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Manganese(II) complexes of hydrazone based NNO-donor ligands and their catalytic activity in the oxidation of olefins

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The reaction between tridentate NNO donor hydrazone ligands, (*E*)-2-cyano-*N*'-(phenyl(pyridin-2-yl)methylene)acetohydrazide (HL¹) and (*E*)-2-cyano-*N*'-(1-(pyridin-2-

yl)ethylidene)acetohydrazide (HL²), with MnCl₂·4H₂O in methanol resulted in

 $[Mn(HL^1)Cl_2(CH_3OH)]$ (1) and $[Mn(HL^2)Cl_2(CH_3OH)]$ (2). Molecular structures of the complexes were determined by single-crystal X-ray diffraction. All of the investigated compounds were further characterized by elemental analysis, FT-IR, TGA and UV-Vis spectroscopy. These complexes were used as catalysts for olefin oxidation in the presence of *tert*-butylhydroperoxide (TBHP) as an oxidant. Under similar experimental conditions with equal manganese loading, the presence of $[Mn(HL^2)Cl_2(CH_3OH)]$ (2) resulted in higher conversion than $[Mn(HL^1)Cl_2(CH_3OH)]$ (1).

Keywords: Manganese(II) complex; Crystal structure; Spectroscopic studies; Oxidation; Catalyst

1. Introduction

The central role played by epoxides in all areas of synthetic organic chemistry [1] caused the expansion of new sustainable and environmentally friendly processes for olefin oxidation [2]. In this regard, researchers have focused on replacing methods based on rare and potentially toxic metals such as chromium, ruthenium and osmium with metals of less toxicity such as iron,

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titanium, manganese, tungsten, and molybdenum [3]. In the area of oxidative transformations, one major aim is replacement of classical toxic waste-producing oxidants, with catalytic procedures using an environmentally safe oxidant. In bulk chemistry, stoichiometric reagents (such as K₂CrO₇, KMnO₄ and derivatives) are regularly applied in these reactions. Nevertheless, these reagents are expensive and produce a stoichiometric amount of (often toxic) inorganic salts as waste [4]. Other suitable oxidants being considered include molecular oxygen, hydrogen peroxide and *tert*-butyl hydroperoxide (TBHP) where there is either no by-product, the by-product is environmentally benign, or the by-product can be easily recovered and recycled [5]. *tert*-Butanol, a useful high-octane compound, is formed as the by-product when *tert*-butyl hydroperoxide is used as the oxidant [6].

Synthesis of coordination compounds based on hydrazone ligands have been reported [7, 8]. Metal complexes of aroylhydrazone ligands have remained an attractive area of research for inorganic chemists due to their versatile coordination chemistry and ability to generate different molecular structures [9, 10]. Aroylhydrazone metal complexes have biological and pharmacological applications [11, 12]. The biological activity associated with these compounds is attributed to the presence of the -C(=O)-NH-N=CH- moiety [13]. Aroylhydrazone Schiff base complexes of transition metals have shown high catalytic activities in chemical reactions such as C–N bond formation using Chan-Lam coupling [14], *trans* amidation of carboxamides with amines [15], epoxidation of olefins [16, 17] and polymerization of ethylene [18]. A series of Mn(II) complexes containing substituted aroylhydrazone ligands have been used in catalytic epoxidation of olefins with *tert*-butylhydroperoxide [19-21].

As a result of our ongoing investigations of the structural and catalytic properties of transition metal complexes with hydrazone ligands, we report here the synthesis, characterization and efficiency in hydrocarbon oxidation of two manganese complexes (scheme 1). These complexes were obtained by coordinated single condensation products of 2-cyanoacetohydrazide with 2-benzoylpyridine or 2-acetylpyridine and characterized by spectroscopic methods and single crystal X-ray analysis.

