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# Efficient oxidation of benzylic and aliphatic alcohols using a bioinspired, cross-bridged cyclam manganese complex with H<sub>2</sub>O<sub>2</sub>

Zhan Zhang,<sup>[a]</sup> Lhoussain Khrouz,<sup>[b]</sup> Guochuan Yin,<sup>[c]</sup> and Bruno Andrioletti \*<sup>[a]</sup>

**Abstract:** The cross-bridged cyclam manganese complex  $Mn(Me_2EBC)Cl_2$  efficiently catalyzes the oxidation of benzylic and aliphatic alcohols at pH 3 in a mixture of acetonitrile and water at room temperature. The environmentally benign and high oxygen content oxidant  $H_2O_2$  was adopted. Conversions of the alcohols to the corresponding carbonyl compounds reached 98% with good to excellent selectivity. In addition, several lignin model compounds were also catalytically oxidized under these conditions, with excellent conversion (up to 96%) and selectivity (up to 99%).

### Introduction

The oxidation of alcohols is an important transformation in organic synthesis that can be achieved by various methods such as chromium-based oxidation, TPAP or Swern oxidations or using periodiane derivatives as the resulting products (aldehydes, carboxylic acids or ketones) are key intermediates for the chemical industry.<sup>[1,2]</sup> However, most of the aforementioned transformations display a very poor environmental impact because heavy and toxic metals and/or multi component systems are often used.

Conversely, metalloenzymes exhibit generally high efficiency and selectivity for some specific substrates under very mild conditions.<sup>[3]</sup> As the development of sustainable oxidation conditions remain highly challenging,<sup>[4]</sup> substantial efforts have been made to develop biomimetic oxidation reactions, using environmentally benign metals (e.g. manganese and iron) and oxidants (e.g. dioxygen and hydrogen peroxide). Consequently, a large variety of bio-inspired catalysts have been synthesized and applied for the catalytic oxidation of alcohols during the past decades. Hence, Sekino et al.<sup>[5]</sup> reported that a  $\mu$ -peroxo diiron(IV) complex generated in situ from  $[Fe_2(L^{Ph4})(O_2)(Ph_3CCO_2)]^{2+}$  (Figure 1. a,  $L^{Ph4} = N, N, N', N'$ tetrakis(1-methyl-2-phenyl-4-imidazolyl)methyl-1,3-diamino-2propanolate) with a dinucleating ligand could catalyze the oxidation of benzyl alcohol with dioxygen. Similarly, Nam et al. investigated the oxidation of benzyl alcohol by oxoiron(IV) complexes based on non-haem ligands such as N<sub>4</sub>Py (Figure 1. b) and TPA (Figure 1, c) and revealed detailed mechanistic insights.<sup>[6]</sup> The Fe-TAML iron complex (Figure 1. d, TAML) was

 [a] Univ Lyon, Université Claude Bernard Lyon 1, ICBMS-UMR 5246, Campus Lyon-Tech la Doua, Bât. Curien/CPE, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne, France. E-mail: <u>bruno.andrioletti@univ-lyon1.fr</u> http://www.icbms.fr/casyen/research/andrioletti

 [b] Univ Lyon, Ecole Normale Supérieure de Lyon, Laboratoire de Chimie, UMR-CNRS 5182, 46 allée d'Italie, 69364 Lyon 07, France.

[c] School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China; Key laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, PR China. Supporting information for this article is given via a link at the end of

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proven very efficient for the catalytic oxidation of benzyl alcohols, and for some lignin model compounds, in the presence of (diacetoxyiodo)benzene.<sup>[7]</sup> With biomimetic manganese-based catalysts, Shen *et al.* reported that the complex Mn(S-PMB)(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (Figure 1. e, S-PMB) efficiently oxidizes a large range of secondary alcohols to the corresponding ketones with hydrogen peroxide in the presence of acetic acid.<sup>[7]</sup> A manganese complex based on the BQEN ligand (Figure 1. f), was also proven to efficiently promote the oxidation of alcohols with peracetic acid as the oxidant.<sup>[9]</sup> The catalytic oxidation of alcohols by other non-haem complexes was also investigated.<sup>[10]</sup>



Figure 1. Examples of bio-inspired ligands used for the catalytic oxidation of alcohols.

