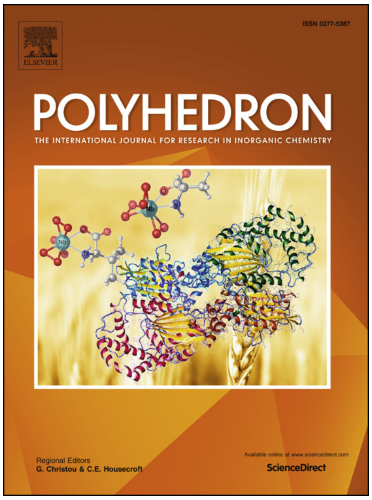

Selective Catalytic Oxidation of Alkenes Employing Homobinuclear Manganese(II) Catalysts with TBHP

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Selective Catalytic Oxidation of Alkenes Employing Homobinuclear Manganese(II) Catalysts with TBHP

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Abstract

The two novel homobinuclear compounds [Mn_2 $^{(II,II)}$ ($\mu_{1,1}$-4-CH_3-$C_6H_4COO)_2(phen)_4]$ $(ClO_4)_2$ (**1**) and [Mn_2 $^{(II,II)}$ ($\mu_{1,3}$-4-CH_3-$C_6H_4COO)_2(bipy)_4]$ $(ClO_4)_2$ (**2**), where bipy = 2,2-bipyridine and phen = 1,10-phenanthroline, have been synthesized and characterized by elemental analyses and spectral methods (UV-vis, FTIR, and X-ray). A single-crystal X-ray diffraction structure analysis of the compounds revealed that the manganese atom is octahedrally coordinated. In compound **1**, the binuclear(II) structure is monodentate, bridged with one oxygen atom of carboxylate ligand in $\mu_{1,1}$ mode, and each Mn(II) center is coordinated with two phen ligands. In compound **2**, the binuclear(II) structure is *syn-anti* bidentate, bridged with two oxygen atoms of carboxylate ligand in $\mu_{1,3}$ mode, and each Mn(II) center is coordinated with two bipy ligands. The Mn–Mn separation is 3.441 (1) Å and 4.450 (1) Å for **1** and **2**, respectively. The catalytic potentials of these compounds have been tested for the oxidation reaction of various olefins (i.e., styrene, cyclohexene, ethyl benzene, 1-hexene, 1-octene). The oxidation reactions were carried out in the presence of catalytic amounts of **1** and **2** with a peroxide oxygen donor (TBHP=*tert*-Butyl hydroperoxide) in acetonitrile at 70^{o}C. On comparing the catalytic activities of **1** and **2**, both catalysts showed good activity (~100% conv. in 24 h.) in the oxidation of studied alkenes, and excellent conversion was obtained for cyclohexene (~100% conv. in 3 h.; TON = 265 and TON = 257, respectively, for **1** and **2**).

Keywords: catalysis, manganese, oxidation, alkene

1. Introduction

The catalytic selective oxidation of hydrocarbons in particular, the alkenes to their corresponding diols or epoxides is of great interest in synthetic and industrial chemistry [1]. A major challenge in industrial chemistry is replacing economically and environmentally friendly catalytic systems with ordinary ones. A primary goal is to develop catalytic systems that show high atom efficiency and minimal formation of side products. Indeed, it is this aspect that places low-cost first-row transition metal complexes instead of high-cost active Rh, Pd, Ru, and other metal complexes. In this respect, the coordination chemistry of manganese has been an interesting and attractive research subject for two decades. This is not only because of the structural and functional mimics for manganese catalases [2], superoxide dismutase [3], but also because of their extraordinary magnetic properties [4] and macromolecular structures [5]. Manganese compound derivatives, especially with chelating neutral N-based ligands, have been used as active catalysts in hydrocarbon oxidations. The interest from the inorganic point of view is that there is considerable challenge in the use of Mn(II,III) complexes as catalyst precursors in synthetic organic chemistry because of the remarkably versatile redox chemistry of manganese [6]. Therefore, the coordination chemistry of multinuclear μ-chlorido-, μ-oxido- and μ-carboxylato-bridged manganese complexes has attracted extensive interest in recent decades owing to the bioinorganic relevance of these complexes [7] and their applications in selective catalytic oxidations and bulk oxidation chemistry [8].Some manganese complexes (i.e., Mn(III)-salen type and Mn(II,III)-Schiff type) are very well studied [9,10] because of easy synthesis and also because they suitably biomimic the structural feature of their active center, but the chemistry of binuclear Mn(II,III) complexes with carboxylate, bridged and coordinated with neutral chelating N,N base ligands, is not relatively studied. Therefore, in general, manganese complexes and the binuclear Mn(II,III) bridging compounds in particular, with N/O donor ligands have received much attention in recent years [11]. In this respect, the main purpose of this work would be the synthesis of manganese binuclear complexes with N,O donor ligands as catalysts for oxidation reactions. This work also focuses on their catalytic performance in the oxidation of alkenes under mild reaction conditions. In this work, we report on the synthesis, crystal structure, and catalytic performance of two novel binuclear Mn(II) complexes with mixed ligands 5-methyl benzoic acid and N,N chelating phen and/or bipy. Moreover, the catalytic performance of the compound is examined in the oxidation of various alkenes with TBHP in acetonitrile.

