

Synthesis, structural characterization, and benzyl alcohol oxidation activity of mononuclear manganese(II) complex with 2,2'-bipyridine: $[\text{Mn}(\text{bipy})_2(\text{ClO}_4)_2]$

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A manganese(II) complex of 2,2'-bipyridine (bipy) was synthesized and characterized by X-ray diffraction, IR, and UV-vis spectroscopy. The activity of the complex was tested for oxidation of benzyl alcohols using *t*-BuOOH as an oxidant in organic solvents and in an organic/water biphasic system (hexane/H₂O, toluene/H₂O). The effect of solvent, temperature, oxidant, and some additives (KBr, N(C₄H₉)Br, and N-bromosuccinimide) on the oxidation of benzyl alcohol is reported. The results show that benzyl alcohol was selectively converted to benzaldehyde in 71.9% yield within 4 h in acetonitrile. Control experiments performed without catalyst and the corresponding metal salt as catalyst produced no benzaldehyde in the reaction mixture. Mild reaction conditions, high yields of the products, short reaction time, no further oxidation to the corresponding carboxylic acids, high selectivity, and inexpensive reagents make this catalytic system a useful oxidation method for benzyl alcohol.

Key Words: Catalysis, oxidation, 2,2'-bipyridine, manganese, benzyl alcohol

Introduction

Selective oxidation of alcohols to the corresponding aldehydes and ketones is one of the most important functional group transformations with significant biological and mechanistic interest in modern organic synthesis.^{1–5} The traditional reactions are often performed with stoichiometric amounts of strong oxidants such as KMnO₄, CrO₃, and HNO₃ in environmentally undesirable solvents.^{6,7} These reagents are toxic, corrosive, unstable, show no selectivity, produce many side products, and require dangerous procedures for preparation. In terms of atom

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efficiency and environmentally friendliness, after oxygen, *t*-BuOOH (TBHP) and H₂O₂ (HP) are attractive oxidants for industrial catalytic applications.^{8–16} Both are desirable oxidants because they are relatively cheap and nontoxic, and produce fewer by-products, which are easy to deal with after the reactions. Moreover, another important concept is that finding an efficient catalyst for the selective oxidation of bulk chemicals into useful products is an interesting field of current chemistry.^{17–21} The use of transition metal complexes is an alternative way of obtaining effective and selective homogeneous catalysts. To date, although some cheap metals such as Fe, Cu, Cr, Co, and Mn have been developed on the liquid-phase oxidation of benzyl alcohol, the studies mainly focus on expensive metals, such as Ru, Mo, V, W, Pd, or Pd–Ag.^{22–40} As well as being expensive, these metals are toxic. Therefore, economical and more efficient alternative catalysts are still desirable. Many catalytic studies in recent years showed that manganese complexes can exhibit a diversity of catalytic oxidation reactions on organic substrates in organic solvents.^{41–44} Much effort has been exerted to develop manganese catalysts for oxidation reactions since they are inexpensive and less toxic than other transition metal complexes.

On the basis of the above considerations, in this work, we synthesized a complex of manganese(II) with 2,2'-bipyridine and characterized its structure. The complex was successfully applied as catalyst precursor for the oxidation of benzyl alcohol to its corresponding aldehyde by using TBHP as an oxygen source under mild conditions in acetonitrile.

Experimental

Materials and methods

All chemicals were purchased from Aldrich and were used as received. FT-IR spectra of compounds were recorded on a Jasco FT/IR-300 E spectrophotometer. The products obtained from the catalytic reaction were determined using a Thermo Finnigan Trace GC/GC-MS using a Permabond SE-54-DF-0.25 25 m × 0.32 mm ID column attached to a flame ionization detector with He as carrier gas.

Catalyst synthesis

A mixture of Mn(ClO₄)₂·6(H₂O) (0.100 g, 0.387 mmol) with bipy (1.394 g, 0.774 mmol) in the molar ratio 1:2 and methanol (30 mL) was placed in a Schlenk vessel (50 mL). The mixture was refluxed for 4 h. The resulting solution was allowed to stand in air and crystals of the title complex were deposited after a week (color: green, mp 320 °C, 0.91 g, yield 90%). FTIR (KBr pellet, $\nu_{\max}/\text{cm}^{-1}$): 1599 (s), 1756 (m), 1494 (w), 1476 (s), 1441 (s), 1321 (m), 1138 (s), 1048 (w), 1029 (s), 919 (s), 764 (s), 737 (m), 652 (w), 630 (s), 624 (s). UV-vis (λ_{\max}/nm): 207, 244, 294 (in methanol).

