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Effective catalytic oxidation of alcohols and alkenes with monomeric versus dimeric manganese(II) catalysts and *t*-BuOOH

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Two new Mn(II) complexes, $[Mn(C_6H_5COO)(H_2O)(phen)_2](CIO_4)(CH_3OH) (1)$ and $[Mn_2(\mu-C_6H_5COO)_2(bipy)_4] \cdot 2(CIO_4) (2)$ (phen = 1,10phenanthroline; bipy = 2,2'-bipyridine), were synthesized and characterized using UV-visible and infrared spectroscopies and single-crystal X-ray diffraction analyses. Complexes 1 and 2 have six-coordinate octahedral geometry around the Mn(II) centre. Complex 1 is a monomer and consists of a deprotonated monodentate benzoate ligand together with two neutral bidentate amine ligands (phen) and a water molecule. Complex 2 has a dinuclear structure in which two Mn(II) ions share two carboxylate groups, adopting a two-atom bridging mode, and two chelated bipy ligands. Both complexes catalyse the oxidation of alcohols and alkenes in a homogeneous catalytic system consisting of the Mn(II) complex and *tert*-butyl hydroperoxide (TBHP) in acetonitrile. The system yields good to quantitative conversions of various alkenes and alcohols, such as styrene, ethylbenzene and cyclohexene to their corresponding ketones, and primary alcohols and 1-octanol, 1-heptanol, cyclohexanol, benzyl alcohols and cinnamyl alcohol to their corresponding aldehydes and carboxylic acids. Complexes 1 and 2 exhibit very high activity in the oxidation of cyclohexene to cyclohexanone (*ca* 80% selectivity) as the main product (*ca* 94% conversion in 1 h) and of cinnamyl alcohol to cinnamaldehyde (*ca* 64% selectivity) as the main product (*ca* 100% conversion in 0.5 h) with TBHP at 70°C in acetonitrile. In addition, optimum reaction conditions were also determined for benzyl alcohol with complexes 1 and 2 and TBHP. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: manganese; complex; benzoic acid; catalysis; oxidation

Introduction

Selective liquid-phase catalytic oxidation, in particular the oxidation of alkenes to their corresponding diols or epoxides or of alcohols to aldehydes, ketones or carboxylic acids, is an important reaction usually used in the industrial synthesis of organics.^[1] The resultant carbonyl compounds are used to manufacture a wide range of fine chemicals and pharmaceuticals. Traditionally, strong oxidants such as KMnO₄, CrO₃, peracetic acid, *m*-chlorobenzoic acid and HNO₃^[2] are used in stoichiometric amounts as the oxidizing agent for liquid-phase oxidation reactions, which might result in serious pollution and have potential risks. In the last few years, much attention has been paid to catalytic oxidation reactions in the presence of various environmentally friendly oxidants, such as hydrogen peroxide, tert-butyl hydroperoxide (TBHP) and oxygen.^[3] Hydrogen peroxide is a very attractive oxidant for industrial applications because it is inexpensive and mild and water is the only by-product, which is easily dealt with after reactions.^[4]

The oxidation of alcohols catalysed by inorganic–organic hybrid compounds is of current interest, and various effective catalysts have been reported, such as those based on molybdenum and tungsten,^[5] ruthenium,^[6] cobalt,^[7] manganese,^[8] iron^[9] and titanium.^[10] However, because most metal-containing catalysts are expensive and may cause environmental pollution, poisonous reagents are required as solvents for use in time-consuming procedures, making the development of a more efficient and environmentally friendly catalytic system an urgent matter.

As a continuation of our recent oxidation studies of various homogeneous catalysts, the aim of the study reported here was

to obtain new Mn(II) complexes with mixed benzoate and nitrogenous base ligands as oxidation catalysts for various alcohols and alkenes. We used benzoic acid and bidentate amines (2,2'-bipyridine and 1,10-phenanthroline) as terminal ligands to complete the manganese coordination. We synthesized two new complexes formulated as mononuclear [Mn(C₆H₅COO)(H₂O)(phen)₂](ClO₄)(CH₃OH) (1) and binuclear [Mn₂(μ -C₆H₅COO)₂(bipy)₄]-2(ClO₄) (2) (phen = 1,10-phenanthroline; bipy =2,2'-bipyridine). The complexes were characterized using X-ray crystallography and successfully applied as catalysts in the oxidation of various alcohols and alkenes with TBHP in a variety of solvents.

Experimental

Materials, instrumentation, physical measurements

All chemicals were purchased from Aldrich and used as received. Fourier transform infrared (FT-IR) spectra were recorded with a Jasco FT/IR-300 E spectrophotometer using the KBr pellet technique in the range 400–4000 cm⁻¹. Electronic spectra were recorded with a Shimadzu UV-2450 spectrophotometer.