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Scheme 1. Schematic representation of the synthesis of ligands and complexes,

2. Experimental

2.1. Materials

All chemicals and solvents were purchased from Merck and used as received. FT-IR spectra were recorded in KBr disks with a Bruker FT-IR spectrophotometer. Elemental analyses (carbon, hydrogen and nitrogen) were obtained applying a Carlo ERBA Model EA 1108 analyzer. Atomic absorption analysis was carried out using Varian Spectra AA 220 equipment. Thermogravimetric analysis (TGA) was performed on a STA409PC Netzsch thermal analyzer in flowing N₂ (60 mL min⁻¹) at a heating rate of 5 °C min⁻¹. ¹H and ¹³C NMR spectra of the ligands in DMSO-*d*₆ solution were recorded on a Bruker 250 MHz spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane (TMS). The reaction products of oxidation were determined and analyzed using an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μ m × 0.25 μ m) and gas chromatograph-mass spectrometry (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector).

2.2. Synthesis of (E)-2-cyano-N'-(phenyl(pyridin-2-yl)methylene)acetohydrazide (HL^1)

 HL^4 was synthesized by refluxing a mixture of 2-cyanoacetohydrazide (10 mmol, 0.99 g) with 2-benzoylpyridine (10 mmol, 1.83 g) in 20 mL of methanol for 5 h [22]. The volume of the solution was decreased to 5 mL by removing the solvent under reduced pressure as the solution was cooled to room temperature. The obtained solids were separated and filtered off, washed

with cooled methanol and then dried in air. Yield 85.1% (2.25 g). *Anal*. Calcd. for C₁₅H₁₂N₄O (%): C, 68.17; H, 4.58; N, 21.20. Found: C, 68.13; H, 4.61; N, 21.27. Selected FT-R (KBr, cm⁻¹): 3103 (m, NH), 2998 (w), 2918 (w, C-H aliphatic), 2260 (m, C \equiv N), 1686 (vs, C=O), 1665 (vs), 1598 (s, C=N), 1567 (s), 1472 (w), 1384 (w, C–O), 1282 (s), 1247 (vs), 1121 (m), 940 (m), 799 (s), 744 (s), 696 (vs), 661 (s), 452 (m), 412 (s). ¹H NMR (250.13 MHz, DMSO-d₆, 25 °C, TMS, ppm): δ = 4.36 (2H, s, CH₂-CN), 7.36-7.48 (3H, m), 7.89-8.05 (3H, m), 8.43 (1H, d, *J* = 8.00 Hz), 8.68 (1H, d, *J* = 4.50 Hz), 9.16 (1H, d, *J* = 7.50 Hz), 10.54 ppm (1H, s, NH). ¹³C NMR (62.9 MHz, DMSO-d₆, 25 °C, TMS, ppm): δ = 25.4 (-CH₂CN), 121.0, 124.5, 128.7, 128.9, 129.2, 129.3, 129.6, 129.9, 137.1, 138.5, 149.0 and 165.9 ppm. UV-Vis (MeOH, λ_{max} (ϵ , M⁻¹cm⁻¹): 204 (30400), 292 nm (17200).

2.3. Synthesis of (E)-2-cyano-N'-(1-(pyridin-2-yl)ethylidene)acetohydrazide (HL^2)

HL² was synthesized by refluxing a mixture of 2-cyanoacetohydrazide (10 mmol, 0.99 g) with 2-acetylpyridine (10 mmol, 1.21 g) in 20 mL of methanol for 5 h with the same procedure used for HL¹. Yield 88.5% (1.79 g). *Anal*. Calcd. for C₁₀H₁₀N₄O (%): C, 59.40; H, 4.98; N, 27.71. Found: C, 59.37; H, 5.03; N, 27.80. Selected FT-IR (KBr, cm⁻¹): 3208 (w), 3150 (w, NH), 2976 (w), 2934 (w, C-H aliphatic), 2264 (m, C=N), 1690 (vs, C=O), 1578 (s, C=N), 1460 (s), 1393 (s, C–O), 1316 (s), 1249 (s), 1108 (m), 1047 (m), 928 (m), 852 (s), 786 (vs), 728 (vs), 702 (vs), 626 (s), 568 (s), 474 (w), 439 (s), 406 (s). ¹H NMR (250.13 MHz, DMSO-d₆, 25 °C, TMS, ppm): δ = 2.29 (3H, s, CH₃), 4.27 (2H, s, CH₂-CN), 7.37 (1H, t, *J* = 7.25 Hz), 7.79 (1H, t, *J* = 7.25 Hz), 8.05 (1H, d, *J* = 7.75 Hz), 8.55 (1H, d, *J* = 7.50 Hz), 11.19 ppm (1H, s, NH). ¹³C NMR (62.9 MHz, DMSO-d₆, 25 °C, TMS, ppm): δ = 12.6 (-CH₃), 25.4 (-CH₂CN), 116.6, 120.7, 124.5, 137.0, 148.9, 150.2, 155.0 and 166.4 ppm. UV-Vis (MeOH, λ_{max} (ε, M⁻¹cm⁻¹): 212 (13080), 289 nm (19780).