2. Experiment

2.1. Materials–instrumentation–physical measurements

All chemicals were purchased from commercial sources and used as received. IR spectra were measured with Jasco FT/IR-300 E Spectrophotometer using the KBr pellet in the range of 4000 - 400 cm^{-1}. UV-vis spectra of **1** were recorded on a Shimadzu UV-2450 spectrophotometer. Crystallographic data were collected at room temperature with a Bruker APEX II CCD using Mo-Ka radiation and corrected for absorption with SADABS. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F2.

2.2 Synthesis of [$Mn_2(\mu_{1,1}$-4-$CH_3C_6H_4COO)_2(phen)_4](ClO_4)_2$, (1)

$Mn(ClO_4)_2{\cdot}6H_2O$ (291.3 mg; 1.15 mmol), 4-methyl benzoic acid (150 mg; 1.15 mmol), and 1,10-phenanthroline (413.6 mg; 2.30 mmol), all dissolved in methanol, were mixed (total volume: ~25 mL) and stirred for 5 h. The yellow solid formed was isolated by filtration, washed with diethyl ether, and air-dried. (320 mg; yield: 42.8% m.p.; 348°C; Λ_m: 295.2 mS L/mol.cm). Yellow crystals suitable for X-ray diffraction were obtained after several days by slow evaporation. Found: % N:8.70, % C:58.96, % H:3.44; Calc.: % N:8.62, % C:59.08, % H:3.57). (Significant IR bands (KBr, ν cm^{-1}) (s, strong; m, medium; w, weak): 1604m; 1569m; 1519m; 1429m; 1307m; 1294s; 1144m; 1077s; 849s; 773s; 722s. UV–Vis λ_{max} nm (CH_3CN): 200, 229, 294.

2.3 Synthesis of [$Mn_2(\mu_{1,3}$-4-$CH_3C_6H_4COO)_2(bipy)_4](ClO_4)_2$, (2),

$Mn(ClO_4)_2{\cdot}6H_2O$ (347.19 mg, 0,96 mmol) and 4-methyl benzoic acid (130.7 mg, 0.96 mmol) and 2,2-bipyridine (150 mg; 0.96 mmol), all dissolved in methanol, were mixed (total volume ~25 mL) and stirred for 5 hours. The yellow solid formed was isolated by filtration and washed with diethyl ether and dried in air. Yield 140 mg; Yield % 48,4 e.n.: 280°C; Λm: 305.6 mS L / mol.cm; Found: (%) N:7.80, C:57.98, H:2.96; Calc.: N:9.31, C:55.87, H:3.85. Yellow crystals suitable for X-ray diffraction were obtained after several days by slow evaporation. (Significant IR bands (KBr, ν cm^{-1}) (s, strong; m, medium; w, weak): 1595s; 1555m; 1474m; 1437m; 1395s;

1315w; 1247w; 1161w; 1082s; 1015s; 846w; 761s; 734m. UV–Vis λ_{max} nm (CH_3CN): 198, 295, 309.

2.4. X-ray Crystallography

Diffraction data for the complex collected with Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 296 (2) K (for compound 1) and at 100 (K) (for compound 2), respectively using graphite monochromated Mo Kα radiation at λ=0.71073 Å. The data reduction was performed with the Bruker SMART program package [12]. The structures were solved by direct methods and the non-hydrogen atoms were located through subsequent difference Fourier syntheses. Structure solution was found with the SHELXS- 97 package using the direct methods and were refined SHELXL-2014. [13] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model at calculated positions. The molecular drawing was obtained using MERCURY [14]. Geometric calculations were performed with PLATON [15].

2.5 General Procedure of the Catalytic Oxidation Experiments

The oxidation of alkenes with TBHP catalyzed by **1** and **2** was carried out in acetonitrile at 70°C. In a 50 mL Schlenk tube were mixed 5 mg of the catalyst, 2 mL of a solution of TBHP 2.97 M in water, and 100–150 µL of alkene (substrate/cat. = 265). The final volume of the reaction mixture was 15 mL. The reaction was carried out at 70°C for 1–24 h. under stirring. The reactions were monitored by withdrawing small aliquots at certain time intervals and analyzed on a GC with an HP-5 quartz capillary column (30 m × 0.32 mm × 0.25 µm) and a flame ionization detector (FID). To analyze the reaction mixture during and after the reaction period, 2–3 drops of the reaction mixture were taken and then mixed with acetone 1:4 (v/v). Each sample was repeated twice. The identification of peaks was made by comparing chromatograms of authentic samples.