During the course of our studies on the development of environmentally benign oxidation of alcohols, we selected the manganese(II) complex containing a cross-bridged cyclam ligand  $Mn(Me_2EBC)Cl_2$  (Figure 2), which had been fully characterized previously<sup>[11]</sup> and used for hydrogen abstraction,<sup>[12]</sup> oxygen transfer,<sup>[13]</sup> C-H bond activation<sup>[14]</sup> and some other applications.<sup>[15]</sup> Herein, we disclose that  $Mn(Me_2EBC)Cl_2$  efficiently catalyzes the oxidation of a series of benzylic and aliphatic alcohols (including lignin model compounds) with 35%  $H_2O_{2(aq)}$  as a green oxidant at pH= 3 in a mixture of acetonitrile and water at room temperature.



Figure 2. Structure of cross-bridged cyclam  $\mathsf{Me}_2\mathsf{EBC}$  and the corresponding manganese(II) complex.

### **Results and Discussion**

Veratryl alcohol being a common model substrate for studying the oxidative degradation of lignin,<sup>[16]</sup> it was chosen for determining the optimal conditions, using Mn(Me<sub>2</sub>EBC)Cl<sub>2</sub> as the catalyst and

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 $\rm H_2O_2$  as the oxidant at different pH values (Table 1). In agreement with preliminary observations,  $^{[8\cdot9,\ 17]}$  we found that at pH 1, 2 or 3, the conversion of veratryl alcohol was quantitative affording the corresponding aldehyde and acid in up and to 80% and 12% yield, respectively, in the presence of 1 mol% of catalyst and 4 eq. of H\_2O\_2 in 4 hours (Table 1, entries 1–3). Conversely, at higher pH, the conversion dropped significantly to 51% at pH 4 and 22% at pH 5 (Table 1, entries 4-5). Therefore, we could infer that at pH > 3, the reactivity decreases. Due to the better selectivity observed at pH 3 and relatively milder conditions, we fixed the working pH at 3.

Table 1. Oxidation of veratryl alcohol with $Mn^{II}(Me_2EBC)CI_2$ and $H_2O_2$ at different pH.							
ОН	Mn(Me <sub>2</sub> EBC)Cl <sub>2</sub> 1 mol% H <sub>2</sub> O <sub>2</sub> 4 eq., 30 °C, 4 h						
Entry	рН	Conversion (%)	Yield of aldehyde (%) <sup>[a]</sup>	Yield of acid (%) <sup>[a]</sup>			
1 <sup>[b]</sup>	1	99	72	11			
2	2	98	70	12			
3	3	99	80	12			
4	4	51	47	0			
5	5	22	19	0			
6 <sup>[c]</sup>	3	98	83	9			
7 <sup>[d]</sup>	3	99	81	11			

[a] GC yields. Conditions: solvent CH<sub>3</sub>CN/ H<sub>2</sub>O: 5 mL (4:1), substrate 100 mM,  $Mn^{II}$ (Me<sub>2</sub>EBC)Cl<sub>2</sub> 1 mol%, H<sub>2</sub>O<sub>2</sub> 0.17 mL 4eq., 303 K, 4 h, pH: adjusted with HCI. [b] 3 h; [c] pH adjusted with H<sub>2</sub>SO<sub>4</sub>; [d] pH adjusted with HNO<sub>3</sub>.