2.4. Synthesis of $[Mn(HL^1)Cl_2(CH_3OH)]$ (1)

HL¹ (1.0 mmol, 0.26 g) and MnCl₂·4H₂O (2.0 mmol, 0.39 g) were dissolved in 20 mL of CH₃OH and the resulting solution refluxed for 8 h. The solution was left at room temperature for two days and the obtained crystalline dark brown material was filtered off and dried in air. Yield: (63%, 0.26 g). *Anal.* Calcd. for C₁₆H₁₆Cl₂MnN₄O₂ (%): C, 45.52; H, 3.82; N, 13.27; Mn, 13.01. Found: C, 45.59; H, 3.85; N, 13.32; Mn, 12.96. Selected FT-IR (KBr, cm⁻¹): 3478 (m, br, OH),

3319 (m, br, OH), 3196 (m, NH), 2947 (w), 2911 (w, C-H aliphatic), 2262 (w, C=N), 1667 (vs, C=O), 1616 (s, C=N), 1525 (s), 1465 (m), 1392 (m, C–O), 1329 (s), 1262 (s), 1228 (s), 1193 (s), 1057 (m), 917 (w), 792 (s), 745 (s), 705 (vs), 665 (s), 574 (Mn-O), 436 (Mn-N).; UV-Vis (MeOH): λ_{max} , nm (ε, M⁻¹cm⁻¹): 205 (30240), 289 (17240), 350 nm (7320).

2.5. Synthesis of $[Mn(HL^2)Cl_2(CH_3OH)]$ (2)

Complex **2** was synthesized by reaction of HL^2 (1.0 mmol, 0.20 g) and $MnCl_2 \cdot 4H_2O$ (2.0 mmol, 0.39 g) in methanol applying the same procedure as reported for **1**. Dark brown crystals of **2** were obtained by slow solvent evaporation during three days. Yield: (71%, 0.26 g). *Anal*. Calcd. for $C_{11}H_{14}Cl_2MnN_4O_2$ (%): C, 36.69; H, 3.92; N, 15.56; Mn, 15.26. Found: C, 36.63; H, 3.88; N, 15.49; Mn, 15.32. Selected FT-IR (KBr, cm⁻¹): 3364 (br, w, OH), 3162 (w, NH), 2941 (w), 2859 (w, C-H aliphatic), 2259 (m, C=N), 1658 (vs, C=O), 1596 (m, C=N), 1538 (s), 1471 (m), 1387 (w, C–O), 1205 (s), 1001 (s), 808 (s), 566 (Mn-O), 429 (Mn-N). UV-Vis (MeOH): λ_{max} , nm (ϵ , M⁻¹cm⁻¹): 214 (12860), 276 (17340), 339 nm (5220).

2.6. X-ray diffraction data collection and refinement

A summary of the crystal data and refinement details for the compounds discussed in this paper is given in table 1. Only special features of the analyses are mentioned here. Single crystals of **1** and **2** were selected directly from the mother liquors under a microscope and sealed in thinwalled glass capillaries. Their quality was checked on a single-crystal X-ray diffractometer (Stoe Image Plate Diffraction System, IPDS 2T) and complete intensity data sets were collected using graphite-monochromated Mo-K_{α} radiation. All data sets were corrected for Lorentz, polarization and absorption effects. The structures were solved by direct methods using SHELXS97 [23] and SIR92 [24] for **1** and **2**, respectively, completed with difference Fourier synthesis and refined with full-matrix least-square procedures based on F² using SHELXL97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C-bonded hydrogens were placed in idealized positions and constrained to ride on their parent atoms. The molecular structure plots were prepared using Diamond [25].