3. Results and Discussion

3.1. Synthesis and Characterization of the Compounds

In the infrared spectrum of **1** (SP1), the observed two strong peaks at ~1429 and ~1604 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of the carboxylate group, respectively. The magnitude of separation (~175 cm^{-1}) indicates the bidentate ($\mu_{1,3}$) coordination of the carboxylate ion, according to Nakamoto's method [16]. However, in the spectrum of **2** (SP2), the bands at 1437 and 1595 cm^{-1} are assigned to νas(CO_2) and νs(CO_2); the Δ value (153 cm^{-1}) is not as large as expected ($\Delta > 250$ cm^{-1}) for monodentate bridging ($\mu_{1,1}$) modes of benzoate ligation. This is because the carboxylate oxygen (O(6) in Fig. 2) not coordinated to Mn(II) is hydrogen bonded to the neighboring groups, giving what can be regarded as a "pseudo-bridging" arrangement. The medium bands at 722 cm^{-1} may be assigned to stretching vibration Mn–O–Mn, respectively [17]. This fact implies the existence of a binuclear manganese core. The IR spectra of the compounds are all similar apart from bands because of vibrations of the N,N ligand and the coordination mode of the carboxylate groups. The bands centered at ∼1569, 1519, 1307, and 1144 cm^{-1} and 1555, 1474, 1395, 1315, and 1247 cm^{-1} are assigned to the phen and bipy, respectively. In the spectrum of **1** and **2**, the observed bands of around 1082 cm^{-1} and 623 cm^{-1} are assigned to the perchlorate anion.

The UV spectrum of the compounds was taken in acetonitrile (SP3). The observed maximum absorptions at 190–300 nm may be assigned to π-π* transitions of the K band of the benzene rings and the charge transfer band to ligand from metal (MLCT)[18].

The stability and degree of dissociation of the compounds in acetonitrile were verified with molar conductivity measurement. Compounds **1** and **2** with two perchlorate anions have Λ_M values close to the expected for 1:2 electrolytes (one cation and two anion) in acetonitrile 295.2 and 305.6 S cm^2 mol^{-1}, respectively. Thus, the compounds retain their binuclear structures in acetonitrile solution, and the perchlorate anions are not coordinated with the manganese ions.

3.2 Crystal Structure Analysis

Suitable crystals of **1** and **2** were obtained by slow evaporation of their solutions in methanol at room temperature. The crystallographic data and processing parameters are summarized in SP4.

The molecular structure of compound **1** is demonstrated in Fig. 1. The compound consists of a dinuclear C2-symmetric $[Mn_2(\mu_{1,1}\text{-}4\text{-}CH_3C_6H_4COO)_2(phen)_4]$ cation and a perchlorate counter ion. The selected angles and bond lengths are depicted in Table 1. The compound 1 crystallizes in the space group C2/m. The Mn(II) atoms are coupled with two carboxylate oxygens of *p*-

touluic acid in a monobidentate $\mu_{1,1}$ bridging mode. The Mn(II) centers have distorted octahedral geometry. The equatorial plane is formed by the two nitrogen atoms of phen ligands and two carboxylate oxygen atoms coming from the two ligands [N1–Mn1–N1 = 160.85(12)^{o}]. The apical positions are occupied by a nitrogen of phen [Mn1–N1 = 2.267(2) Å, N2–Mn1–O1 = 160.33 (9)^{o}]. The Mn–N [2.273(2) Å and 2.267(2) Å] and Mn–O [2.185(2) Å] bond lengths are in agreement with analogous structures [19]. In the toluic acid ligand, the OH group is deprotonated (Fig. 2). Within the dimer, the two Mn(II) ions are bonded through the carboxylate oxygen atoms; the angles of Mn1–O1–Mn1i and O1–Mn1–O1 are 103.91^{o} (10) and 76.09^{o} (10), respectively, and the Mn–Mn distance is 3.4413(7) Å (Fig. 2 a). In the asymmetric unit of cation, intramolecular π-π-interaction is observed between the aryl ring plane of *p*-toluic acid (C14/C14/C15/C16/C17/C19) and the phen ligands ring (N2/C7/C10/C9/C8/C7), with a short centroid–centroid distance of 3.948(3) Å. The ring of p-toluic acid is perfectly linear, whereas the phen ligand has a torsion angle of 2.35^{o} (36) (N1C12C11N2). Within the metallacyclic cation, the O ··· O distance is 2.6930 (34) Å.

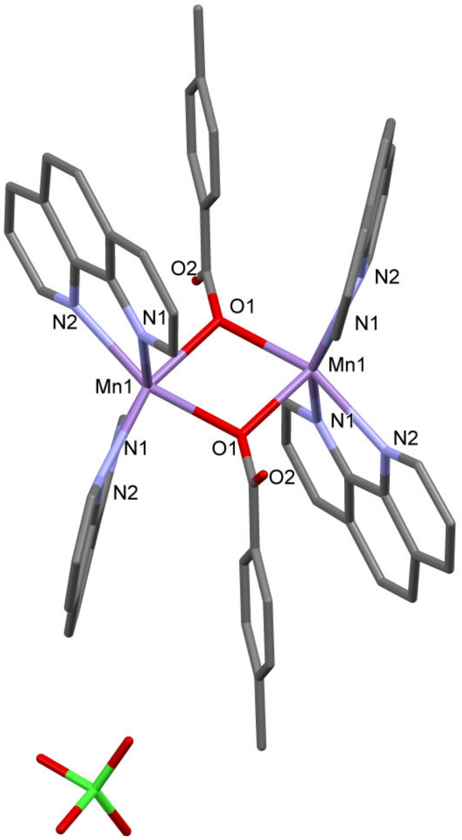
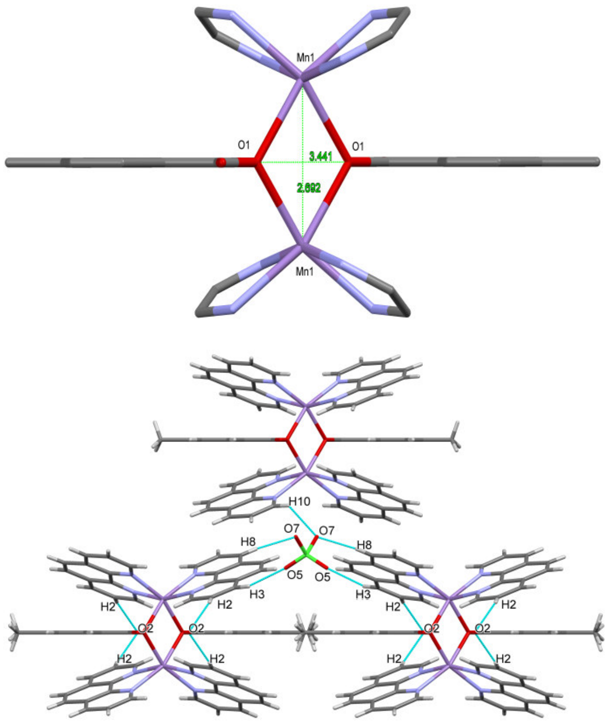