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Synthesis of complexes

Synthesis of $[Mn(C_6H_5COO)(H_2O)(phen)_2](ClO_4)(CH_3OH)$ (1)

A solution of manganese(II) perchlorate (Mn(ClO₄)₂·6(H₂O)) and H₂O (311.8 mg, 1.23 mmol) in methanol (10 ml) was added to a neutralized solution of benzoic acid (150 mg, 1.23 mmol) with NaOH (2.5 ml, 0.489 M). The reaction mixture was stirred for 1 h at room temperature, and then a solution of phen (221.6 mg, 1.23 mmol) in methanol (2 ml) was added to the mixture. The final solution was refluxed for 5 h. The mixture was filtered over Celite, and the solvent was evaporated to dryness. The crude product was washed with diethyl ether and then dried under vacuum. The yellow product was recrystallized from methanol by ether diffusion. Yield 276.6 mg, 65.5%; m.p. 330 °C. Anal. Found (%): N, 8.64; C, 58.05; H, 3.25. Calcd for $C_{32}H_{27}CIMnN_4O_8$ (%): N, 8.17; C, 56.16; H, 3.96. Significant IR bands (KBr pellet, cm⁻¹): 3050 (vs), 1990 (s), 1581 (vs), 1396 (s), 1307 (s), 1083 (vs), 825(s), 694 (s). The complex is soluble in polar solvents and slightly soluble in CH₂Cl₂ and CHCl₃.

Synthesis of $[Mn_2(\mu-C_6H_5COO)_2(bipy)_4] \cdot 2(CIO_4)$ (2)

The procedure for the synthesis of complex **2** was similar to that of complex **1**. Yield 56.7%; light yellow colour; m.p. 260 °C. Anal. Found (%): N, 9.31; C, 55.33; H, 3.52. Calcd for $C_{54}H_{42}Cl_2Mn_2N_8O_{12}$ (%): N, 9.53; C, 55.16; H, 3.60. Significant IR bands (KBr, cm⁻¹): 3085 (s), 1997 (s), 1612 (s), 1550 8w), 1461 (s), 1103 (vs), 821 (s), 605 (s). The complex is soluble in dimethylformamide (DMF), MeOH, EtOH, (CH₃)₂CO and MeCN and slightly soluble in CH₂Cl₂.

X-ray crystallography

Diffraction data for the complexes were collected using a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 296(2) K using graphite-monochromated Mo Ka radiation at $\lambda = 0.71073$ Å. Diffraction data were collected over the full sphere and were corrected for absorption. Unit cell dimensions were determined by least-squares refinement of the complete data set, and an empirical absorption correction was made based on psi-scans. The data reduction was performed with the Bruker SMART^[11] program package. Structure solutions were found with the SHELXS-97^[12] package using direct methods and refined with SHELXL-97^[13] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structural model at calculated positions. Geometric calculations were performed with PLATON.^[14]

General procedure for catalytic oxidation experiments

Notably, only harvested crystals of the complexes were used for the catalytic activity studies to exclude the effects of impurities. Catalytic oxidation reactions were carried out in 50 ml two-neck flasks equipped with a reflux water condenser. The whole assembly was placed in a temperature-controlled oil bath. The reaction mixture was heated at 70 °C for 6 h. The general procedure for alcohol/alkene oxidation was as follows. A solution of substrate and catalyst was purified with nitrogen via bubbling to remove the dissolved oxygen in the solvent. A solution of oxidant (2 ml, 70%) in solvent (10 ml) was added to a stirred mixture of substrate (0.2 ml) and catalyst Mn(II) (*ca* 0.5–1%) at 70 °C. The homogeneous mixture was oxidized on a magnetic stirring apparatus at a stirring speed of 1200 rpm. Samples of the products (0.1 ml) were collected at certain time intervals and analysed using a Thermo Finnigan Trace GC with an HP-5 quartz capillary column

(30 m × 0.32 mm × 0.25 μ m) and a flame ionization detector using ultrapure nitrogen as the carrier gas (at a rate of 1.0 ml min⁻¹). Each sample was injected twice. Both the injector and detector temperatures were 250 °C, and the column temperature was between 100 and 180 °C. The products were confirmed using GC–MS. All catalytic experiments were performed at least twice.

Results and discussion

Synthesis of complexes 1 and 2

The synthesis of the complexes is shown in Scheme 1. X-ray analysis and spectral data confirm the assigned composition of the complexes. The electronic spectra of the complexes were recorded in methanol. The crystallographic data and corresponding selected bond lengths and angles of **1** and **2** are given in Tables 1, 2.

The crystal structure of complex **1** shows a mononuclear cation with benzoic acid and phen ligands, one perchlorate and a methanol molecule. The molecular structure of **1** is shown in Fig. 1. Within the complex cation, the Mn atom is coordinated by four N atoms from two bidentate chelating phen ligands, a carboxylate oxygen atom from the benzoic acid ligand, and an oxygen atom from a water molecule to complete a significantly distorted MnN₄O₂ octahedral environment with (Mn–N) in the range 2.262(2)–2.278(2) Å and (Mn–O) of 2.108(1) and 2.162(2) Å. A perchlorate anion and a methanol molecule make up the outside of the complex cation. The phen ligands are almost planar (torsion angle N1C1C9N2 = $-0.7(2)^{\circ}$ and N3C13C21N4 = $1.3(2)^{\circ}$), and the mean plane angle between ligands is 74.56°. The *cisoid* angles range from 73.1(5)° to 103.4(5)°, whereas the *transoid* angles are 160.9(5)° (O1–Mn1–N2), 161.2(5)° (N1–Mn1–N4) and 163.2(6)° (N3–Mn1–O8).

