Accepted Manuscript

Accepted Date:

Synthesis, characterization and catalytic reactivity of Mn(III) complexes with a Scorpion-like bis(phenolate) ligand: Selective oxidation of primary alcohols to aldehydes

Nader Noshiranzadeh, Marzieh Emami, Rahman Bikas, Katarzyna Ślepokura, Tadeusz Lis

PII:	\$0277-5387(14)00041-2
DOI:	http://dx.doi.org/10.1016/j.poly.2014.01.020
Reference:	POLY 10518
To appear in:	Polyhedron
Received Date:	14 November 2013

18 January 2014

<page-header><image><section-header><image><image><image><image>

Please cite this article as: N. Noshiranzadeh, M. Emami, R. Bikas, K. Ślepokura, T. Lis, Synthesis, characterization and catalytic reactivity of Mn(III) complexes with a Scorpion-like bis(phenolate) ligand: Selective oxidation of primary alcohols to aldehydes, *Polyhedron* (2013), doi: http://dx.doi.org/10.1016/j.poly.2014.01.020

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Synthesis, characterization and catalytic reactivity of Mn(III) complexes with a Scorpion-like bis(phenolate) ligand: Selective oxidation of primary alcohols to aldehydes

Nader Noshiranzadeh,^{a,*} Marzieh Emami, Rahman Bikas,^a Katarzyna Ślepokura,^b and Tadeusz Lis^b

^a Department of Chemistry, Faculty of Sciences, University of Zanjan 45195-313, Zanjan, Iran

^b Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, Wroclaw 50-383, Poland

Abstract

Two new mononuclear complexes of manganese(III), $[Mn(bp)(N_3)(CH_3OH)] \cdot 0.5CH_3OH$ (1) and $[Mn(bp)(NCS)_{0.9}(NO_3)_{0.1}(CH_3OH)] \cdot CH_3OH$ (2), have been synthesized, where H_2bp is 6,6'-(pyridin-2-ylmethylazanediyl)bis(methylene)bis(2,4-di-tert-butylphenol). The complexes were characterized by elemental analyses and spectroscopic methods, and fully characterized by X-ray diffraction analysis. Single-crystal X-ray diffraction structure analysis of the complexes revealed that the manganese atom is octahedrally coordinated, where the bis(phenolate) ligand (bp²⁻) is N_2O_2 -bonded to the Mn(III) center in a tetradentate dinegative fashion. The catalytic potential of these complexes has been tested for the oxidation of primary alcohols using H_2O_2 as the oxidant. The effects of various parameters, including the molar ratio of oxidant to substrate, the temperature and the solvent, have been studied. On comparing the catalytic activity of 1 and 2, catalyst 2 showed the most powerful activity in the oxidation of alcohols. Excellent conversions have been obtained for the oxidation of benzyl alcohols containing electron-donating groups at the *para*-position.

Keywords: Bis(phenolate) ligands; Mn(III) complex; Catalytic oxidation; Crystal structure; Scorpion-like ligands, Oxidation of alcohols

1. Introduction

Due to wide application of carbonyl compounds as intermediates for many drugs, vitamins and fragrances, both in manufacturing and scientific researches [1], the oxidation of alcohols to their corresponding carbonyl compounds is one of the most important and fundamental reactions in organic synthesis [2]. However, the selective oxidation of primary alcoholic compounds to their corresponding aldehydes remains relatively difficult because in the oxidation of primary alcohols, the corresponding carboxylic acids can also form [3]. The selective catalytic oxidation of primary alcohols to aldehydes has attracted a great deal of attention in the last decade and in this context a variety of methods have been reported. Most of reported methods have to be performed with a stoichiometric amount of the oxidants [4]. The development of newer catalysts, methods and methodologies are gaining much attention currently due to the significance of this reaction [5]. In terms of economical benefit and environmental impact, catalytic oxidations processes based on H_2O_2 as an oxidant are extremely valuable [6]. Recently, the catalytic oxidation of alcohols employing transition metal complexes, such as Fe, V [7], Cu [8], Co [9], Ag [10], Pd [11], Mn [12] etc., using H₂O₂ have been developed. Among these, manganese complexes have attracted much attention because of (i) the variable structures of manganese complexes with various accessible oxidation states (e.g. 2+, 3+, 4+, 7+) [13], (ii) the wide occurrence of manganese in enzymes, plants and

bacteria [14] and (iii) its potential for use as an industrial catalyst [15]. In addition, manganese based catalysts are generally known as environmentally benign catalytic systems [16].