CCDC 1504221 and 1504222 contain supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

2.7. General oxidation procedure

Oxidation reactions were carried out under air with acetonitrile as solvent and TBHP (80% solution in water) as oxidant. In a typical experiment, a mixture of 2.4×10^{-3} mmol of **1**, 2.0 mL solvent and 1.0 mmol of cyclohexene was placed in a 25 mL round bottomed glass flask. The mixture was heated to the desired temperature and after addition of TBHP, the solution was placed in an oil bath. At appropriate intervals, aliquots were removed and analyzed immediately by GC. The oxidation products were identified by comparison of their retention times with those of authentic samples. Yields are based on cyclohexene.

3. Results and discussion

3.1. Preparation and characterization of 1 and 2

The reaction of 2-cyanoacetohydrazide with 2-benzoylpyridine or 2-acetylpyridine in methanol gave the desired tridentate Schiff bases (HL¹ or HL²) in high yield and purity. Elemental analysis together with ¹H NMR and ¹³C NMR spectra of HL¹ and HL² in DMSO- d_6 confirmed the proposed structure of the ligands (scheme 1). In the ¹H NMR spectrum of these ligands the signal of the N*H*-group appears at δ 10.54 (in HL¹) and 11.9 (in HL²) which are substantially broadened, indicating their involvement in hydrogen bonding interactions.

The infrared spectra of HL^1 and HL^2 (figures S1 and S2) display bands at ~3150, ~2260, ~1690 and ~1590 cm⁻¹, which are assigned to v(N-H), v(C=N), v(C=O) and v(C=N) of the free Schiff base, respectively. Complexes **1** and **2** were synthesized by reaction of the corresponding Schiff bases, HL^1 and HL^2 , with $MnCl_2 \cdot 4H_2O$ in methanol. Dark brown crystals of **1** and **2** grew by slow evaporation of methanol and were collected by filtration. The C=O bands of the free ligands are shifted to lower frequencies in the FT-IR spectrum of **1** and **2** (figures S3 and S4), which confirm coordination of HL^1 and HL^2 as neutral ligands in the keto form [26]. Moreover, there is a band at 3150 cm⁻¹ in the FT-IR spectrum of **1** and **2** which is due to the presence of an amidic N-H bond and confirms coordination of ligands in the keto form. In the FT-IR spectra of the complexes, the presence of Mn-O and Mn-N are indicated by weak bands at ~570 and ~430 cm⁻¹, respectively [27]. The very broad band at 3400 cm⁻¹ in the FT-IR spectrum of **1** and **2** is attributed to O-H of coordinated water or methanol molecules involved in hydrogen bonding interactions [28].

The UV–Vis spectra of HL^1 and HL^2 and of **1** and **2** were obtained in methanolic solutions and are shown in figure 1. The complexes exhibit intense bands at ~350 nm, attributed to charge transfer (CT) transitions [29]. The intense higher-energy bands at ~270 nm can be attributed to intra-ligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions [30].

3.2. Thermal investigation

To examine thermal stabilities of complexes, thermogravimetric analysis (TGA) of **1** was made at a heating rate of 5 °C/min from 30–800 °C. TGA curve of **1** (figure S5) shows that **1** is stable to 115 °C, where the coordinated CH₃OH is removed [observed (7.79%), calculated (7.58%)] between 115–145 °C, then at 270 °C the Cl ligands are removed [observed (16.35%), calculated (16.80%)]. Finally, hydrazone ligand is removed during third step up to 440 °C. The overall mass loss to 800 °C is 80% of starting mass and indicates that the final product should be oxides of manganese.