An intramolecular hydrogen bond is found between the coordinated carboxylic acid group of benzoic acid moiety and the coordinated water with an O2–O8 distance of 2.612(2) Å. Moreover, intermolecular hydrogen bonds (O8–O7 = 2.724(2) Å, O7–O6 = 2.748(3) Å) exist in the uncoordinated methanol, perchlorate anion and coordinated water molecule.



Scheme 1. Synthesis of complexes 1 and 2.

Table 1.	Crystal	data	and	structure	refinement	parameters	of	com-
plexes 1 a	nd 2							

	1	2
Empirical formula	$C_{32}H_{27}CIMnN_4O_8$	$C_{54}H_{42}CI_2Mn_2N_8O_{12}$
MA (g mol ⁻¹)	685.97	1175.74
Refinement method	Full-matrix leas	st-squares on F ²
Temperature (K)	106(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Colour	Yellow	Yellow
Crystal system	Monoclinic	Triclinic
Space group	P121/c1	P-1
a (Å)	11.6192(3)	9.0291(3)
b (Å)	16.0932(6)	11.6096(4)
<i>c</i> (Å)	16.9741(6)	13.3884(4)
α (°)	90	65.727(2)
β (°)	108.8220(10)	84.269(2)
γ (°)	90	87.897(2)
Volume, V (Å ³)	3004.26(17)	1272.95(7)
Ζ	4	1
Density (mg m $^{-3}$)	1.517	1.534
Absorption coefficient (mm ⁻¹)	0.589	0.675
heta range for data collection (°)	1.85 to 28.45	1.68 to 28.39
Goodness-of-fit on F ²	0.999	1.060
R indices (all data)	$R_1 = 0.0491,$	$R_1 = 0.0784,$
	$wR_2 = 0.0984$	$wR_2 = 0.2030$
Largest diff. Peak	0.787 and –	2.515 and –
and hole	0.456 e A ⁻³	0.854 e A ⁻³
Final R indices	$R_1 = 0.0372,$	$R_1 = 0.0699,$
$[l > 2\sigma(l)]$	$wR_2 = 0.0917$	$wR_2 = 0.1947$

Table 2. Selected	bond lengths (Å	À) and angles (°)	
Complex 1			
Mn(1)–O(8)	2.162(15)	Mn(1)–N(2)	2.269(16)
Mn(1)–O(1)	2.107(12)	Mn(1)–N(3)	2.261(16)
Mn(1)–N(1)	2.277(15)	Mn(1)–N(4)	2.268(15)
O(8)-Mn(1)-O(1)	86.51(5)	O(1)-Mn(1)-N(4)	103.45(5)
O(8)-Mn(1)-N(1)	102.84(6)	N(1)-Mn(1)-N(2)	73.10(5)
O(8)-Mn(1)-N(2)	88.91(6)	N(1)-Mn(1)-N(3)	93.66(5)
O(8)-Mn(1)-N(3)	163.19(6)	N(1)–Mn(1)–N(4)	161.21(5)
O(8)-Mn(1)-N(4)	91.29(6)	N(2)-Mn(1)-N(3)	99.10(6)
O(1)-Mn(1)-N(1)	89.89(5)	N(2)-Mn(1)-N(4)	95.14(5)
O(1)-Mn(1)-N(2)	160.93(5)	N(3)–Mn(1)–N(4)	73.38(5)
O(1)-Mn(1)-N(3)	90.35(5)		
Complex 2			
Mn(1)–O(2 ⁱ)	2.127(4)	Mn(1)–N(1)	2.261(4)
Mn(1)–O(1)	2.136(3)	Mn(1)–N(2)	2.280(4)
Mn(1)–N(4)	2.253(4)	Mn(1)–N(3)	2.284(4)
O(2 ⁱ)–Mn(1)–O(1)	103.92(14)	N(4)-Mn(1)-N(2)	96.38(15)
O(2 ⁱ)–Mn(1)–N(4)	92.48(15)	N(1)-Mn(1)-N(2)	72.71(15)
O(1)-Mn(1)-N(4)	88.61(14)	O(2 ⁱ)–Mn(1)–N(3)	80.83(14)
O(2 ⁱ)–Mn(1)–N(1)	98.01(15)	O(1)-Mn(1)-N(3)	161.21(14)
O(1)-Mn(1)-N(1)	92.57(14)	N(4)-Mn(1)-N(3)	72.92(15)
N(4)-Mn(1)-N(1)	168.83(15)	N(1)-Mn(1)-N(3)	104.88(15)
O(2 ⁱ)–Mn(1)–N(2)	168.25(15)	N(2)-Mn(1)-N(3)	94.40(14)
O(1)-Mn(1)-N(2)	84.04(14)		



Figure 1. Molecular structure of 1.

The crystal structure of complex **2** consists of a dinuclear cation, $[Mn_2(\mu-C_6H_5COO)_2(bipy)_4]^{2+}$, and two perchlorate anions, as shown in Fig. 2. It has a centre of symmetry. The carboxylate group of the benzoic acid ligand acts as the mono-bidentate bridging ligand, and bridges two Mn atoms in a syn-anti fashion to form a dimer. The Mn–O bond length is similar (2.136(3) Å) and comparable to that of related compounds ($[Mn_2(OAc)_2(4-aba)_2(2,2'-bpy)_2]^{115}$ (average Mn–O: 2.109(8) Å), $[Mn(2,2'-bipy)_2(2,6-dhba)_2]^{[16]}$ (average



Figure 2. Molecular structure of **2** ((i) 2 - x, 1 - y, 2 - z).