It is obvious that the product selectivity depends on the catalyst, oxidant, solvent and the reaction conditions. It is well established that Mn(III) salen complexes are good candidates for the selective oxidation of organic substrates [17]. Investigations on MnIII(salen)-catalyzed oxidations have shown that specific steric and electronic properties of the substituents on the salen ligands (Scheme 1) are essential in order to achieve high enantioselectivity [18]. Previous reports note that the effect of substituents at the *ortho-* and *para*-positions with respect to the phenolic group is more effective than for other sites. Incorporation of bulky substituents at the *ortho*-positions improves selectivity dramatically by directing the substrate approach to the vicinity of the metal core, while the effect of *para*-substituents is based on the electronic nature of the substituents (electron-donating substituents show higher enantioselectivity). The *tert*butyl and *tert*-Ph groups are simple but unique directing substituents for selective oxidation [19]. There are many reports on the application of catalysts containing the *tert*butyl group as a directing group [20].

In the present work, we report the synthesis, characterization, crystals structures and catalytic reactivity of two new manganese(III) complexes of a tetradentate ligand including two phenolic rings bearing the bulky *tert*-butyl substituent at the *ortho-* and *para-* positions with respect to the phenolic oxygen. This ligand has been prepared by a simple one-pot reaction through the Mannich condensation of 2,4-di-*tert*-butylphenol, formaldehyde and 2-(aminomethyl)pyridine. The catalytic reactivity of these complexes

has been investigated in the selective oxidation of primary alcohols in the presence of H_2O_2 as a highly selective, atom economic and environmental oxidant. When this ligand coordinates to the metal ion, only one side of metallic core is available for catalytic reactions and the other sites are closed by substituents or donor atoms of the ligand. Having no need for axial ligands, which are usually use as a co-catalyst in Mn-salen complexes, is one of the most remarkable features of this catalytic system.

Scheme 1.

2. Experimental

All starting chemicals were commercially available reagents and were used without further purification. IR spectra were recorded in KBr discs with a Bruker FT-IR spectrophotometer. UV-Vis solution spectra were recorded using a thermo-spectronic Helios Alpha spectrometer. The elemental analyses (carbon, hydrogen and nitrogen) of the compounds were obtained from a Carlo ERBA Model EA 1108 analyzer. The manganese percentage of the complexes was measured by a Varian spectrometer AA 220 equipment. ¹H and ¹³C NMR spectra were measured with a Bruker Spectrospin spectrometer at 500 and 125 MHz, respectively. The molecular mass was determined with an HP-MS model 5973, Network Mass Selective Detector with an electron impact 70 eV and Quadru-pole analyzer. The reaction products of oxidation were determined and analyzed by an HP Agilent 6890 gas chromatograph equipped with an HP-5 capillary column (phenyl methyl siloxane 30 μ 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).

2.1. Synthesis of 6,6'-(pyridin-2-ylmethylazanediyl)bis(methylene)bis(2,4-di-tertbutylphenol) (H₂bp)

For the synthesis of the amine-bis(phenolate) ligand, H_2 bp, methanol (35 mL) was added to 2-(aminomethyl)pyridine (5.407 g. 0.05 mol) and the rapidly stirred solution was cooled to 0 °C, after which aqueous formaldehyde (37%) solution (8 mL, 0.1 mol) was added dropwise. The mixture was stirred for 15 minutes, then 2,4-di-tert-butylphenol (20.63 g, 0.1 mol) was added and the mixture was refluxed for 48 h. The resultant solution was evaporated on a steam bath to 5 mL and cooled to room temperature. The resulting white precipitate was separated and filtered off, washed with 20 mL of cooled methanol and re-crystallized from methanol. Yield 85% (23.15 g). M.p. 188-193 °C. *Anal.* Calc. for C₃₆H₅₂N₂O₂ (MW = 544.81): C, 79.36; H, 9.62; N, 5.14. Found: C, 79.38; H, 9.61; N, 5.17%. FT-IR (KBr, cm⁻¹): 3100 (s, br), 2949 (s, br), 2864 (s), 1597 (vs), 1571 (s), 1509 (s), 1482 (s), 1467 (s), 1435 (s), 1415 (s), 1387 (m), 1362 (m), 1293 (w), 1254 (m), 1221 (s), 1202 (s), 1164 (w), 1154 (w), 1141 (s), 1133 (s), 1120 (w), 1090 (s), 1049 (m), 1041 (w), 1004 (m), 996 (m), 985 (w), 974 (m), 956 (w), 937 (s), 875 (m), 861 (m), 821 (m), 799 (w), 760 (m), 755 (m), 725 (w), 699 (w), 685 (w), 668 (w), 648 (w), 625 (w). ¹H NMR (500 MHz, DMSO-d₆, 25 °C, TMS, ppm) δ: 1.23 (s, 18 H, CH₃ of t-Bu), 1.35 (s,18 H, CH₃ of t-Bu), 3.93 (s, 2 H, Ar-CH₂), 3.96 (s, 2 H, Ar-CH₂), 4.89 (s, 2H, py-CH₂), 6.81 (d, ${}^{4}J$ = 2.40 Hz, 2H, aryl), 7.14 (d, ${}^{4}J$ = 2.45 Hz, 2 H, aryl), 7.29 (tm, ${}^{3}J = 7.50$ Hz, 1 H, py), 7.52 (d, ${}^{4}J = 7.80$ Hz, 1H, py), 7.81 (td, 1 H, py), 8.49 (dd, ${}^{3}J =$