3.3. X-ray crystal structures of 1 and 2

In order to define the coordination sphere of Mn in 1 and 2, single-crystal X-ray diffraction analyses were performed. The molecular structure of 1 and 2 are shown in figures 2 and 3, respectively. Selected bond lengths and angles are given in table 2. The manganese(II) in both complexes has distorted octahedral coordination with one oxygen and two nitrogen donors provided by the Schiff base ligands, one oxygen, provided by coordinated water in 1 and methanol in 2, and two chlorides. In both complexes, the two chlorides are located *cis* with respect to each other with Cl1-Mn1-Cl2 angles of 97.81(3)° and 94.02(2)° in 1 and 2, respectively. One Cl is axial and the other is equatorial. The Mn–Cl, Mn–N and Mn–O bond lengths are in normal ranges as reported for Mn(II) complexes [31]. In 1 the C110=O110 and C110–N19 bond lengths are 1.227(3) and 1.350(3) Å, respectively, and in 2 these bond lengths are 1.227(2) and 1.350(2) Å, respectively. These bond lengths are close to those observed in hydrazone ligands coordinated in the keto form [32]. Although the value of the C=O bond length is considerably shorter than the C–O bond length in reported complexes containing the enol form of hydrazone ligands, they are relatively longer than the C=O bond lengths of free hydrazones [33]. Moreover, the C–NH– bond lengths in both 1 and 2 are considerably longer that the C=N bond lengths in coordinated hydrazones in the enol form [34]. All these observations indicate

coordination of both HL^1 and HL^2 as neutral tridentate ligands in the keto form, which is also confirmed by the IR spectrum. A coordinated water or methanol is present in the crystal structures of **1** and **2**, respectively. These molecules are engaged in O–H···Cl hydrogen bonding interactions. Moreover, there are N–H···Cl and several directed C–H···Cl interactions which further stabilize the crystal structures of both **1** (figure S6) and **2** (figure S7).

3.4. Catalytic activity

The oxidation of cyclohexene as a substrate with H_2O_2 (30%) and TBHP (80% solution in water) was carried out in the presence of **1** as a catalyst precursor. In order to find the optimum conditions for the oxidation reactions, oxidation of cyclohexene was studied under various conditions. The oxidation of cyclohexene in the presence of H_2O_2 was not significant which can be attributed to degradation of H_2O_2 in the presence of manganese [19]. Oxidation of cyclohexene was significant when TBHP was used as oxidant, so, it was selected as oxidant in the rest of the reactions. The conversion increased with increasing amounts of *tert*-butylhydroperoxide from 0.5 mmol to 1 mmol, but further increase resulted in no notable increase of conversion (table 3, entries 1-3).

It may be pointed out that the addition of the catalyst led to an increase in conversion of cyclohexene. A relatively low conversion (36%) was obtained with 1.2×10^{-3} mmol catalyst, but a higher conversion (71%) with 2.4×10^{-3} mmol catalyst. A still larger quantity resulted in lower conversion, 67% with 4.8×10^{-3} mmol catalyst. This may be due to increased degradation of the oxidant at a higher concentration of the catalyst [35]. In the blank reaction under similar conditions with cyclohexene, only 5% of cyclohexene was oxidized after 24 h [36]. Thus, the presence of **1** as a catalyst precursor is necessary for the oxidation reaction.

When the temperature was increased (from 40 to 80 °C), the conversion correspondingly increased from 28% to 71%, as shown in table 3 (entries 2, 6 and 7). Solvent in the catalytic oxidation of cyclohexene was examined in the current catalytic system (table 4). It was found that the cyclohexene oxidation reaction had the highest reactivity and selectivity when the reaction was performed in 1,2-dichloroethane, whereas methanol and ethanol were not the most suitable solvents for [Mn(HL¹)Cl₂(CH₃OH)]. The efficiency of the catalysts in different solvents decreases in the order 1,2-dichloroethane > acetonitrile > methanol > CCl₄, indicating

a significant role of solvent for the oxidation reactions as investigated in this work (conversion 7–71%).