Table 3. Oxidation of	various alkenes with homoge	neous complex 1 /TB	HP system			
Substrate	Products	Conv. (%)	Time (h)	Total conv. (%)	TON	Solvent
Cyclohexene	Cyclohexene oxide	4.6	1.5	94.3	251	Acetonitrile
	2-Cyclohexene-1-one	76.0				
	2-Cyclohexene-1-ol	2.5				
	1,2-Cyclohexanediol	11.2				
Styrene	Styrene oxide	1.0 ^b	6	40.1	107	DMF
	Acetophenone	25.9				
	2-Phenylethanol	11.7				
	Benzaldehyde	1.5				
Ethylbenzene	Acetophenone	10.0	6	10.0 ^a		Acetonitrile

^a3 ml addition of oxidant after 1 h of reaction increased the conversion to 44.3%, and a further increase in the oxidant (2 ml) increased the conversion to 69.1% after 24 h of reaction.

^bAfter 24 h of reaction, total conversion increased to 52.4% (styrene oxide 1.2%, acetophenone 42.7%, 2-phenylethanol 6.4%, benzaldehyde 2.1%). Reaction conditions: 1.46 × 10⁻² mol of oxidant, 7.3 × 10⁻³ mmol of catalyst (0.8 mol% vs. substrate), substrate/catalyst =266, 70 °C, TON = number of moles of product per mole of catalyst.

Mn–O: 2.112(2) Å) and $[Mn(4-hba)(H_2O)(1,10-phen)_2](4-hba)$ (H₂O)^[17] (average Mn–O: 2.10(6) Å)). Each manganese ion is further coordinated by two bipy ligands (average Mn–N: 2.269(2) Å), leading to a distorted octahedral geometry around the metal ion with average Mn–O distances that are much longer than the Mn–N distances (2.524 and 2.269 Å, respectively). All distances agree with those reported for analogous compounds.^[15–17] The Mn–O bond lengths range from 2.436(2) to 2.691(19) Å, with an average value of 2.524 Å. The Mn–Mn distance (4.465(8) Å) is significantly longer than those found in $[Mn_2(OAc)_2(4-aba)_2-(2,2'-bipy)_2]$ (4.081 Å) and $[Mn_3(4-aba)_6]_n$ (3.452(2) Å). The oxygen atoms of the carboxylate group and perchlorate anions form intermolecular C–HO hydrogen bonds with the –CH groups of coordinated bipy molecules. The compound is further stabilized by π – π aromatic stacking interactions between the rings of ligands.

Spectroscopic study of complexes

The FT-IR spectra of the compounds contain two strong bands at *ca* 1563 and *ca* 1394 cm⁻¹ due to the asymmetric and symmetric vibrations of the COO groups (Fig. 9 (SP5)). The values of $\Delta = v_a$ (COO) – v_s (COO), *ca* 200 cm⁻¹ for compounds **1** and **2**, are indicative of

carboxylate ligands coordinated in a bidentate bridging mode $(\mu_{1,3})$, whereas higher values are expected for compound **1** with a monodentate coordination, although hydrogen bonds may decrease this Δ value. Broad bands at *ca* 1100 cm⁻¹ and a moderate intensity band at 623 cm⁻¹ in the spectra of compounds **1** and **2** are assigned to the perchlorate anions. The phen ligand produces characteristic bands at *ca* 1516, 1428, 863, 848 and 727 cm⁻¹, and the bipy ligand produces characteristic bands at *ca* 1500, 1474 and 1439 cm⁻¹.

The UV–visible spectroscopic data are very similar for both complexes, indicating that each of the Mn(II) complexes behaves as a high-spin octahedral d⁵ system (Fig. 10 (SP6)). The absorption bands in the UV region at *ca* 235, *ca* 270 and *ca* 300 nm are assigned to ligand-centred $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions in the bipy and phen ligands, respectively. Due to the d⁵ configuration of the Mn²⁺ ion, no absorptions are expected in the visible region of the spectrum.

Catalytic studies

Complexes 1 and 2 are highly soluble in CH_3CN . The complexes produce a light-brown-coloured solution in solvent after dissolution. The colour is intensified upon addition of the terminal oxidants. When the substrates are added, the colour begins to fade,

Table 4. Oxidation of	various alkenes with homoge	neous complex 2 /TB	HP system			
Substrate	Products	Conv. (%)	Time (h)	Total conv. (%)	TON	Solvent
Cyclohexene	Cyclohexene oxide	3.8	1	92.9	241	Acetonitrile
	2-Cyclohexene-1-one	75.1				
	2-Cyclohexene-1-ol	2.8				
	1,2-cyclohexanediol	11.8				
Styrene	Styrene oxide	1.2 ^b	6	25.3	78	DMF
	Acetophenone	18.4				
	2-Phenylethanol	3.9				
	Benzaldehyde	1.3				
Ethylbenzene	Acetophenone ^a	11.0	6	11.0	32	Acetonitrile

^a3 ml addition of oxidant after 1 h of reaction increased the conversion to 61.9%, and a further increase in the oxidant (2 ml) increased the conversion to 84.1% after 24 h of reaction.