Catalytic tests

Experiments were carried out in a thermostated glass reactor equipped with a condenser and stirrer. Solution of benzyl alcohol and catalyst in acetonitrile was purified with nitrogen to remove the oxygen. The crystals of the manganese complex were used as catalyst in all catalytic experiments. A mixture of benzyl alcohol (9.6×10^{-4} mol, 0.1 mL), catalyst (8.34×10^{-6} mol, 5 mg), and acetonitrile (15.0 mL) was stirred in a 50 mL glass reactor for a few minutes at room temperature. The oxidant *t*-BuOOH (1.42×10^{-2} mol, 2 mL) was then added and the reaction mixture was stirred for the desired time. After certain time intervals, samples

(0.5 mL) were taken. Each sample was injected in the GC twice, 1 μ L each time. Formation of products and consumption of substrates were monitored by gas chromatography. All catalytic experiments were performed at least twice.

General biphasic oxidation procedure

In a typical experiment, a solution of oxidant (1.42×10^{-2} mol, 2 mL) in H₂O (5 mL) at room temperature was added to a solution of alcohol (9.6×10^{-4} mol, 0.1 mL) and complex (8.34×10^{-6} mol, 5 mg) in hexane (5 mL). The biphasic mixture was stirred vigorously. The oxidation products were isolated by the phase separation of the resulting biphasic system. The upper organic layer was removed by syringe. The water phase was extracted with acetone. The collected acetone and the separated organic phase were combined and analyzed by GC.

X-ray crystallography

Diffraction data for the compounds were collected with a Bruker SMART APEX CCD diffractometer equipped with a rotation anode at 100 K using graphite monochromated Mo K radiation (0.71073 Å). SAINT, SHELXTL,

Table 1. Crystal data and structure refinement for Mn(II) complex.

Empirical formula	C ₂₀ H ₁₆ Cl ₂ MnN ₄ O ₈
Formula weight	566.21
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P</i> 21 / <i>n</i>
Unit cell dimensions (Å, °)	<i>a</i> = 8.2272(5) α = 90
	<i>b</i> = 13.3691(9) β = 100.05(3)
	<i>c</i> = 21.0132(14) γ = 90
Volume	2275.8(3) Å ³
Z, Calculated density	4, 1.653 Mg/m ³
Absorption coefficient	0.871 mm ⁻¹
F(000)	1148
Theta range for data collection	1.81 to 28.38 deg.
Limiting indices	-10 \leq <i>h</i> \leq 11, -17 \leq <i>k</i> \leq 17, -28 \leq <i>l</i> \leq 25
Reflections collected/unique	31,590/5689 [R(int) = 0.0467]
Completeness to theta	28.38 99.3%
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	5652/0/316
Goodness-of-fit on F ²	1.062
Final R indices [I > 2 σ (I)]	R1 = 0.062, wR2 = 0.213
R indices (all data)	R1 = 0.0730, wR2 = 0.2782

and SHELXS 97⁴⁵ were used for cell refinement, data reduction and structure solving, and refinement of structure. Molecular graphics and publication materials were prepared using SHELXTL.⁴⁶ Crystallographic data and structure refinements parameters are listed in Table 1. Hydrogen atoms were added to the structure model on calculated positions. Geometric calculations were performed with Platon.⁴⁷ The refinement converged with the residuals summarized in Table 1. The structure of **1** has been deposited at CCDC with the deposition number 798813. The data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Characterization of catalyst

The synthesis of complex is shown in Scheme 1. The X-ray analysis and spectral data confirm the assigned composition of the complex. The electronic spectrum was taken in methanol. The IR spectrum of the complex shows that peaks revealing the presence of bipy in the complex occur at around 1599-1576 cm⁻¹ [(C=N) and (C=C) stretches], 1476-1048 cm⁻¹ [(C-C) and (C-N) vibrations], and 920-737 cm⁻¹ (aromatic C-H deformation vibrations). In the IR spectrum, the (C=C/C=N) bands were shifted to higher wavenumbers in the complex.⁴⁸ The strong nonsplitting absorption band of uncoordinated perchlorate anion (at about 1100 cm⁻¹) is distinctly split into 2 components observed at around 1029 and 1138 cm⁻¹. Moreover, a strong absorption band characteristic of uncoordinated perchlorate ion, centered at 620 cm⁻¹, is significantly split into 2 (624 and 630 cm⁻¹) in the spectrum of the compound. These features indicate monodentate coordination of the perchlorate group.⁴⁹ The absorption bands in the UV region between 232 and 280 nm are assigned to ligand-centered $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the 2,2'-bipyridine ligand. Due to the d⁵ configuration of Mn²⁺ ion, no absorptions are expected in the visible region of the spectrum.



Scheme 1. The synthesis of complex.