To establish the scope for the activity of $[Mn(HL^1)Cl_2(CH_3OH)]$, this study was further extended to the catalytic oxidation of linear and cyclic olefins, namely styrene, α -methyl styrene, 1-octene, 1-decene, cyclooctene and indene, using $[Mn(HL^1)Cl_2(CH_3OH)]$ (table 5). Generally, excellent epoxide selectivity was observed for the tested aliphatic and aromatic substrates (table 5, entries 1-7). The present catalytic system is completely selective for epoxidation of cyclooctene, 1-octene, 1-decene and indene, but is not selective for styrene and α -methyl styrene because benzaldehyde and acetophenone were byproducts, respectively. The production of benzaldehyde in the oxidation of styrene is due to over-oxidation of styrene oxide in the presence of TBHP. The lower catalytic activity of α -methyl styrene compared to styrene seems to be due to the steric hindrance of the methyl substituent of the former [37]. It should be noted that if electronic effects due to the methyl substituent were important, then, α -methyl styrene as a more electron-rich olefin would be expected to show higher reactivity than styrene.

In the following, to investigate substituent effects on catalytic activity, we have examined the catalytic activity of $[Mn(HL^2)Cl_2(CH_3OH)]$ (2) under the same conditions as were optimized for $[Mn(HL^1)Cl_2(CH_3OH)]$ (1) as the catalyst (table 6, entries 1-7). It is clear from the table that the percentage conversion of olefins varies in the order 2 > 1. Both electron donation and steric effect of the phenyl substituent rather than methyl in the hydrazone Schiff base ligand decrease the catalytic activity of 1 relative to 2 [38]. Steric effect of the phenyl substituent rather than methyl in the hydrazone Schiff base ligand decrease the catalytic activity of 1 relative to 2 [38]. Electron-donor substituents (such as methyl) seem to facilitate oxidation of M(II) to M(III) [39, 40]. It should be noted that the oxidation of Mn(II) to Mn(III) has been proposed as an important step in the Mn-hydrazone catalyzed oxidation of hydrocarbons with TBHP. In general, electronic and steric effects of the ligand substituent are rather obvious since they are near the Mn(II) center.

Although the details of catalytic mechanism are not studied in the present work, on the basis of the electronic absorption spectroscopy studies (figure S8) and also by considering the previous studies on catalytic oxidation by manganese complexes [41-43], it is predicted that the key step in this catalytic process is the oxidation of substrates by a Mn-(oxido/peroxido)-hydrazone Schiff base species formed after addition of TBHP to solution of complex.

4. Conclusion

Two new manganese(II) complexes were synthesized and characterized by various analyses and their structures were determined by single crystal X-ray analysis. These complexes were used as catalysts in oxidation of olefins in the presence of TBHP as oxidant. The catalytic potential of the manganese(II) complexes in oxidation of olefins was studied, choosing oxidation of cyclooctene, styrene, α -methyl styrene, indene, cyclohexene, 1-octene and 1-decene as model reactions. These complexes catalyze the oxidative conversion of styrene to styrene oxide and its successive products, and cyclohexene to cyclohexene oxide, 2-cyclohexene-1-ol, indene to indene oxide and ketone, α -methyl styrene to α -methyl styrene epoxide and acetophenone, while the present catalytic system was selective for epoxidation of cyclooctene, 1-octene and 1-decene. All the catalytic processes have clean, safe and operationally simple characteristics.

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Figure 1. UV-Vis spectra of (a) HL^1 , (b) $[Mn(HL^1)Cl_2(CH_3OH)]$ (1), (c) HL^2 and (d) $[Mn(HL^2)Cl_2(CH_3OH)]$ (2).



Figure 2. Molecular structure of 1; thermal ellipsoids are drawn at 50% probability level.