^bAfter 24 h of reaction, total conversion increased to 29.6% (acetophenone 24.2%, 2-phenylethanol 2.7%, others not changed).

Reaction conditions: 1.46 × 10⁻² mol of oxidant, 4.3 × 10⁻³ mmol of catalyst (0.45 mol% vs. substrate), substrate/catalyst =266, 70 °C, TON = number of moles of product per mole of catalyst.

and, after complete consumption of the substrates, the intensity of the colour turns back nearly to the original intensity, indicating catalyst regeneration. Mn(ClO₄)₂ was also examined as a catalyst for oxidation reactions: no reaction occurred. Furthermore, we examined the Lewis acid co-catalyst used by others as an additive, i.e. ascorbic acid and oxalate buffer, trichloroacetic acid and salicylic acid, and the results are in contrast to those of previous reports: the additives are not effective in the epoxidation of alkenes and alcohols.^[18] Shul'pin and co-workers reported a dinuclear Mn(IV) complex that efficiently catalysed various oxidation reactions with H₂O₂ or *t*-BuOOH oxidants.^[19] The system requires a carboxylic acid co-catalyst, preferably oxalic acid, to control the solubility and oxidation state of the Mn species. Our catalytic system contains carboxylic acid as a coordinating ligand in the complex structure, which is probably the reason for the ineffectiveness of the co-catalyst. Moreover, the results of control experiments reveal that the presence of catalyst and oxidant is essential for the oxidation.

Mono- (1) and homodinuclear (2) manganese complexes were tested as catalysts for the oxidation of alcohols (cinnamyl alcohol, cyclohexanol, 1-heptanol, 1-octanol and benzyl alcohol) to the respective aldehydes and carboxylic acids and of alkenes (cyclohexene, styrene and ethylbenzene) to the corresponding ketones and alcohols using TBHP as an oxidizing agent. Typically, we dissolved 5 mmol of a substrate in 15 ml of acetonitrile with a catalytic amount $(7.3 \times 10^{-3} \text{ mol and/or } 4.3 \times 10^{-3} \text{ mol})$ of the Mn(II) complexes. The solution was heated to 70 °C and treated with 2 ml (9.7 × 10⁻³ mmol) of the TBHP (70%, aqueous) oxidant.

Oxidation of alkenes

The olefins (cyclohexene, styrene and ethylbenzene) are practically active without adding any additives. The system has highest activity with electron-rich alkenes, i.e. cyclohexene, and relatively little activity with the electron-deficient alkenes styrene and ethylbenzene. Tables 3, 4 and Fig. 3 present the maximum conversion and time required to obtain the maximum yield for cyclohexene, styrene and ethylbenzene epoxidation using TBHP as the terminal oxidant in the presence of two solvents, acetonitrile and DMF (only for styrene). From the obtained data, complexes **1** (94.3%, after 1.5 h) and **2** (92.9% after 1 h) clearly exhibit the highest efficiency in the reaction of cyclohexene in acetonitrile (Tables 3, 4).

Complexes 1 and 2 show the highest activity for the oxidation of cyclohexene in acetonitrile, affording cyclohexanone as a major product with the formation of small amounts of cylohexenol, 2-cyclohexene-1-one, cyclohexene oxide and 1,2-cyclohexanediol (due to allylic oxidation) (Tables 3, 4). Cyclohexene has two fragments accessible to attack by the catalytically active species (the double bond and relatively weak C-H bonds). Comparison of the rates of epoxidation and C-H bond oxygenation could give valuable information on the nature of the oxidizing species. The very low yield of the epoxidation product indicates that the catalytic activity of our system proceeds through C-H bond activation. The oxidation of cyclohexene to the allylic ketone and the very low epoxide formation strongly imply that the system involves a radical oxidant via one-electron oxidation. Complex 1 oxidizes cyclohexene to the corresponding epoxide (4.6%), 2-cyclohexen-1-one (76.0%), 2-cyclohexen-1-ol (2.5%) and 1,2-cyclohexanediol (11.2%) after 1.5 h of reaction. Complex 2 exhibits very rapid oxidation under the same conditions (reaction almost completed in 1 h) with 92.9% conversion: cyclohexene oxide (3.8%), 2-cyclohexen-1-one (75.1%), 2-cyclohexen-1-ol (2.8%) and 1,2-cyclohexanediol (11.8%).



Figure 3. Comparison of complexes (a) 1 and (b) 2 in alkene oxidation.



Figure 4. Comparison of complexes (a) 1 and (b) 2 in alcohol oxidation.

Table 5. Oxidation of var	rious alcohols with homogeneous comple	x 1 /TBHP system			
Substrate	Products	Product distribution (%)	Time (h)	Total conv. (%)	TON
Cinnamyl alcohol	Cinnamaldehyde	30.0	0.5	98.2	261
	Benzaldehyde	32.8			
	Styrene	13.5			
	3-Phenylglycidol	21.9			
Cyclohexanol	Cyclohexanone	43.0	6	43.0 ^a	114
Heptanol	Heptanal, Heptanoic acid	4.9;1.3	6	6.2 ^{b,c}	17
1-Octanol	Octanal, Heptanal, Heptanoic acid	1.8;4;1;2.7	6	8.6 ^d	92
Benzyl alcohol	Benzaldehyde, Benzoic acid	53.4;3.63	6	57 ^{e,f}	152

^a2 ml addition of oxidant after 1 h of reaction increased the conversion to 75.4%.