X-ray structure of cis-(2,2'-bipyridine- κ^2 -N,N)bis(perchlorate)manganese(II)

The ligand 2,2'-bipyridine (bipy) and its derivatives are widely used in the construction of novel metallorganic complexes.^{50,51} Because the inter-ring C-C bond of bipy can rotate freely, bipy cannot just be considered as a chelating ligand^{52,53}, but also a potential spacer between metal centers by acting as a bridging ligand with an anti configuration to form stable polymeric complexes.⁵⁴ In addition, bipy ligand is capable of giving very stable species in solution^{55,56} due to π -back bonding from metal to the aromatic amine and also π -aromatic systems are stabilized by stacking due to non-covalent interactions involving the π systems in solid state.⁵⁷

The molecular geometry of the title compound is illustrated in Figure 1 and crystal data listed in Table 1. The Mn(II) atom is coordinated by 4 N atoms from bidentate chelating bipy ligands and 2 oxygen atoms from 2 perchlorate ions in an irregular octahedral geometry. The distortion is reflected on the cisoidal angles [74.2 (1)-109.2 (1)°] and trans angles [156.8 (1)-169.1 (1)°]. The differences in N...N bite distances (2.671 (4) and 2.670 (4) Å) as well as the N—Mn—N bite angles (74.4 (1) and 74.2 (1)°) deviate greatly from the ideal

angle of 90° because of the constraint geometry of the bipy ring system.⁵⁸ The average C—C (1.385 Å) and C—N (1.344 Å) bond lengths within the rings, and the inter-ring C—C bonds (1.493 Å) are in good agreement with those given in the literature for non-coordinated bipy.^{59–61} The Mn—N bond distances (2.205–2.218 Å) (Table 2) for the bidentate bipy ligands are close to those of similar Mn(II) complexes.⁶⁰ The 2 bipy ligands around the Mn(II) atom are almost perpendicular to each other. The 5-membered chelating rings of Mn(II) and bipy N atoms are considerably planar; the N1—C5—C6—N2 and N4—C15—C16—N4 torsion angles are $2.3(5)^\circ$ and $6.4(4)^\circ$, respectively.