5.75 Hz, 2H, ${}^{4}J = 1.75$ Hz, 1 H, py), 9.04 (s, broad, 2 H, OH). ${}^{13}C$ NMR (125 MHz, DMSO-d₆, 25 °C, TMS, ppm) δ : 30.2 (-*C*H₃ of t-Bu), 32.3 (-*C*H₃ of t-Bu), 39.5 (-*C*Me₃ of t-Bu), 39.7 (-*C*Me₃ of t-Bu), 50.4 (Ar-*C*H₂), 57.3 (Ar-*C*H₂), 82.2 (py-*C*H₂), 116.2, 123.1, 124.0, 130.9, 134.6, 136.2, 137.4, 142.1, 147.1, 154.0, 159.2. Mass spectrum [m/z (%)]: 546 (M+1, 65.9), 453 (M⁺ - C₆H₆N⁻, 80.8), 325 (M⁺ - C₁₅H₂₃O⁻, 100), 234 (C₁₅H₂₃NO⁺, 61.7), 219 (C₁₅H₂₃O⁺, 20.2), 203 (14.9), 189 (4.2), 161 (7.4), 116 (7.4), 107 (C₆H₆N₂⁺, 17), 93 (C₆H₆N⁺, 28.7), 57 (t-Bu⁺, 27.6). UV-Vis (5×10⁻⁵ M, CH₃OH) λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 228 (39 500), 268 (30 400), 278 (30 200).

2.3. Synthesis of $[Mn(bp)(N_3)(CH_3OH)] \cdot 0.5CH_3OH(1)$

The appropriate amount of the ligand H_2 bp (0.45 g, 1 mmol) and NaN₃ (0.13 g, 2.00 mmol) were dissolved in CH₃OH (30 mL) in association with $Mn(NO_3)_2 \cdot 4H_2O$ (0.502 g, 2.00 mmol). The solution was gently refluxed for 12 h under an aerobic atmosphere. After cooling, the resulting solid was filtered off, washed with cooled absolute ethanol and dried 60 °C. Suitable single crystals of at $[Mn(bp)(N_3)(CH_3OH)] \cdot 0.5CH_3OH$ (1) were grown from a concentrated methanol solution following slow evaporation at room temperature. Yield 78% (0.54 g). Anal. Calc. for $C_{375}H_{56}MnN_5O_{35}$ (MW = 687.81): C, 65.48; H, 8.21; N, 10.18; Mn, 7.99. Found: C, 65.55; H, 8.19; N, 10.15; Mn, 8.03%. FT-IR (KBr, cm⁻¹): 3426 (w, br), 2952 (s), 2925 (s), 2861 (w), 2055 (vs), 1604 (w), 1477 (m), 1469 (m), 1438 (m), 1412 (w), 1387 (w), 1361 (w), 1304 (w), 1262 (m), 1239 (m), 1202 (w), 1169 (w), 1019 (w), 835 (m), 763 (w), 750 (w), 606 (w), 577 (w). Mass spectrum [m/z (%)]: 688 (M⁺, 2.5), 648 (3.14), 545 (H₂bp⁺, 5.5), 453 (40.94), 325 ($C_{21}H_{29}N_2O^+$, 100), 234 ($C_{15}H_{23}NO^+$, 62.99), 203 (26.77), 187

(3.93), 161 (12.59), 133 (8.66), 109 ($C_6H_6N_2^+$, 18.11), 93 ($C_6H_6N^+$, 59.8), 77 ($C_6H_5^+$, 3.93), 57 (t-Bu⁺, 43.3). UV-Vis (2.5×10⁻⁵ M, CH₃OH) λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 224 (71 000), 259 (52 800), 375 (13 400), 520 (7 300).