^b2 ml addition of oxidant after 1 h of reaction increased the conversion to 18.7%: heptanal (14.6%), heptanoic acid (4.1%).

^cAfter 24 h of reaction, total conversion increased to 36.1% (heptanal 24.1%, heptanoic acid 12.0%).

^d2 ml addition of oxidant after 1 h of reaction increased the conversion to 34.7%: heptanal (22.4%), heptanoic acid (6.8%), octanal (0.8%), octanoic acid (4.7%).

^e2 ml addition of oxidant after 1 h of reaction increased the conversion to 76.8%: benzaldehyde (47.3%), benzoic acid (29.5%).

^fAfter 24 h of reaction, total conversion increased to 89.8% (benzaldehyde 46.5%, benzoic acid 43.3%).

Reaction conditions: 1.46×10^{-2} mol of oxidant, 7.29×10^{-3} mmol of catalyst (0.8 mol% vs. substrate), substrate/catalyst =266, 70 °C, solvent = acetonitrile, TON = number of moles of product per mole of catalyst.

The oxidation of styrene was carried out in DMF because styrene polymerizes in acetonitrile, and was catalysed by complexes **1** and **2** using TBHP as the oxidant to yield the following products: styrene oxide, benzaldehyde, 2-phenylethanol and acetophenone (Tables 3, , 4). The efficiency of the mononuclear catalyst (40.1%) in styrene epoxidation is better than that of the binuclear catalyst (25.3%) under the same conditions. For both complexes, the main product is acetophenone (65% selectivity with **1** and 62% selectivity with **2**) in 6 h. Further increasing the reaction time to 24 h and the ratio of oxidant from 1:4 to 1:16 increases the total conversion of styrene to 69.1 and 29.5% for **1** and **2**, respectively.

Ethylbenzene exhibits a low conversion for both complexes (*ca* 10%) with TBHP in acetonitrile at 70 °C. However, increasing the TBHP concentration in the reaction mixture considerably increases the conversion of ethylbenzene due to an increased consumption of oxidant. The conversion of ethylbenzene to acetophenone with 100% selectivity increases with TBHP, varying from *ca* 10.0% (at an ethylbenzene-to-TBHP mole ratio of 1:6) to 44.3% (for **1**) and

61.9% (for **2**) (at an ethylbenzene-to-TBHP mole ratio of 1:16) and 69.1% (for **1**) and 84.1% (for **2**) (at an ethylbenzene-to-TBHP mole ratio of 1:30) without changing the selectivity. This excellent selectivity in the oxidation of ethylbenzene to acetophenone is very remarkable.

Oxidation of alcohols

Complexes 1 and 2 are effective in the oxidation of primary alcohols. A comparison of the time-dependent conversion using 1 and 2 is shown in Fig. 4 and Tables 5, 6. Among the studied alcohols, cinnamyl alcohol is the most reactive and results in 100% conversion in 0.5 h (turnover number (TON) of *ca* 266) with both complexes. Notably, primary aliphatic alcohols are inevitably oxidized to form their secondary oxidation products, carboxylic acids, with low to moderate conversion using a range of reaction conditions, whereas secondary alcohols (cyclohexanol) are oxidized to only the corresponding ketones (cyclohexanone) (43.0% for

Table 6. Oxidation of variation	ous alcohols with homogeneous complex	2 /TBHP system			
Substrate	Products	Conv. (%)	Time (h)	Total conv. (%)	TON
Cinnamyl alcohol	Cinnamyl aldehyde	30.9	0.5	100	266
	Benzaldehyde	45.9			
	Styrene	8.8			
	Benzoic acid	7.1			
	3-Phenylglycidol	9.9			
Cyclohexanol	Cyclohexanone	48.1	6	48.1 ^a	128
Heptanol	Heptanal	14.9	24	50.3 ^b	17
1-Octanol	Octanal ^c , Heptanal, Heptanoic acid	1.3;6.8;3.2	6	11.3 ^c	92
Benzyl alcohol	Benzaldehyde, Benzoic acid	39.2;5.40	6	44.6 ^d	152

^a2 ml addition of oxidant after 1 h of reaction increased the conversion to 79.5%.

^b2 ml addition of oxidant after 1 h of reaction increased the conversion to 50.3%.

^c2 ml addition of oxidant after 1 h of reaction increased the conversion to 53.0% in 24 h of reaction (octanal 1.0%, heptanal 38.0%, heptanoic acid 14.0%).

^d2 ml addition of oxidant after 1 h of reaction increased the conversion to 70.6% in 24 h of reaction (benzaldehyde 45.8%, benzoic acid 24.8%). Reaction conditions: 1.46×10^{-2} mol of oxidant, 4.25×10^{-3} mmol of catalyst (0.45 mol% vs. substrate), substrate/catalyst =266, 70 °C, solvent = acetonitrile, TON = number of moles of product per mole of catalyst. complex 1 and 48.1% for complex 2 in acetonitrile in 6 h of reaction) without C–C chain cleavage. This is in agreement with reports that aliphatic alcohols are less reactive than benzylic substrates.