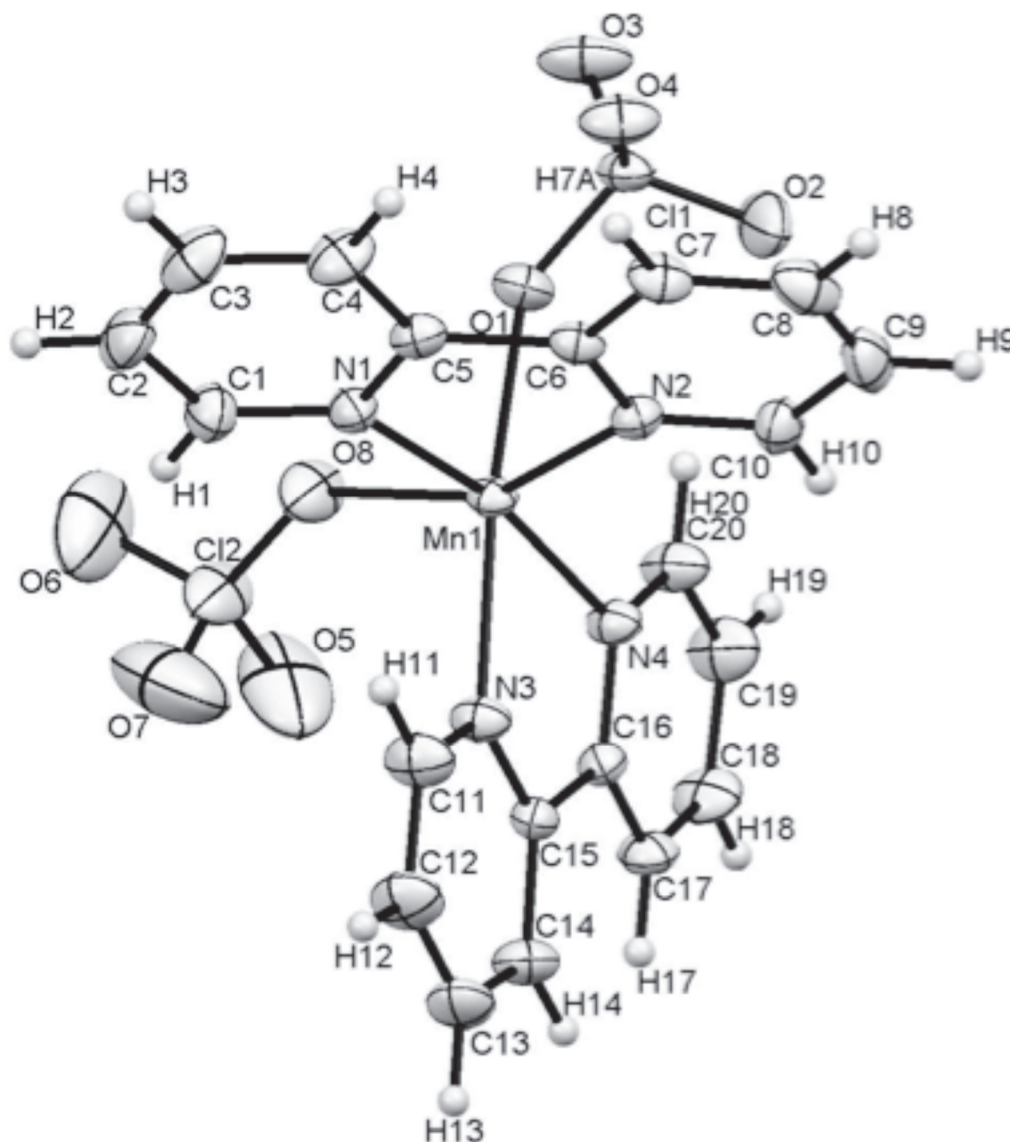


Figure 1. Molecular structure of Mn(II) complex.

Table 2. Selected geometric and hydrogen-bond parameters (Å, °).

Mn1—O8	2.193 (3)	N2—Mn1—N3	97.20 (10)	
Mn1—N4	2.205 (3)	O8—Mn1—N1	89.30 (11)	
Mn1—N2	2.206 (3)	N4—Mn1—N1	169.12 (10)	
Mn1—N3	2.218 (3)	N2—Mn1—N1	74.43 (10)	
Mn1—N1	2.219 (3)	N3—Mn1—N1	95.29 (10)	
Mn1—O1	2.279 (2)	O8—Mn1—O1	77.26 (10)	
O8—Mn1—N4	89.86 (11)	N4—Mn1—O1	94.64 (9)	
O8—Mn1—N2	156.84 (10)	N2—Mn1—O1	87.89 (9)	
N4—Mn1—N2	109.21 (10)	N3—Mn1—O1	168.74 (9)	
O8—Mn1—N3	100.68 (11)	N1—Mn1—O1	95.76 (9)	
N4—Mn1—N3	74.21 (10)			
D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
C1—H1 \cdots O7	0.95	2.65	3.506(6)	149
C1—H1 \cdots O8	0.95	2.66	3.179(46)	114
C14—H1 \cdots O4 ⁱ	0.95	2.68	3.613(4)	166
C17—H17A \cdots O4 ⁱ	0.95	2.52	3.465(4)	172
C10—H10 \cdots O7 ⁱⁱ	0.95	2.59	3.349(6)	136
C3—H3 \cdots O8 ⁱⁱⁱ	0.95	2.64	3.277(5)	124
C13—H13 \cdots O3 ^{iv}	0.95	2.69	3.231(5)	116
C18—H18 \cdots O6 ^v	0.95	2.41	3.238(6)	145
C19—H19 \cdots O5 ^v	0.95	2.69	3.418(6)	133
C7—H7A \cdots O3 ^{vi}	0.95	2.46	3.384(4)	162

Symmetry codes: (i) $x + 1/2, -y + 1/2, z + 1/2$ (ii) $-x + 1/2, +y + 1/2, -z + 1/2$ (iii) $-x, -y, -z$ (iv) $x - 1/2, -y + 1/2, z + 1/2$ (v) $-x + 1/2, +y + 1/2, -z + 1/2$ (vi) $x - 1, +y, +z$

No classical hydrogen bonding was found in the crystal structure. Furthermore, the occurrence of C—H \cdots O hydrogen bond interactions link the complex molecules into a 3-dimensional polymer network (Table 2). Nonclassical C_{bipy}—H \cdots O hydrogen bonds [average C—O distance = 3.280 (9) Å] link adjacent columns to form the resulting 3-dimensional network. The shortest Mn1 \cdots Mn1 interaction is 7.864 (8) Å. In nitrogen-containing molecules, the inductive effect of neutral or charged N atoms decreases the electron density in adjacent CH groups (C atoms) and enhances the facility with which they participate in C—H \cdots X hydrogen bonds, being usually the shortest ones. In the present case, all C atoms participated in hydrogen bonds. The substructure is generated by C—H \cdots O hydrogen bonds; atom C7 in the molecule acts as a hydrogen bond donor, via H7A to atom O3 ($2 + x, y, z$) and atom C14 acts as a hydrogen bond donor, via H14 to atom O4 ($-1/2 + x, 1/2 - y, -1/2 + z$) and atom C17 in the molecule acts as hydrogen bond donor, via H17 to atom O4 ($1/2 + x, 1/2 - y, -1/2 + z$), thus forming a chain running parallel to the b direction (Figure 2a). Another substructure is generated by C—H \cdots O hydrogen bonds; atom C18 in the molecule acts as a hydrogen bond donor, via H18, to atom O6 ($-1/2 - x, -1/2 + y, 1/2 - z$) and atom C19 in the molecule acts as a hydrogen bond donor, via H19, to atom O5 ($1/2 - x, -1/2 + y, 1/2 - z$), thus forming a chain running parallel to the a direction (Figure 2b). The remaining contacts involve the C atoms to N atoms whose H atoms are outer and have been determined to be the most acidic protons on the ring. In the structure of Mn(II)-complex, there are also relatively strong C—H \cdots π interactions between neighboring bipy rings and H atoms. The shortest $\pi \cdots$ H