Figure 1 Binuclear structure of compound **1**.



a) b)

Figure 2 a) Binuclear structure of compound **1**. b) Intermolecular interaction of perchlorate ion.

The crystal structure of compound **2** consists of a centrosymmetric binuclear unit [$Mn_2(\mu_{1,3}$-4-$CH_3C_6H_4COO)_2(bipy)_4$] as shown in Fig. 3. Some selected angles and bond distances are given in Table 1. Compound **2** crystallizes in the space group P-1. The asymmetric unit contains two bipy ligands chelating through N atoms, one *p*-toluate ligand coordinated through an oxygen atom, and one perchlorate as a counter ion. The Mn(II) atom centers have distorted octahedral geometry, with angles of 72.28(15)^o and 101.61(16)^o as well as 168.9(1)^o and 161.67(15)^o deviates from 90^o and 180^o, respectively. The Mn(II) atoms are coupled with two carboxylate oxygen atoms of *p*-toluate in the *syn-anti* bidentate $\mu_{1,1}$ bridging mode. The Mn–O and Mn–N bond lengths are in well agreement with the published analogous structures (Table 3). Within the dimer, the Mn(II) ions are bonded through the carboxylate oxygen atoms; the angle of Mn(1)–O(2)–Mn(1i) is 108.31(8)^o, and the Mn–Mn separation is 4.450 (1) Å (Fig. 4 a). In the asymmetric unit of cation, intramolecular π-π-interaction is not observed between the aryl ring plane of *p*-toluate and the phen ligands; their positions are almost perpendicular to each other. Within the metallacyclic cation, the O–O distances are 4.248 (6) Å (O6 ··· O6), 3.6671 (46) Å

(O5 ··· O5), and 4.414 (7) Å (C21··· C21). We observed large torsion angles of bipy ligands of 16.76^{o}(58) (N3C15C16N4) and 12.95^{o}(58) (N2C5C6N1).

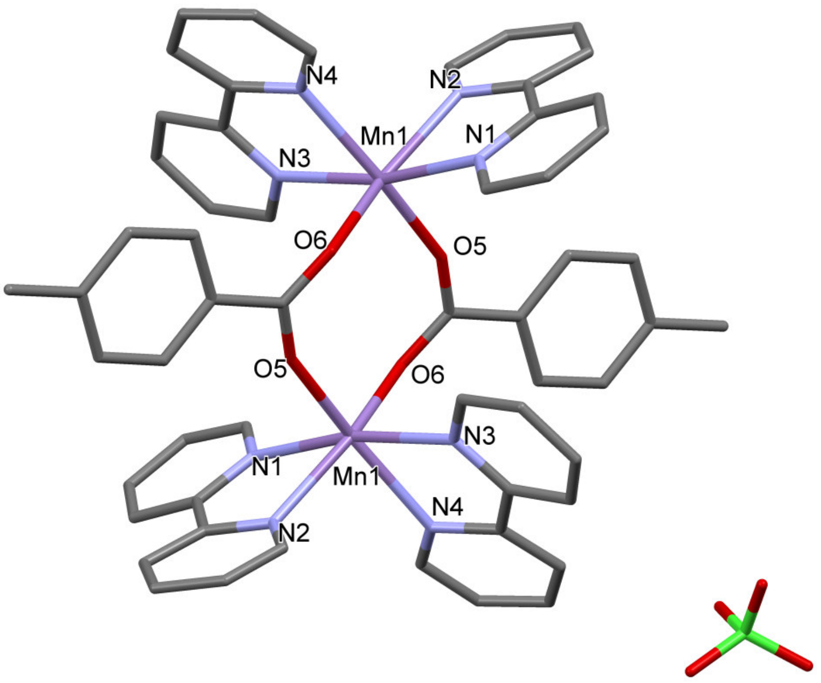
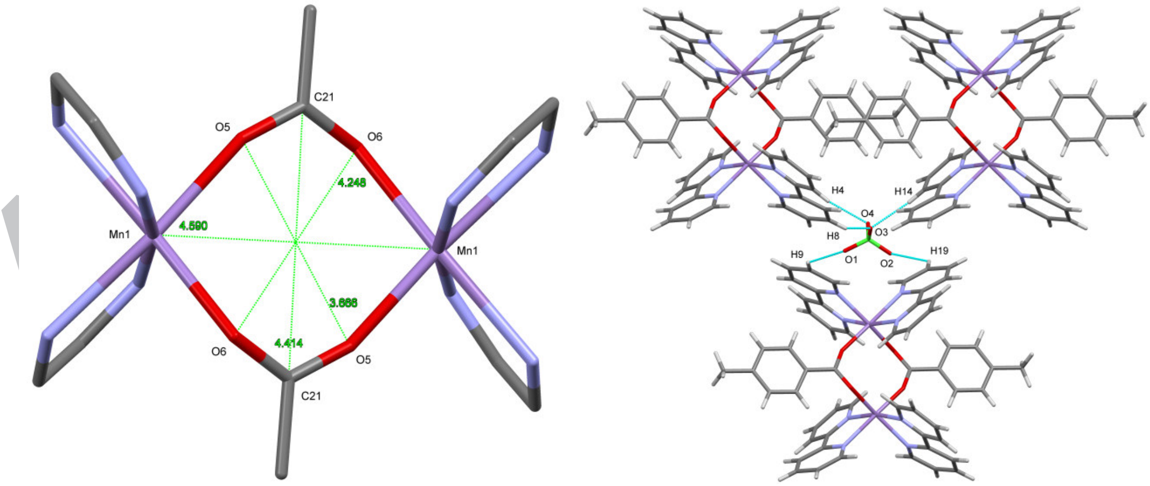