In addition, we studied the influence of the chloride counter anion. Hence,  $H_2SO_4$  and  $HNO_3$  were also investigated for adjusting the working pH at 3. In the presence of  $H_2SO_4$  or  $HNO_3$ , both the conversions and the yields were similar to that determined in the presence of HCI (Table 1, entry 6 – 7). Accordingly, contrary to former reports from the literature revealing that the nature of the counter-anion could accelerate the alcohol oxidation,<sup>[8,10e,18]</sup> in our conditions, the nature of the counter anion (i.e. Cl<sup>-</sup> vs. HSO<sub>4</sub><sup>-</sup> or  $NO_3^-$ ) did not affect significantly the outcome of the reaction.

Next, we investigated the effect of the catalytic charge and the optimal amount of  $H_2O_2$  at pH 3 at 30°C (Table 2). Firstly, a control experiment carried out with  $H_2O_2$  only confirmed that the manganese catalyst was crucial in the transformation (Table 2 entry 1). Entries 2 to 5 reveal that the conversions improve dramatically from 36 to 99% when increasing the amount of catalyst from 0.1 to 1 mol%. Hence, a minimum catalytic charge of 0.5 mol% appeared necessary for ensuring the efficient conversion of the substrate. On this basis, we also investigated the effect of the amount of oxidant (Table 2, entries 5 – 8). With 3 or 4 equivalents of  $H_2O_2$ , conversions were excellent, up to 99%.

By taking into account the efficiency, the selectivity and the costeffectiveness of the transformation, we selected the conditions used in the entry 4, namely 0.5 mol% of catalyst and 4 equivalents of oxidant as the best compromise.

Table 2. Oxidation of veratryl alcohol with different amounts of  $\mathsf{Mn}^{ll}(\mathsf{Me}_2\mathsf{EBC})\mathsf{Cl}_2$  and oxidant.

	OH	e <sub>2</sub> EBC)Cl <sub>2</sub> x mol eq., pH 3, 30 °C,	% 0 0		ОН
Entry	Amount of catalyst /mol%	Amount of H <sub>2</sub> O <sub>2</sub> / eq.	Conversion /%	Yield of aldehyde /% <sup>[a]</sup>	Yield of acid /% <sup>[a]</sup>
1	0	4	9	5	0
2	0.1	4	36	28	1
3	0.3	4	75	61	3
4	0.5	4	89	76	7
5	1	4	99	80	12
6	1	1	77	61	1
7	1	2	89	68	3
8	1	3	95	75	9

[a] GC yields. Conditions: solvent CH\_3CN/ H\_2O: 5 mL (4:1) substrate 100 mM, Mn<sup>II</sup>(Me\_2EBC)Cl\_2, H\_2O\_2, pH 3, 303 K, 4 h. pH adjusted with HCl.



Figure 3. Kinetics of the oxidation of veratryl alcohol with  $Mn^{II}(Me_2EBC)Cl_2$  in the presence of  $H_2O_2$ . Conditions: solvent  $CH_3CN$  and  $H_2O$  5 mL (4:1), substrate 100 mM,  $Mn^{II}(Me_2EBC)Cl_2$  0.5 mol%,  $H_2O_2$  0.17 mL, pH 3, 303 K, pH adjusted with HCI.

The effect of the reaction time was also investigated (Figure 3). When the reaction was run for 6 hours, the conversion went up to

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99% but at the expense of the selectivity. Indeed, upon running the reaction for an additional 2 hours (from 4 to 6 h), the selectivity went down from 9/1 to 5/1. Hence the quantity of aldehyde is maximized after 5 h before slowly decreasing upon oxidation to the corresponding acid.

In conclusion, this preliminary study reveals that the optimal conditions for oxidizing veratryl alcohol to the corresponding aldehyde involves the use of 0.5 mol% of catalyst, 4 equivalents of  $H_2O_2$  and a 5 h reaction at pH 3 and 303 K, knowing that the maximum conversion is reached after 6 h.

Table 3. Oxidation of different types of alcohols with  $Mn^{II}(Me_2EBC)CI_2$  and  $H_2O_2$ .