Figure 3. Molecular structure of 2; thermal ellipsoids are drawn at 50% probability level

	1	2
Empirical formula	$C_{15}H_{14}Cl_2MnN_4O_2$	$C_{11}H_{14}Cl_2MnN_4O_2$
Formula weight	408.14	360.10
Temperature (<i>K</i>)	293	293
Crystal system	Monoclinic	Monoclinic
Space group	Cc	$P2_1/c$
Crystal size (mm)	$0.3 \times 0.2 \times 0.2$	$0.3 \times 0.1 \times 0.1$
<i>a</i> (Å)	13.4270(7)	7.1368(3)
<i>b</i> (Å)	19.0994(8)	18.0670(7)
<i>c</i> (Å)	7.0430(4)	12.8545(5)
α (°)	90	90
β (°)	108.044(4)	117.114(3)
γ (°)	90	90
$V(Å^3)$	1717.33(15)	1475.30(11)
Ζ	4	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.579	1.621
<i>F</i> (000)	828	732
$\mu (\mathrm{mm}^{-1})$	1.10	1.26
θ range (°)	1,9-26.8	2.1-26.8
Reflections collected	12777	17129
Unique reflections, $R_{(int)}$	3617, 0.068	3112, 0.057
Observed reflections $[I > 2\sigma(I)]$	3564	2859
Goodness-of-fit (GØF)	1.06	1.13
Absorption correction	Numerical	Numerical
T_{\min}, T_{\max}	0.5751, 0.8585	0.6098, 0.9047
Final R_1 , $wR_2 [I > 2\sigma(I)]$	0.035, 0.092	0.029, 0.074
Flackx	0.01	
$I = \frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} +$	1.09 -0.39	0.490.65

Table 1. Crystal data for $[Mn(HL^1)Cl_2(H_2O)]$ (1) and $[Mn(HL^2)Cl_2(CH_3OH)]$ (2).

Complex 1		Complex 2	
Mn1—0005	2.226(2)	Mn1—N8	2.2387(12)
Mn1—N18	2.256(2)	Mn1-0101	2.2495(11)
Mn1—N11	2.272(2)	Mn1—N1	2.2711(13)
Mn1—O110	2.2797(19)	Mn1—O21	2.2717(12)
Mn1—Cl1	2.4048(8)	Mn1—Cl1	2.3757(4)
Mn1—Cl2	2.5015(7)	Mn1—Cl2	2.5312(5)
O005—Mn1—N18	81.34(8)	N8—Mn1—O101	70.99(4)
O005—Mn1—N11	90.50(8)	N8—Mn1—N1	70.36(5)
N18—Mn1—N11	69.54(8)	N8—Mn1—O21	81.71(4)
O005—Mn1—O110	80.35(8)	O101—Mn1—O21	80.11(4)
N18—Mn1—O110	70.36(8)	N1—Mn1—O21	89.21(5)
N11—Mn1—O110	139.75(7)	N1—Mn1—Cl1	101.49(3)
O005—Mn1—C11	99.35(7)	O21—Mn1—Cl1	92.81(3)
N11—Mn1—Cl1	100.26(6)	N8—Mn1—C12	92.53(3)
N18—Mn1—Cl2	83.08(6)	O101-Mn1-Cl2	90.25(3)
N11—Mn1—Cl2	93.64(6)	N1—Mn1—Cl2	96.62(3)
O110-Mn1-Cl2	84.78(5)	O21—Mn1—Cl2	169.96(3)
Cl1—Mn1—Cl2	97.81(3)	Cl1—Mn1—Cl2	94.018(15)

Table 2. Selected bond distances and angles in the molecular structures of 1 and 2.

 \mathcal{Y}^{*}

Entry	[TBHP]/[C ₆ H ₁₀] Molar ratio	Conversion (%) ^b	Epoxide selectivity (%) ^c	TON ^d	TOF ^e (h ⁻¹)
1	0.5	23	73	96	19
2	1	71	71	296	59.2
3	1.5	74	70	308	61.6
4 ^f	1	36	75	300	60
5 ^g	1	67	70	139.6	28
6 ^h	1	28	84	104	21
7 ⁱ	1	53	78	221	44