Figure 3 Binuclear structure of compound **2**.



a) b)

Figure 4 a) Binuclear structure of compound **1**. b) Intermolecular interaction of perchlorate ion.

For both compounds, the crystal structure is stabilized by interionic hydrogen bonds, each uncoordinated perchlorate oxygen atom acting as an acceptor, with the carbon atoms of bipy as donors (Fig. 2b and 4b). Their dimensions are given in Table 2.

Table 1 Some selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

1				2			
Mn1 – N1	2.267 (2)	N1 – Mn1 – N2	73.45(8)	Mn1 – N3	2.259 (4)	N3 – Mn1 – O6	95.33 (16)
Mn1 – N2	2.273 (2)	N1 – Mn1 – O1	96.83(9)	Mn1 – O6	2.122 (3)	N3 – Mn1 – O5	94.76 (17)
Mn1 – 01	2.1849 (15)	N2 – Mn1 – O1	87.06(7)	Mn1 – O5	2.100 (4)	N3 – Mn1 – N4	72.28 (15)
N1 – C1	1.342 (4)	Mn1 – N1 – C1	126.56(19)	Mn1 – N4	2.291 (5)	N3 – Mn1 – N1	169.05 (16)
N1 – C12	1.348 (3)	Mn1 – O1 – C13	126.85 (7)	Mn1 – N1	2.250 (4)	N3 – Mn1 – N2	101.61 (16)
O1 – C13	1.331 (4)	Mn1 – N1 – C12	114.94 (17)	Mn1 – N2	2.291 (4)	O6 – Mn1 – O5	102.67 (16)
C13 – 02	1.208 (5)			N3 – C15	1.354 (7)	O6 – Mn1 – N4	85.03 (15)
C16 – C17	1.417 (8)			N3 – C11	1.331 (7)	O6 – Mn1 – N1	89.28 (15)
Cl1 – 05	1.322 (5)			O5 – C21	1.249 (6)	O6 – Mn1 – N2	161.67 (15)
Cl1 – 07	1.376 (4)			N4 – C20	1.350 (7)	O5 – Mn1 – N4	165.66 (16)
						O5 – Mn1 – N1	93.91 (16)
						N4 – Mn1 – N1	98.31 (15)
						N4 – Mn1 – N2	93.45 (15)
						N1 – Mn1 – N2	72.84 (15)

Table 2. Hydrogen bonding in compounds **1** and **2**.

D – H … A	D – H (Å)	H … A (Å)	D … A (Å)	D – H … A (°)
1				
C3 – H3 ... O5^{i}	0.93	2.51	3.403(7)	161
C8 – H8 ... O7^{i}	0.93	2.29	3.212(11)	173
C10 – H10 ... O7^{ii}	0.93	2.53	3.280(12)	138
2				
C14 – H14 ... O3^{iii}	0.95	2.33	3.260(14)	165
C9 – H9 ... O1^{iv}	0.95	2.57	3.244(13)	129
C8 – H8 ... O3^{v}	0.95	2.62	3.305(11)	129
C4 – H4 ... O4^{vi}	0.95	2.32	3.239(9)	163

Symmetry codes: (i) x, y, 1+z ; (ii) ½+x,½-y,z; (iii) -x+1,-y,-z+1; (iv) x+1,+y,+z-1; (v) -x+1,-y+1,-z+1; (vi) -x,-y+1,-z+1

3.3 Catalytic Studies

Previously, our group and others reported the oxidation of alcohols and alkenes catalyzed by homobinuclear Mn(II) complexes containing dicarboxylic acids employing TBHP as an oxidant in acetonitrile under mild conditions [11,20]. The Mn(II)/TBHP/CH_3CN system shows high activity for cyclohexene, styrene, and, surprisingly, linear alkenes (1-heptene and 1-octene) and shows relatively poor activity with ethyl benzene.

