998)
15. Newcomb, M., Aebisher, D., Shen, R., Chandrasena, R.E.P., Hollenberg, P.F., Coon, M.J.: Kinetic isotope effects implicate two electrophilic oxidants in cytochrome P450-catalyzed hydroxylations. J. Am. Chem. Soc. **125**, 6064–6065 (2003)
16. Toy, P.H., Newcomb, M., Coon, M.J., Vaz, A.D.N.: Two distinct electrophilic oxidants effect hydroxylation in cytochrome P-450-catalyzed reactions. J. Am. Chem. Soc. **120**, 9718–9719 (1998)
17. Bach, R.D., Su, M.D., Andres, J.L., Schlegel, H.B.: Structure and reactivity of diamidoiron(III) hydroperoxide. The mechanism of oxygen-atom transfer to ammonia. J. Am. Chem. Soc. **115**, 8763–8769 (1993)
18. Nam, W., Ho, R., Valentine, J.S.: Iron-cyclam complexes as catalysts for the epoxidation of olefins by 30% aqueous hydrogen peroxide in acetonitrile and methanol. J. Am. Chem. Soc. **113**, 7052–7054 (1991)
19. Sam, J.W., Tang, X.J., Peisach, J.: Electrospray mass spectrometry of iron bleomycin: demonstration that activated bleomycin is a ferric peroxide complex. J. Am. Chem. Soc. **116**, 5250–5256 (1994)
20. Ho, R.Y.N., Roelfes, G., Feringa, B.L., Que Jr., L.: Raman evidence for a weakened O−O bond in mononuclear low-spin iron(III)−hydroperoxidesJ. Am. Chem. Soc. **121**, 264–265 (1999)
21. Nam, W., Lim, M.H., Lee, H.J., Kim, C.: Evidence for the participation of two distinct reactive intermediates in iron(III) porphyrin complex-catalyzed epoxidation reactions. J. Am. Chem. Soc. **122**, 6641–6647 (2000)
22. Wadhwani, P., Mukherjee, M., Bandyopadhyay, D.: The prime reactive intermediate in the iron(III) porphyrin complex catalyzed oxidation reactions by tert-butyl hydroperoxide. J. Am. Chem. Soc. **123**, 12430–12431 (2001)
23. Kim, C., Chen, K., Kim, J., Que Jr., L.: Stereospecific alkane hydroxylation with H_2O_2 catalyzed by an iron(II)−tris(2-pyridylmethyl)amine complex. J. Am. Chem. Soc. **119**, 5964–5965 (1997)
24. Sano, S., Sano, T., Morishima, I., Shiro, Y., Maeda, Y.: On the mechanism of the chemical and enzymic oxygenations of

α-oxyprotohemin IX to Fe-biliverdin IXα. Proc. Natl. Acad. Sci. USA **83**, 531–535 (1986)

25. Ortiz de Montellano, P.R.: Heme oxygenase mechanism: evidence for an electrophilic, ferric peroxide species. Acc. Chem. Res. **31**, 543–549 (1998)

26. Avila, L., Huang, H., Damaso, C.O., Lu, S., Moënne-Loccoz, P., Rivera, M.: Coupled oxidation vs. heme oxygenation: insights from axial ligand mutants of mitochondrial cytochrome *b5*. J. Am. Chem. Soc. **125**, 4103 (2003)