Mn(Me <sub>2</sub> EBC)Cl <sub>2</sub> 0.5/1 mol%								
alcohol pH 3, H <sub>2</sub> O <sub>2</sub> 4/8eq. 30 °C, 6/18 h								
En try	Substrate	Conv. (%)	Aldehyde or ketone	Y. (%) <sup>[a]</sup>	Acid	Y. (%) <sup>[a]</sup>		
1	ОН	98		77	ОН ОН	15		
2	Ъ-СУ-он	69	°-<>-^°	68 (79)	<i>р</i> -С, С, он	(6)		
		(86)		(13)				
3	ОН	73 (89)		69 (81)	OH O	(6)		
4	ОН	40 (78)		37 (59)	OH OH	(11)		
5	СНОН	42 (63)	$\mathbb{O}^{\downarrow_0}$	39 (63)				
6	OH C	(32)		(32)	Z			
7	,() <sub>6</sub> ,,,OH	(24)	,() <sub>6</sub> , <i>⊎</i> 0	(11)	-() <sub>6</sub> =0 OH	(12)		
8	ОН	(60)	$\bigcirc^{\circ}$	(60)				
9	CCC <sup>OH</sup>	100/ 100 <sup>[b]</sup>	ССОН	99/ 99 <sup>[b]</sup>				
10	OH H H	95/ 95 <sup>[b]</sup>	С	95/ 95 <sup>[b]</sup>				
11	COLO CH	58/ 96 <sup>[b,c]</sup>		56/ 95 <sup>[b,c]</sup>		F		
12	HO CON	98	Med CH CH	68	Med C C C C C C C C C C C C C C C C C C C	29		

[a] GC yields. Conditions: solvent CH<sub>3</sub>CN/ H<sub>2</sub>O: 5 mL (4:1) substrate 100 mM, Mn<sup>II</sup>(Me<sub>2</sub>EBC)Cl<sub>2</sub> 0.5 mol%, H<sub>2</sub>O<sub>2</sub> 0.17 mL 4eq., pH 3, 303 K, 6 h. [b] H<sub>2</sub>O<sub>2</sub> 0.34 mL 8 eq.; [c] Mn<sup>II</sup>(Me<sub>2</sub>EBC)Cl<sub>2</sub> 1 mol%; Data in brackets: 18 h.

On the basis of these preliminary studies, we investigated the effect of the substitution on the alcohol (Table 3). As expected, the electron richness of the alcohol seems to be the major parameter of the transformation. Indeed, if the veratryl alcohol was converted to the corresponding aldehyde and acid in 98% in 6 h (Table 3, entry 1), the *para*-methoxy benzyl alcohol lacking one -OMe group in comparison with the parent

compound could not be transformed to the corresponding aldehyde or acid in more than 86% conversion even after 18 h (Table 3, entry 2). The relative position of the substituent did not appear crucial either, as the *ortho*-methoxy benzyl alcohol analogue produced the corresponding aldehyde and acid in similar range (Table 3, entry 3). The benzyl alcohol was proven even less reactive as after 6 h the conversion remained in the 40% range and reached 78% after 18 h (Table 3, entry 4). However, this decent conversion was obtained at the expense of the selectivity as benzoic acid was produced in substantial amount.

When secondary benzylic alcohols were subjected to oxidation (Table 3, entries 5 - 6), the corresponding ketone was isolated in good yield (63%) in the case of the methyl ketone but a relatively long reaction time was proven necessary. However, the diphenylmethanol was more reluctant to oxidation, as the expected ketone was isolated in 32% yield, even after a prolonged reaction time (Table 3, entry 6). Similarly, aliphatic alcohol displaying a long alkyl chain such as 1-octanol (Table 3, entry 7) appeared little reactive under our conditions. Interestingly, cyclohexanol was converted much more efficiently and cyclohexanone was isolated in a decent 60% yield (Table 3, entry 8).