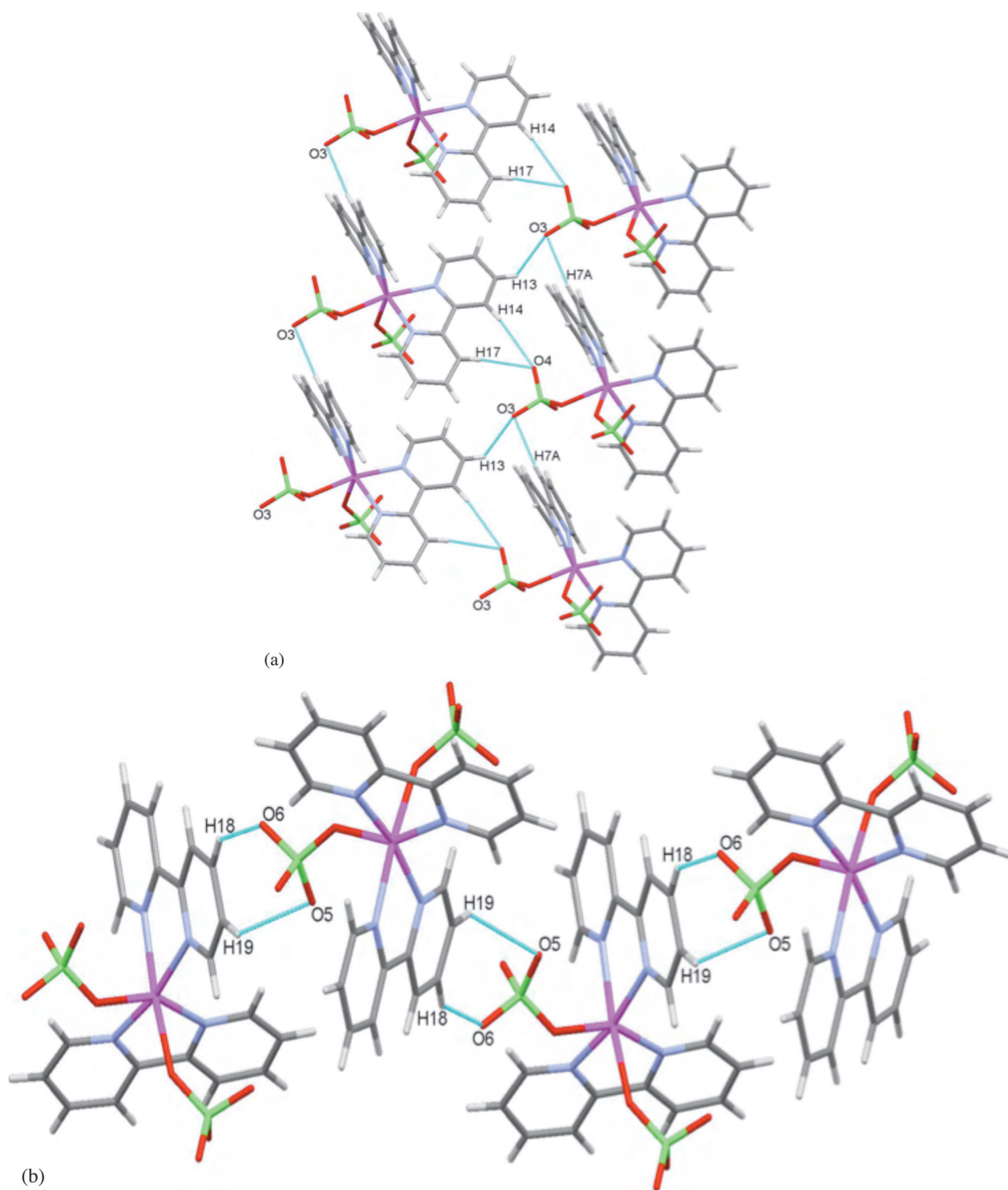


Figure 2. Part of the crystal structure of complex, showing the hydrogen bonding interactions (a) along **b** direction; b) along **a** direction; c) C - H... π interactions along **c** direction.

distance is 3.140 Å. The C19 atom in the molecule acts as a hydrogen bond donor to the bipy ring (N1—C5), thus forming a chain running parallel to the **c** direction (Figure 2c).