Table 3. Catalytic activity of [Mn(HL¹)Cl₂(CH₃OH)] on cyclohexene oxidation.^a

^a *Reaction conditions*: catalyst ([Mn(HL¹)Cl₂(CH₃OH)]) (2.4×10⁻³ mmol); reaction temperature, 80 °C; cyclohexene, 1 mmol; 1,2-DCE (as solvent), 2 mL; reaction time, 5 h; ^b Conversions are based on the starting substrate for homogeneous conditions; ^c The other product is 2-cyclohexene1-ol; ^d Turnover number (TON) = (mmol of product)/(mmol of catalyst); ^e Turnover frequency (TOF) = (mmol of oxide)/(mmol of catalyst × time); ^f catalyst amount = 1.2×10^{-3} mmol; ^g catalyst amount = 4.8×10^{-3} mmol, ^h Temperature = 40 °C; ⁱ Temperature = 60 °C

Entry	Solvent	Conversion (%) ^b	TON ^c	TOF ^d (h ⁻¹)
1	EtOH	16	66	13.2
2	CCl_4	7	29	5.8
3	1,2-DCE	71	296	59.2
4	CH ₃ CN	60	250	50
5	MeOH	28	117	23.4

Table 4. Effect of various solvents on cyclohexene oxidation by [Mn(HL¹)Cl₂(CH₃OH)].^a

^a*Reaction conditions*: catalyst ([Mn(HL¹)Cl₂(CH₃OH)]) (2.4×10^{-3} mmol); reaction temperature, 80 °C; cyclohexene, 1 mmol; solvent, 2 mL; reaction time, 5 h; TBHP, 1 mmol; ^bConversions are based on the starting substrate; ^cTurnover number (TON) = (mmol of product)/(mmol of catalyst); ^dTurnover frequency (TOF) = (mmol of oxide)/(mmol of catalyst × time)

Entry	Substrate	Conversion (%) ^b	Epoxide selectivity (%) ^c	TON ^f	TOF ^g (h ⁻¹)
1	Styrene	67	40 ^c	279	55.8
2	α-Methyl styrene	56	34 ^d	233	46.6
3	Indene	26	>99	108	21.6
4	Cyclooctene	43	100	179	35.8
5	1-Octene	17	>99	71	14.2
6	1-Decene	9	>99	37.5	7.5
7	Cyclohexene	71	71 ^e	296	59,2

Table 5. Oxidation of alkenes with TBHP catalyzed by [Mn(HL¹)Cl₂(CH₃OH)] (1).^a

^a*Reaction conditions:* catalyst $(2.4 \times 10^{-3} \text{ mmol})$, substrate (1.0 mmol), 1,2-dichloroethane (2 mL), TBHP (1 mmol) and temperature 80 °C; ^bConversions are based on the starting substrate; ^c The other product is benzaldehyde; ^d The other product is acetophenone; ^e The other product is 2-cyclohexene1-ol; ^fTurnover number (TON) = (mmol of product)/(mmol of catalyst); ^gTurnover frequency (TOF) = (mmol of oxide)/(mmol of catalyst × time)

Entry	Substrate	Conversion (%) ^b	Epoxide selectivity (%) [°]	TON ^f	TOF ^g (h ⁻¹)
1	Styrene	74	50	308	61.6
2	α-Methyl styrene	68	65 ^d	283	56.6
3	Indene	39	68	162.5	32.5
4	Cyclooctene	50	100	208	41.6
5	1-Octene	25	>99	104	20.8
6	1-Decene	14	>99	58	11.6
7	Cyclohexene	80 ^e	84	333	66.6

Table 6. Oxidation of alkenes with TBHP catalyzed by the [Mn(HL²)Cl₂(CH₃OH)] (2).^a

^a*Reaction conditions:* catalyst $(2.4 \times 10^{-3} \text{ mmol})$, substrate (1.0 mmol), 1,2-dichloroethane (2 mL), TBHP (1 mmol) and temperature 80 °C; ^bConversions are based on the starting substrate; ^c The other product is benzaldehyde; ^d The other product is acetophenone; ^e The other product is 2-cyclohexene1-ol; ^fTurnover number (TON) = (mmol of product)/(mmol of catalyst); ^gTurnover frequency (TOF) = (mmol of oxide)/(mmol of catalyst × time)

Graphical abstract