In contrast, very high conversions and selectivities were obtained with 1,2-cyclohexanediol (Table 3, entry 9) and 1,2diphenyl-ethane-1,2-diol (Table 3, entry 10). In the latter cases, the corresponding mono-ketones were obtained in guantitative yields. Interestingly, even in the presence of a larger excess of H<sub>2</sub>O<sub>2</sub> (8 equiv. vs. 4 equiv.) the mono-ketones were not oxidized further. This observation is in agreement with the former observation regarding the higher reactivity of electron rich alcohols. Hence, an excellent selectivity can be reached in the case of 1,2-diols. For this reason, we investigated the oxidation of lignin model compounds that could be of prime interest for understanding the reactivity of lignin. As in lignins, the  $\beta$ -O-4 moieties are the most abundant,<sup>[19]</sup> we decided to investigate a classical  $\beta$ -O-4 model (Table 3, entry 11). Using our optimized conditions, the desired ketone was isolated in a moderate 56% yield, but with an excellent selectivity. For this reason, we decide to harden the reaction conditions by doubling the amount of catalyst (1 mol%) and H<sub>2</sub>O<sub>2</sub> (8 equiv.). In these conditions, we were delighted to observe that in these conditions the conversion increased dramatically to 96% while maintaining an excellent selectivity (99%). Using the same conditions, we evaluated the reactivity of a  $\beta$ -1 lignin model compound (Table 3, entry 12). After 6 h, the conversion of the starting material was almost complete, but a mixture of mono-ketone and dione was isolated. The mono- and diketone were isolated in 68 and 29% yield, respectively. Interestingly though, no C-C bond cleavage was observed. These promising results suggest that the combination of Mn<sup>II</sup>(Me<sub>2</sub>EBC)Cl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> may constitute an alternative for the valorization of lignin, a bio-source of aromatic compounds.[19b]

In order to gain some insights on the mechanism of the reaction, we first investigated the possible presence of radical intermediates. As *t*-BuOH is an acknowledged radical scavenger,<sup>[20]</sup> we decided to perform the oxidation of veratryl

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alcohol in a *t*-BuOH/H<sub>2</sub>O (4:1) solvent mixture. In these solvent conditions, veratryl alcohol was converted in 67% and afforded veratraldehyde in 65% yield. Hence, this result accounts for a mechanism precluding the presence of hydroxyl radicals.<sup>[15, 20]</sup>

Alternatively, we confirmed the absence of hydroxyl radical intermediates using EPR measurements (see Supporting Information Section). Knowing that DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) traps radicals affording a DMPO radical adduct (that displays a typical four-line EPR spectra)<sup>[12, 21]</sup> we added DMPO to our experimental conditions and followed the reaction using EPR. However, upon adding H<sub>2</sub>O<sub>2</sub> to a solution of Mn(Me<sub>2</sub>EBC)Cl<sub>2</sub> and DMPO at pH 3, only the EPR signal of residual Mn(II) (g~2  $a_{Mn}$ ~90G), was visible.<sup>[22]</sup> Hence, this observation confirmed the absence of hydroxyl radicals in our reaction conditions.

After excluding a radical-mediated oxidation, we investigated the possibility that a highly oxidized Mn species was responsible for the catalytic performance. To this end we synthesized the pure Mn<sup>IV</sup>(Me<sub>2</sub>EBC)(OH)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> metallocomplex from Mn(Me<sub>2</sub>EBC)Cl<sub>2</sub> using a known procedure.<sup>[23]</sup> In the absence of any oxidant, veratryl alcohol was oxidized rather efficiently by a stoichiometric amount of the manganese(IV) complex as the expected aldehyde and acid were isolated in 22 and 7% yield, respectively with a conversion of 40%. This result demonstrates that  $Mn^{V}(Me_2EBC)(OH)_2(PF_6)_2$  is able to oxidize veratryl alcohol even in the absence of any oxidant. Hence, in the presence of H2O2 at Mn(Me<sub>2</sub>EBC)Cl<sub>2</sub> is oxidized bН 3. generating Mn<sup>IV</sup>(Me<sub>2</sub>EBC)(OH)<sub>2</sub><sup>2+</sup>. Next, the Mn<sup>IV</sup> intermediate can directly oxidize a molecule of alcohol through hydrogen atom abstraction or through or the transfer of a hydroxyl as already observed in the literature.<sup>[22a, 24]</sup>.