Catalytic studies

To evaluate the catalytic effect of complex, the oxidation of benzyl alcohol was carried out under different reaction conditions (Tables 3-6). A control experiment was done without catalyst precursor and we did not observe any aldehyde in the reaction mixture (Table 3, entry 1). $\text{Mn}(\text{ClO}_4)_2$ was also examined as catalyst for this reaction. No reaction took place and the starting material was recovered (Table 3, entry 2).

Table 3. The effect of additive and catalyst on oxidation of benzyl alcohol in acetonitrile.

Entry	Additive	T (°C)	T (h)	Tot. conv. ^a (%)	TON	TOF (h ⁻¹)	Products
1	- ^b	80	4	0	-		-
2	- ^c	80	4	0	-		-
3	- ^d	80	4	49	46	12	40.9 (benzaldehyde)
4	- ^e	80	4	71.9	83	21	71.9 (benzaldehyde)
5	KBr	80	4	98	113	28	29.0 (benzaldehyde) 69.0 (benzoic acid)
6	$\text{N}(\text{C}_4\text{H}_9)\text{Br}$	80	4	100	115	29	99.0 (benzaldehyde) 1.0 (benzoic acid)
7	<i>N</i> -Bromsucc.	80	4	30.6	35	9	18.6 (benzaldehyde) 12.0 (benzoic acid)

^aConversion was determined by GC.

^bWithout catalyst

^c $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ as catalyst without complex

^dThe molar ratio of substrate/*t*-BuOOH/catalyst was 230:8:1

^eThe molar ratio of substrate/*t*-BuOOH/catalyst was 115:8:1

The influence of amount of catalyst on the oxidation of benzyl alcohol was carried out under 2 different sets of conditions: the molar ratio of benzyl alcohol, *t*-BuOOH, and the catalyst was 115:8:1 and 230:8:1 and temperature (80 °C) and time (4 h) were kept constant. The yields were reported with respect to the substrate concentration and are illustrated in Table 3 (entries 3 and 4). At low catalyst concentration, moderate conversion of benzyl alcohol was achieved (49%, TON = 46) with 100% aldehyde selectivity and with the double the catalyst concentration the conversion of benzyl alcohol increased up to 71.9% (TON = 83) with aldehyde product (100%). This may be due to the availability of more active sites of the catalyst, which favors the accessibility of a larger number of molecules of substrates and oxidant to the catalyst.

The time dependence of the catalytic oxidation of benzyl alcohol was studied by performing the reaction of benzyl alcohol with TBHP in the presence of 0.88 mmol catalyst at 80 °C. The results are presented in Figure 3. The initiation period was not observed. The benzyl alcohol conversion increased as the reaction time was prolonged. Selectivity of the products did not significantly change with increasing time.

The catalytic experiments were conducted to examine the effect of cation and bromine anion with different additives (Table 3). In the absence of additive, the catalyst activity is moderate under similar conditions. The addition of potassium bromide leads to a substantial increase in conversion and also completes the oxidation processes to benzoic acid (69%) with KBr additive (Table 3, entry 5). A similar effect of bromine anion was

observed for the oxidation of secondary alcohols with Mn(II)(Salen) complexes.⁶² In contrast to KBr, the addition of *n*-Bu₄NBr leads to completion of the reaction with 99% aldehyde selectivity without benzoic acid formation (Table 3, entry 6). The addition of N-bromosuccinimide leads to a decrease in reaction rate (Table 3 entry 7).

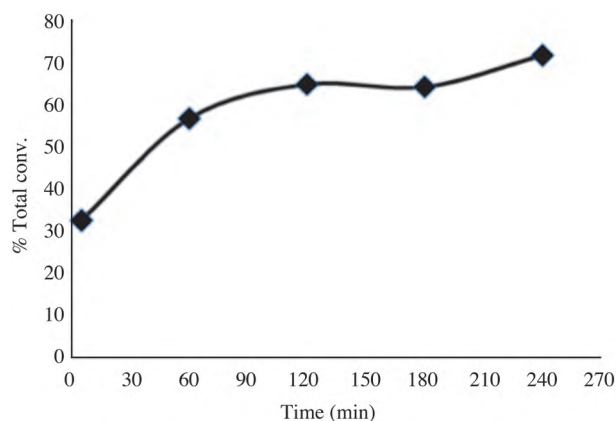


Figure 3. Time dependence of benzyl alcohol oxidation.

The catalyst was also tested for the catalytic oxidation of substituted benzylic alcohols under optimized reaction conditions. The presence of an electron-donating (3,4-dimethoxy-, 4-methoxy-benzyl alcohol) or an electron-withdrawing (4-chloro- and 2-nitrobenzyl alcohol) group in the substrate strongly affected the oxidation reaction and in both cases did not give any oxidation product under the studied conditions.