Two binuclear Mn(II)/carboxylate/N-based ligand compounds have been tested as catalysts for the oxidation of alkenes to diols and epoxides using TBHP at 70°C in 24 h. The oxidation reactions were carried out in acetonitrile using a molar ratio of catalyst/alkene/TBHP of 1/265/3.4. All catalytic data were presented in Table 3. Figures 5 and 6 show the comparison of the alkenes conversion profiles versus the reaction time for compounds **1** and **2**. Under typical conditions, it can be concluded that compounds **1** and **2** exhibit a unique activity in oxidation of cyclohexene, 1-hexene, styrene and 1-octene and yields up to 100% are obtained in 24 h. except ethyl benzene. Ethyl benzene is a poor substrate in Mn(II) catalyzed oxidation with TBHP. Low activity was found for the oxidation of ethyl benzene to one product, benzaldehyde, by TBHP under catalysis with both compounds**,** 27.6% and 24.3% for **1** and **2,** respectively, under studied conditions (TONs up to only 73).

To examine the effect of oxidant activity, we tested the molecular oxygen, H_2O_2 (30% in water), and TBHP (70% in decane) in acetonitrile at 70°C. Oxygen was not effective under studied conditions probably the cause of the low-temperature reaction. The use of H_2O_2, instead of TBHP results in no reaction for all alkenes, possibly with the expected decomposition of H_2O_2 under the applied reaction conditions (70°C). These results were observed in our previous studies of similar Mn(II) binuclear complexes, which are very active for H_2O_2 decomposition to water and oxygen (catalase activity). Moreover, the use of more oxidants and increased temperature do not lead to conversion. TBHP was the most attractive oxidant for our catalytic system. The blanc experiments showed that a very poor conversion ratio of alkenes was observed without any catalysts and $Mn(ClO_4)_2$. It can be seen that the ligands play a significant role in the catalytic properties of the compounds. The control experiments proved that the catalytic activities are derived from compounds **1** and **2** as catalyst precursors.

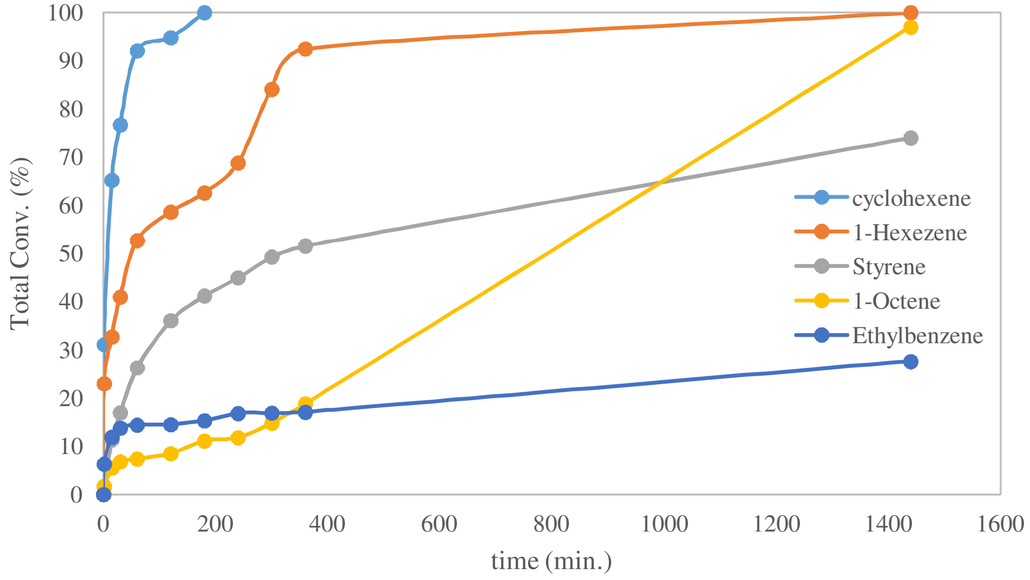


Figure 5 The alkenes conversion profiles versus the reaction time with compound **1.**