1-Octanol, a primary aliphatic alcohol, is generally difficult to oxidize to its carboxylic acid in lower conversion of 8.6% for 1 and 11.3% for 2 in 6 h. Heptanol is oxidized in also very low yield (6.2% for 1 and 14.9% for 2 in 6 h) with both complexes (Tables 5, 6). However, adding the oxidant in small portions (at an alcoholto-TBHP mole ratio of 1:6 to 1:10 in 6 h of reaction) over time in a single experiment improves the conversion of alcohols: 43.0% cyclohexanol to 75.4% cyclohexanone; heptanol to the corresponding aldehyde and acid (total conversion of 6.2 to 18.7%), to heptaldehyde (4.9 to 14.6%) and to heptanoic acid (1.3 to 4.1%); 1-octanol to the corresponding aldehyde and acid (total conversion of 8.6 to 34.7%), heptanal (4.1 to 22.4%) and heptanoic acid (2.7 to 6.8%); and benzyl alcohol to the corresponding aldehyde and acid (total conversion of 57.0 to 76.8), benzaldehyde (53.4 to 47.3%) and benzoic acid (3.6 to 29.5%) (Table 5, for complex 1). After 24 h reaction, the total conversion increases up to 89.8% for benzyl alcohol oxidation.

The same effect is observed for the oxidation of cyclohexanol to cyclohexanone catalysed by complex 2 without changing the 100% selectivity: a conversion of 48.1 to 79.5% (at a cyclohexanol-to-TBHP mole ratio of 1:12 and 1:20) after 6 h of reaction. In addition, 4.9% heptanol was converted to 50.3%, and 11.3% 1-octanol was converted to 53.0% after 24 h of reaction.

Benzyl alcohol oxidation

To determine the suitable reaction conditions, the oxidation of benzyl alcohol was selected as a model reaction. The conversion of benzyl alcohol is nearly quantitative, with benzaldehyde as the major product along with benzoic acid as the minor product. First, the choice of solvent was optimized in the model reaction. Different solvents such as acetone, acetonitrile, dichloromethane and tetrahydrofuran were investigated, and the highest yield of benzaldehyde is obtained with acetonitrile for complex 1 (89.8% after 24 h) and acetone for complex 2 (100% after 24 h) (Table 7 and Fig. 5 (SP1)). The catalytic activity of complex 1 decreases in the order of the relative dielectric constants: acetonitrile (37.5) > acetone (20.7) > dichloromethane (8.9) > tetrahydrofuran (7.6). In general, there is good correlation between the solvent polarity and the benzyl alcohol conversion for complex 1 but not for complex 2 in acetone. The highest conversion in acetonitrile is possibly caused by its high dielectric constant. The fact that activity is observed in several,

quite different solvents indicates that coordination of the organic solvent to the manganese complex is essential to the catalytic cycle.

We also assessed the activity of 1 and 2 in the oxidation of benzyl alcohol with three different oxidants: hydrogen peroxide, TBHP and molecular oxygen. The results are given in Table 8. The oxidation of benzyl alcohol with O₂ (10 bar) as an oxidant was carried out at 70 °C in a stainless steel autoclave using the same amounts of CH_3CN , TBHP and complex **1** as in the general procedure. During the reaction, the samples were taken with a special sampling apparatus and analysed by GC after filtration and dilution. The complexes exhibit a unique activity in alcohol oxidation with only TBHP (TONs of up to 152) and do not show activity with H_2O_2 or molecular oxygen, in agreement with the unproductive decomposition of H₂O₂ with Mn(II) complex under the applied reaction conditions (70 °C).

Furthermore, the effect of the amount of TBHP on the oxidation of benzyl alcohol as a function of time is illustrated in Fig. 6 (SP2), and the results are summarized in Table 9. Four different oxidant/substrate molar ratios of 4, 7, 11 and 15 were considered, while maintaining fixed amounts of benzyl alcohol $(7.3 \times 10^{-3} \text{ mol})$ and catalyst $(7.29 \times 10^{-6} \text{ mol})$ in 20 ml of CH₃CN at 70 °C. A maximum of 51.9% conversion of benzyl alcohol is obtained at an oxidant/substrate molar ratio of 4 (TON =138). This conversion improves to 70.6% at an oxidant/substrate molar ratio of 11. Further increasing the ratio to 15 expedites the conversion to completion within 6 h, but the overall conversion is not affected very much (76.8%, TON =204), which may have been due to the dilution of the reaction mixture by the greater presence of water molecules in the TBHP solution. It is therefore clear that the TBHP-to-benzyl alcohol molar ratio of 15 is optimal for obtaining the maximum benzyl alcohol conversion of 76.8% in 6 h of reaction time.