Effect of solvent, oxidant, and temperature

Generally, solvent plays an important role in the conversion and product distribution of oxidation reactions. In order to study the effect of solvents on the oxidation process, the experiments were carried out with different solvents (acetone, acetonitrile, ethanol, and methanol) and 2 biphasic solvent systems (hexane/H₂O and toluene/H₂O) under similar reaction conditions (TBHP (1.0 mL) at 80 °C) (Table 4). The selected solvent should possess certain criteria, for example it should dissolve the substrate and oxidant and it should be stable. As shown in Table 4, higher conversion was observed in polar aprotic solvent. In acetonitrile, among the tested solvents, we obtained the highest conversion and achieved aldehyde as the main product with 88% selectivity (Table 4, entry 4). Almost no reaction was observed when the polar protic solvents MeOH and EtOH were used (Table 4, entries 1 and 2). In contrast, low conversions were obtained with low polar solvent, like acetone (32.3%), hexane/water (21.5%), and toluene/water (24.7%) biphasic systems (Table 4, entries 5 and 6). The higher catalytic activity in acetonitrile is attributed to the high dielectric constant of solvent. The better solubility of substrate and oxidant in the solvent mean that the substrates and oxidant can easily approach the active sites of the catalyst. As a consequence, in terms of activity, acetonitrile was the best solvent for the studied catalytic system.

In order to design the best catalytic system, the effect of different oxidants such as TBHP, HP, and molecular oxygen was examined on the reaction rate of oxidation of benzyl alcohol. In the absence of oxidant, the reaction did not proceed. TBHP in acetonitrile medium was the most efficient oxidant source to oxidize

benzyl alcohol. Oxidants like HP and molecular oxygen were not effective oxygen sources for our catalytic system. The substrate-to-oxidant ratio is another important parameter influencing the results of this oxidation reaction. The effect of mole ratio of oxidant/benzyl alcohol was investigated in the range of 4-23 (Table 5). Lower conversion of benzyl alcohol was observed with 1:4 mol ratios of benzyl alcohol/TBHP. The conversion of benzyl alcohol increased markedly with increasing substrate-to-oxidant molar ratio. Further increases in this ratio above 1:15 led to decreased conversion but the selectivity for aldehyde did not change. Based on the results, the mole ratio of 1:15 was chosen as the optimal for benzyl alcohol/TBHP.

Table 4. The effect of solvent on oxidation of benzyl alcohol.

Entry	Solvent	T (°C)	t (h)	Total conv. (%)	TON	TOF (h ⁻¹)	Aldehyde selectivity (%)	Products ^a
1	Methanol	80	4	5.6	6	1.5	100	5.60 (benzaldehyde)
2	Ethanol	80	4	6.20	7	1.8	100	6.20 (benzaldehyde)
3	Acetone	60	4	32.3	37	9.3	94	30.4 (benzaldehyde) 1.90 (benzoic acid)
4	Acetonitrile	80	4	60.2	69	17.3	88	52.8 (benzaldehyde) 7.40 (benzoic acid)
5	Hexane/H ₂ O	80	4	21.5	25	6.3	100	21.5 (benzaldehyde)
6	Toluene/ H ₂ O	80	4	24.7	28	7	100	24.7 (benzaldehyde)

Reaction conditions: solvent (10 mL), the molar ratio of substrate/*t*-BuOOH/catalyst was 115:15:1.

^a Conversion was determined by GC.

Table 5. The effect of *t*-BuOOH on oxidation of benzyl alcohol.

Entry	Oxidant	Tot. conv. (%)	Aldehyde selectivity (%)	TON	TOF (h ⁻¹)	Products ^a
1	0.5 mL	43.4	100	49	12.3	41.8 (benzaldehyde)
2	1.0 mL	60.2	88	60	15	52.8 (benzaldehyde) 7.40 (benzoic acid)
3	2.0 mL	71.9	100	83	20.8	71.9 (benzaldehyde)
4	3.0 mL	56.9	100	65	21.7	56.9 (benzaldehyde)

Reaction conditions: Catalyst (8.34×10^{-6} mol), benzyl alcohol (9.6×10^{-4} mol), solvent: acetonitrile (10 mL) at 80 °C, 4 h reaction time.

^a Conversion was determined by GC.

The reaction temperature has a strong influence on the progress of benzyl alcohol oxidation. The oxidation reaction was carried out using 1:8 mol ratio of benzyl alcohol/TBHP in acetonitrile for 4 h with the range of reaction temperatures from 40 to 80 °C and the results are shown in Table 6. As expected, benzyl alcohol conversion increased with increasing reaction temperature. The reaction was carried out by heating the reaction mixture (80 °C) for 4 h, which resulted in 71.9% conversion with 100% aldehyde selectivity (Table 6, entry 4).

Table 6. The effect of temperature on oxidation of benzyl alcohol.