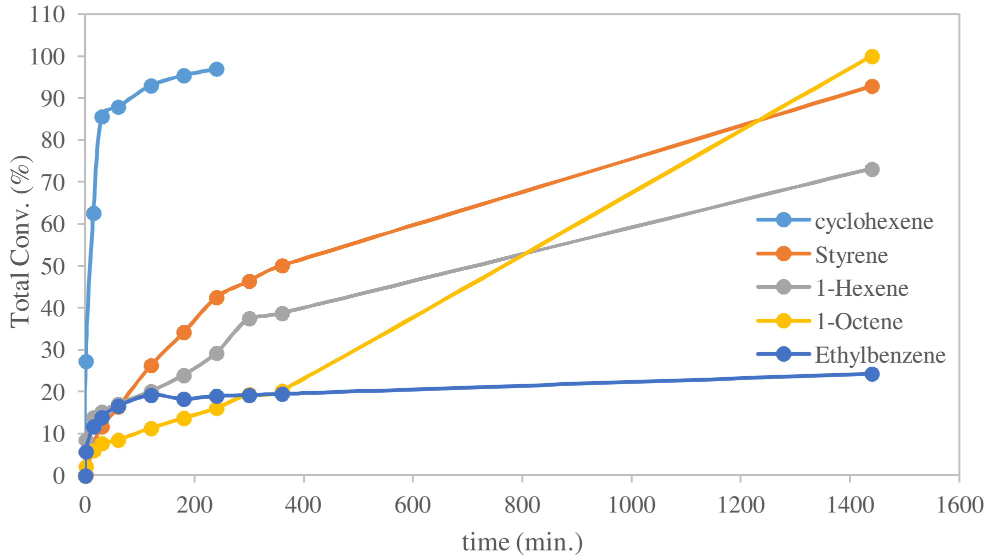
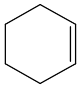
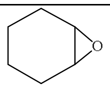
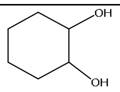
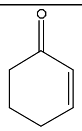
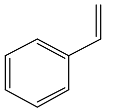
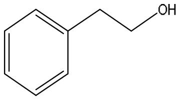
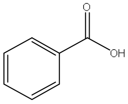
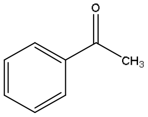
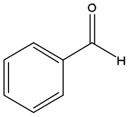
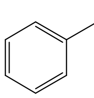
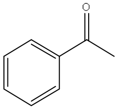
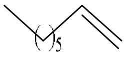
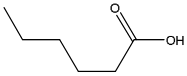
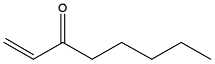
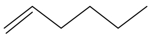
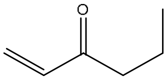
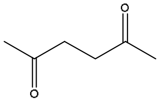


Figure 6. The alkenes conversion profiles versus the reaction time with compound **2.**

Table 3. Compounds **1** and **2** catalyzed oxidation of alkenes to carbonyl compounds.

Entry	**Substrate**	**Product Distrubution, Conv. (%)**[a]				**Total Conv. (%)**	**TON TOF (h^{-1})**
1						100 **1**	265 **1** 83

		(3 h) 5.2 **1** 3.0 **2**	(3 h.) 7.3 **1** 3.7 **2**	(3 h.) 87.5 **1** 93.3 **2**		97.0 **2**	257 **2** 86
2		 (6 h.) 14.2 **1** 6.1 **2** (24 h.) 15.0 **1** 7.7 **2**	 (6 h.) 0 **1** 0 **2** (24 h.) 0 **1** 13.5 **2**	 (6 h.) 32.5 **1** 33.4 **2** (24 h.) 50.3 **1** 48.2 **2**	 (6 h.) 4.9 **1** 10.6 **2** (24 h.) 8.7 **1** 23.5 **2**	74.0 **1** 92.9 **2**	196 **1** 8 246 **2** 10
3		 (6 h.) 17.1 **1** 19.5 **2** (24 h.) 27.6 **1** 24.3 **2**				27.6 **1** 24.3 **2**	73 **1** 3 64 **2** 3
4		 (6 h.) 13.3 **1** 15.1 **2** (24 h.) 64.9 **1** 73.5 **2**	 (6 h.) 5.5 **1** 5.1 **2** (24 h.) 32.1 **1** 26.5 **2**			97.0 **1** 100 **2**	257 **1** 11 265 **2** 11
5		 (6 h.) 32.6 **1** 16.8 **2** (24 h.) 22.8 **1** 16.5 **2**	 (6 h.) 33.5 **1** 10.5 **2** (24 h.) 33.5 **1** 10.9 **2**	 (6 h.) 26.4 **1** 11.4 **2** (24 h.) 43.7 **1** 45.7 **2**		100 **1** 72.2 **2**	265 **1** 11 191 **2** 8

[a] Conversion due to GC results.

Reaction conditions: 1.46 x 10^{-2} mol of oxidant, 4.3 x 10^{-3} mmol of catalyst, subst. /cat. =266, T = 70 °C, TON = number of moles of product per mole of catalyst

In particular, electron-rich alkene, cyclohexene, converts relatively faster than the other studied alkenes to related products for both compounds (~100% conv.; TOF = 83–86). The reaction was completed in 3 h. In cyclohexene, the carbon–carbon double bond undergoes oxidation by TBHP in very low yields (3–5 % in 3 h.) of cyclohexene oxide (epoxide), which, upon further reaction with water, produces 1,2-cyclohexanediol (diol) (4–7% in 3 h.). Selective epoxidations over transition metal systems occur via a heterolytic cleavage of the O–O bond by a hydroperoxo-/superoxo-metal species. The oxidation of the allylic C–H bond via a homolytic O–O bond cleavage results in 2-cyclohexene-1-ol, which is further oxidized to 2-cyclohexene-1-one. The 2-cyclohexene-1-one selectivity is ~96%.