Table 8. and 2	Oxidant effec	t on ber	nzyl a	cohol o	kidatior	n with c	omple	exes 1
Oxidant	Substrate/ catalyst	Time (h)	Tota	al conv. (%)	T	NC	TOF	(h ⁻¹)
			1	2	1	2	1	2
t-BuOOH	266	6	57	44.6	152	119	25	20
H_2O_2	266	6	0	0	0	0	0	0
O ₂	266	6	0	0	0	0	0	0
Reaction o	conditions: 70	°C, solv	ent =	acetoni	trile, 1.	46 × 10) ⁻² m	ol of

HP.			

Table 7. Solvent effe	ct on benzyl alcohol	oxidation wit	h complexes 1 a	nd 2						
Oxidant Dielectric	Dielectric	T (K)	T (K) Time (h)	Total	Total conv. (%)		TON		TOF (h^{-1})	
	constant (E)			1	2	1	2	1	2	
Acetonitrile	37.5	70	6	57	44.6	152	119	25	20	
			24	89.8	70.6					
Acetone	20.7	70	6	37.2	57.7	99	154	17	26	
			24	79.6	100					
Dichloromethane	8.93	70	6	17.6	23	47	61	8	10	
			24	64.2	62.5					
Tetrahydrofuran	7.58	70	6	8.2	6.1	22	16	4	3	
			24	17.4	27.2					

Reaction conditions: 1.46×10^{-2} mol of oxidant, substrate/catalyst = 266, solvent = acetonitrile, TON = number of moles of product per mole of catalyst, TOF = number of moles of product/(number of mole of catalyst × time).

Table 9. Effect of ox	kidant addition on benz	yl alcohol oxic	lation with complex 1			
Oxidant/substrate	Substrate/catalyst	Time (h)	Product distribution	Total conv. (%)	TON	TOF (h^{-1})
4	266	6	47.0% benzaldehyde; 4.9% benzoic acid	51.9	138	23
7	266	6	53.4% benzaldehyde; 3.6% benzoic acid	57.0	152	25
11	266	6	52.4% benzaldehyde; 18.2% benzoic acid	70.6	188	31
15	266	6	47.3% benzaldehyde; 29.5% benzoic acid	76.8	204	34
Reaction conditions:	70 °C, solvent = aceton	itrile.				

Table 10.	Effect of substrate/catalyst ratio on benzyl alcohol oxidation
with comp	lex 1

Oxidant	Substrate/ catalyst	Т (°С)	Time (h)	Total conv. (%)	TON	TOF (h ⁻¹)
t-BuOOH	66	70	6	97	64	11
t-BuOOH	166	70	6	95.1	158	26
t-BuOOH	266	70	6	57	152	25
t-BuOOH	366	70	6	45.4	166	28
Reaction conditions: 70 °C, solvent = acetonitrile, benzyl alcohol						

=10 mmol, TBHP =14.6 \times 10⁻³ mol.

The effect of the amount of **1** on the oxidation of benzyl alcohol was studied considering four different substrate/catalyst molar ratios of 66, 166, 266 and 366, while maintaining the amounts of benzyl alcohol (1.04 g, 10 mmol) and TBHP (14.6×10^{-3} mol, 2 ml) in 20 ml of CH₃CN, and the reaction was carried out at 70 °C. As shown in Fig. 7 (SP3) and Table 10, a maximum conversion of 45.4% is achieved with a substrate/catalyst ratio of 366, whereas a substrate/catalyst ratio of 166 gives a maximum conversion of 95.1% in 6 h of reaction time. A further increase in the catalyst amount (substrate/catalyst ratio of 66) results in little increase in conversion to 97.0%.

The effect of temperature on benzyl alcohol oxidation with **1** and **2** was investigated with substrate/catalyst ratio = 266 at various temperatures over the range 50–80 °C (Fig. 8 (SP4)). The conversion rate is rapid, up to *ca* 30% conversion in the first minute of reaction, after which the reaction proceeds slowly with both catalysts at all temperatures. The reaction at 60 °C is slow and yields only 41 and 36.7% benzaldehyde from benzyl alcohol after 6 h with **1** and **2**, respectively. However, the conversion increases markedly at a MeCN reflux temperature of 80 °C to yield 67.7% benzaldehyde with **1**, but the conversion with **2** does not show significant enhancement (47.5%).

Conclusions

In summary, mono- and carboxylate-bridged dinuclear Mn(II)/ benzoic acid/phen or bipy complexes were synthesized, characterized using X-ray crystallography and successfully applied in the catalytic oxidation of alcohols and alkenes. The complexes exhibited good catalytic activities in the oxidation of cinnamyl alcohol, cyclohexanol, benzyl alcohol, cyclohexene and styrene when TBHP was used as an oxidant in the absence of any additive in an acetonitrile medium. We observed that in terms of the comparison of catalytic performance, mono- and dinuclear complexes are quite close to each other. In particular for cyclohexene, a conversion of up to ca90% and selectivity up to 80% were observed after 1 h at 70 °C in acetonitrile with both complexes. In addition, with the optimized conditions for benzyl alcohol oxidation with complex **1**, the maximum conversion was obtained at 97% (substrate/catalyst =66, TBHP =1.46 \times 10⁻² mol, at 70 °C). Moreover, the present catalytic oxidation system has the following distinct characteristics: (a) requires only acetonitrile as a solvent without any additives; (b) employs a very small amount of catalyst; (c) produces a high TBHP efficiency; and (d) is safe, clean, inexpensive and operationally simple.

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