### Conclusions

In conclusion, we have developed an efficient catalytic system from a bioinspired manganese(II) complex Mn(Me<sub>2</sub>EBC)Cl<sub>2</sub> and an environmentally benign oxidant H<sub>2</sub>O<sub>2</sub> at pH 3. This new catalytic system displays a high efficiency for the oxidation of a variety of benzylic alcohols and some aliphatic alcohols. More interestingly, it was proven very powerful for the oxidation of lignin model compounds. In particular,  $\beta$ -O-4 lignin model molecule was converted almost quantitatively to the corresponding ketone without C-C bond cleavage. In addition, a mixture of H<sub>2</sub>O and MeCN was used at the expense of acetone and advantageously precluded the possible oxidation of acetone with H<sub>2</sub>O<sub>2</sub>. Substrates displaying electron enriched alcohols were proven more reactive and allowed obtaining high selectivities for the oxidation of unsymmetrical 1,2-diols. At last, we have proven that the oxidation process does not involve any radical and most likely relies on a high valent manganese(IV) complex. Additional investigations are currently underway in our Laboratory in order to totally ascertain the mechanism of oxidation.

### **Experimental Section**

 $\begin{array}{lll} Mn(Me_2EBC)CI_2 \text{ was kindly provided by Prof. Guochuan Yin. The corresponding manganese(IV) compound, \\ Mn(Me_2EBC)(OH)_2(PF_4)_2 \text{ was synthesized according to a known procedure from the literature.}^{10,22a} All the chemical reagents used were commercially available except for lignin model compounds, which were synthesized and characterized before in our group.}^6 \end{array}$ 

# General procedure for the oxidation of alcohols using $Mn(Me_2EBC)Cl_2$ in the presence of $H_2O_2$ .

Under Ar, a 25 mL round bottom flask was charged with acetonitrile (4 mL) and water (1 mL) before the pH was adjusted at 3 with HCl. Next, the substrate (100 mM) and 0.5 mol% of Mn(Me<sub>2</sub>EBC)Cl<sub>2</sub>, 0.17 mL or 0.34 mL of 35% of H<sub>2</sub>O<sub>2</sub> aqueous solution (35%) and diphenyl ether as the internal standard were added. The reaction was kept under vigorous stirring for 6 h or 18 h at 303 K in a water bath. Next, the solution was extracted with dichloromethane. After drying, the organic phase was analyzed by GC/MS.

The kinetic follow-up was carried out according to the same protocol, but aliquots were taken every hour.

# Experiment protocol for hydroxyl radical trapping with *t*-BuOH.

The protocol for this reaction was the same as the one described above but MeCN (4 mL) was replaced by *t*-BuOH (4 mL).

# Stoichiometric oxygenation of veratryl alcohol with manganese(IV) complexes.

5 mL of the mix solvent containing acetonitrile (4 mL) and water (1 mL) at pH 3 (pH adjusted with HCl) was charged with 1 mM of substrate, 1 mM of Mn(IV) complex and diphenyl ether. The reaction was kept stirring for 6 h at 303 K in a water bath. The conversion and the yields were detected by GC/MS using the internal standard method.

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**Keywords:** Green oxidation • Manganese complex • cyclam • lignin models • benzyl alcohols

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# Sustainable oxidation of benzyl alcohols

Zhan Zhang, Lhoussain Khrouz, Guochuan Yin, and Bruno Andrioletti\*

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Efficient oxidation of benzylic and aliphatic alcohols using a bioinspired, cross-bridged cyclam manganese complex with H<sub>2</sub>O<sub>2</sub>