Entry	T (°C)	t (h)	Total conv. (%)	Aldehyde selectivity (%)	TON	TOF (h ⁻¹)	Products ^a
1	40	4	53.6	100	62	15.5	53.6 (Benzaldehyde)
2	50	4	59.0	100	68	17	59.0 (Benzaldehyde)
3	60	4	63.9	100	73	18.3	63.9 (Benzaldehyde)
4	80	4	71.9	100	83	20.8	71.9 (Benzaldehyde)

Reaction conditions: oxidant:*t*-BuOOH solvent:acetonitrile (10 mL), 4 h, the molar ratio of substrate/*t*-BuOOH/catalyst was 115:8:1.

^a Conversion was determined by GC.

UV-visible spectroscopy of reaction intermediates

The oxidation system was further examined by UV-vis spectroscopy in order to investigate the catalytic mechanism for the Mn(II)-catalyzed benzyl alcohol oxidation in acetonitrile and the results are illustrated in Figure 4. The spectrum of the complex shows absorption bands at around 294 nm and 244 nm, which are assigned to the LMCT.⁴⁸ When the solution was treated with aqueous *t*-BuOOH, the LMCT absorbance decreased with a shift to 238 nm and 285 nm, which may be due to the cleavage of an axial Mn–O bond of the

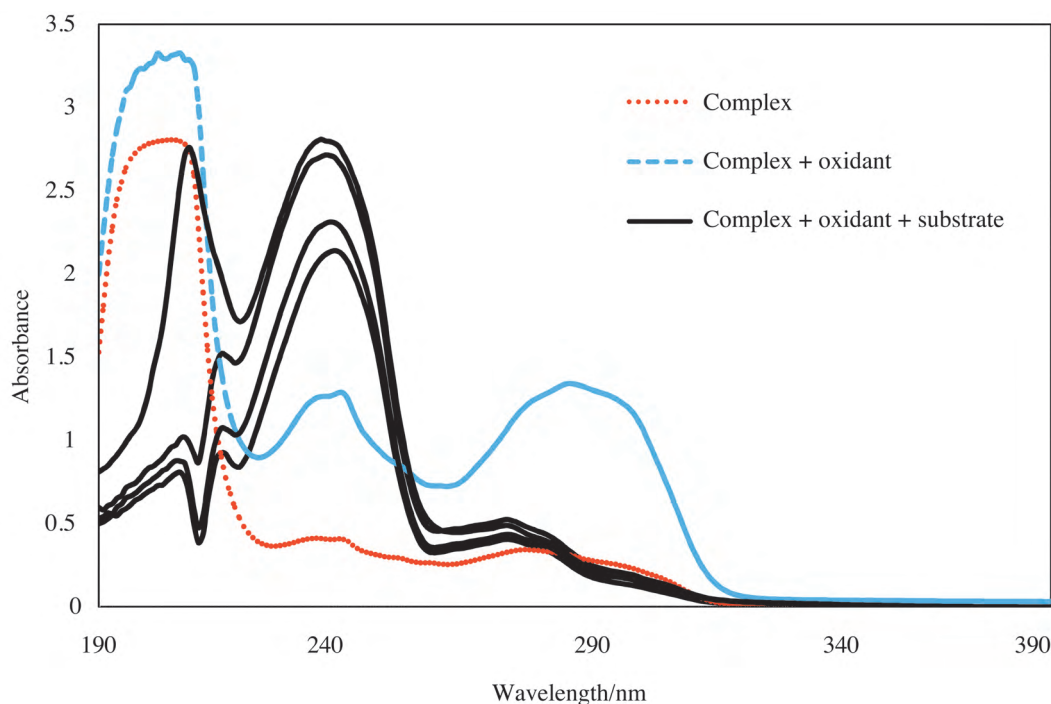


Figure 4. ···· Spectra of complex in acetonitrile, ---- Spectra immediately after addition of *t*-BuOOH, ——— time evolution of spectra accompanying the oxidation of benzyl alcohol after addition of substrate.

complex to form an intermediate. Then, when adding benzyl alcohol to the solution further, the maxima around 240 nm rapidly increased and a new absorption band centered around 216 nm developed in 5 min, implying that benzyl alcohol interacted with this intermediate to form a new intermediate. The spectra did not change as the reaction proceeded. We must note that there is no clear absorbance around 500-600 nm assigned to the ligand to metal charge transfer of the high valent manganese, indicating that the Mn(V) = O should not be responsible for the oxidation of alcohols using *t*-BuOOH as an oxidant.

Conclusion

In summary, we synthesized and characterized a new manganese complex, [Mn(bipy)₂(ClO₄)₂], and demonstrated its catalytic activity in the selective oxidation of benzyl alcohol to aldehyde under mild homogeneous conditions with environmentally benign *t*-BuOOH in acetonitrile. The high selectivity, efficiency, safety, and low cost of this complex make it a good choice for oxidant of benzyl alcohol.

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