After a runtime of 24 h., acetophenone is a major product in styrene oxidation, with total conversions of 50.3% and 48.2% and selectivities of 68% and 52% for **1** and **2**, respectively. The results dictate that the selectivity to acetophenone was changed from 63% to 68% in 6 h. for **1**, whereas the selectivity to acetophenone decreased from 52% to 67% for **2** after 6 h. (Table 3). The formation of benzaldehyde following the radical mechanism by the direct C=C bond cleavage of styrene is very low compared the other products (8.7% and 23.5% for **1** and **2,** respectively).

Moreover, in contrast to reported Mn(II) complexes, very high activity was obtained for the electron-poor aliphatic alkenes such as 1-octene and 1-hexene, which tend to be the least reactive olefins in metal-catalyzed epoxidation and are readily oxidized to corresponding carbonyl products, ~ 100% conversions of olefins with **1** and **2**. Also, 1-octene converts to hexanoic acid as a major product, 64.9% and 73.5%, and the second product, 1-octene-3-one, 32.1% and 26.5% with **1** and **2,** respectively, after 24 h. at 70°C. Compounds **1** and **2** exhibited very high activity for the oxidation of 1-hexene, affording 43.7%;45.7% 2,5 hexanedione as a major product, with the formation of other products: 22.8%;16.5% 1-hexene-1-one and 33.5%;10.9% hexanal for **1** and **2**, respectively, in 24 h. With a further increase in reaction time, the conversion ratio of aldehyde did not change.

In general, compounds **1** (monodentate, one-oxygen bridged, Mn–Mn distance of 3.441 Å) and **2** (bidentate, two-oxygen bridged, Mn–Mn distance of 4.590 Å) showed very similar activity for alkene oxidation. These results revealed that the Mn–Mn separation distance has no effect on the oxidation activity of the catalyst. In addition, the basic character of N,N chelating ligands (a less basic character of bipy ligand than phen) also has no effect in terms of an overall conversion ratio of alkene oxidation in studied conditions.

4. Conclusion

In this contribution, we report on the synthesis and complete characterization of two homobinuclear carboxylate–bridged Mn(II) compounds with hybrid p-toluic acid and phen/bipy ligands. Remarkably, these complexes all showed very good catalytic activity in the oxidation of the cyclic alkene cyclohexene and styrene and terminal alkenes. Here, 1-octene and 1-hexene with TBHP were used as oxidants in an acetonitrile solvent at 70°C. In addition to the chemical simplicity and easy synthesis of **1** and **2**, the compounds have also the ability to form active intermediate Mn(II)/Mn(III) compounds to catalase alkene oxidation in the TBHP/catalyst/alkene system.

Acknowledgment

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Supplementary material

CCDC 1014102 and 994266 contains the supplementary crystallographic data for compound **1** and **2** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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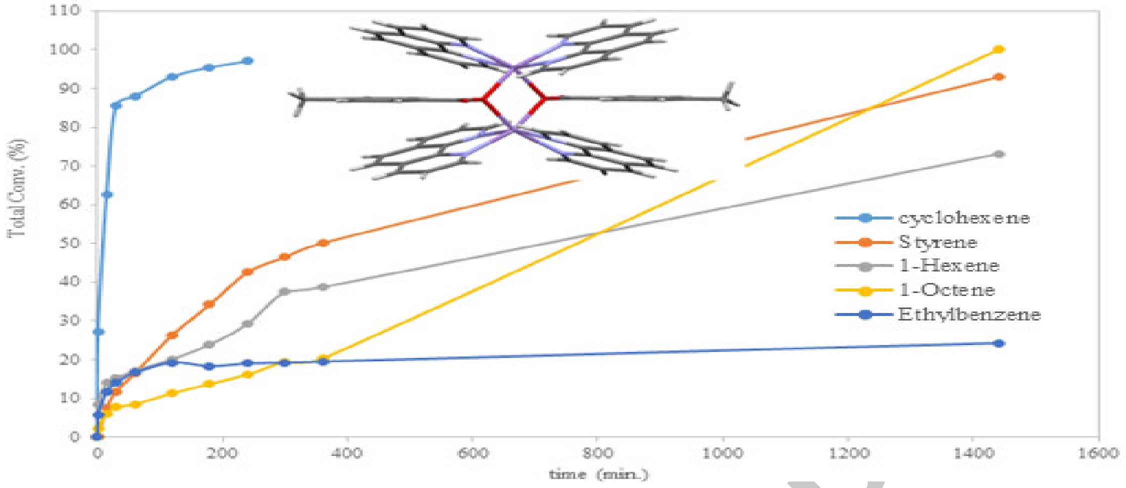
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1400
1600
time (min.)
cyclohexene
Styrene
1-Hexene
1-Octene
Ethylbenzene

Selective Catalytic Oxidation of Alkenes Employing Homobinuclear Manganese(II) Catalysts with TBHP

Yalçın Kılıç, Ibrahim Kani

The two novel homobinuclear compounds of Mn(II) with *p*-toluic acid and N-heterocyclic amine has been synthesized and characterized. The complexes exhibited good catalytic activity in oxidation of alkenes in acetonitrile with TBHP as an oxidant at 70 ^{o}C; cyclohexene to cyclohexanone (> 97 % conversion in 3 h, TOF ~265) without any promoter.