2.3. Synthesis of $[Mn(bp)(NCS)_{0.9}(NO_3)_{0.1}(CH_3OH)] \cdot CH_3OH(2)$

The complex $[Mn(bp)(NCS)_{0.9}(NO_3)_{0.1}(CH_3OH)] \cdot CH_3OH$ (2) was formed by a similar procedure to that used for complex **1**, with azide replaced by potassium thiocyanate (H₂bp, 1 mmol; Mn(NO₃)₂·4H₂O, 2.00 mmol; KSCN, 2.00 mmol). Yield 70% (0.50 g). *Anal*. Calc. for C_{38.9}H₅₈MnN₃O_{4.3}S_{0.9} (MW = 720.28): C, 64.86; H, 8.12; N, 5.83; Mn, 7.63. Found: C, 64.93; H, 8.10; N, 5.78; Mn, 7.69%. FT-IR (KBr, cm⁻¹): 3431 (m, br), 2954 (s), 2923 (m), 2865 (w), 2068 (vs), 1605 (w), 1477 (w), 1466 (m), 1438 (m), 1411 (w), 1384 (s), 1362 (w), 1261 (m), 1169 (w), 1019 (w), 837 (m), 611 (w). Mass spectrum [m/z (%)]: 720 (M⁺, 2.5), 598 (Mnbp⁺, 4.4), 545 (H₂bp⁺, 10.8), 453 (49), 325 (C₂₁H₂₉N₂O⁺, 100), 234 (C₁₅H₂₃NO⁺, 68.7), 203 (30.5), 161 (12.1), 106 (C₆H₆N₂⁺, 13.4), 93 (C₆H₆N⁺, 45.8), 57 (t-Bu⁺, 25.5). UV-Vis (2.5×10⁻⁵ M, CH₃OH): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 230 (69 600), 256 (61 400), 375^{broad} (31 900), 515 (5 200).

2.4. X-ray crystallography

Data collection for the X-ray structure determinations was performed on an Xcalibur R four-circle diffractometer with a Ruby CCD detector with graphite monochromatized Mo*K* α radiation. The data were collected at 100(2) K using an Oxford Cryosystems cooler. Data collection, cell refinement, data reduction, analysis and absorption corrections were carried out with the Xcalibur R software, CrysAlis^{Pro} [21]. The

structures were solved by direct methods with SHELXS [22] and refined by a full-matrix least-squares technique on F^2 using SHELXL-97 [22] with anisotropic thermal parameters for the non-H atoms (except for some positions of disordered atoms). The H atoms were found in the difference Fourier maps, but in the final refinement cycles they were repositioned in their calculated positions and refined using a riding model, with C-H = 0.95-0.99 Å, and with $U_{iso}(H) = 1.2U_{ea}(CH, CH_2)$ or $1.5U_{ea}(CH_3)$, except for methanol hydroxyl H atoms, which were located in the Fourier maps, refined isotropically with O-H distances restrained to 0.840(2) Å and then constrained to ride on their parent atoms (AFIX 3 instruction in SHELXL-97). Ye uncoordinated methanol molecule and one of the *tert*-Bu groups in 1 are disordered and refined into two sites with s.o.f. = 0.604(8) and 0.396(8) for MeOH, and 0.922(6) and 0.078(6) for tert-Bu. Two different ligands share the same coordination site in the complex molecule of 2: NCS⁻ [additionally disordered into two positions with s.o.f. = 0.54(2) and 0.34(2) and NO₃⁻ with s.o.f. = 0.114(4)]. Thus, the crystals of 2 are of a solid solution type – two different complex molecules may be distinguished in the same, symmetrically equivalent position: $[Mn(bp)(NCS)(CH_3OH)]$ $[Mn(bp)(NO_3)(CH_3OH)],$ and and the formula [Mn(bp)(NCS)_{0.9}(NO₃)_{0.1}(CH₃OH)]·CH₃OH, accepted in the final model, corresponds to the existence of these two complexes, randomly occupying the crystallographic sites of the unit cell in a 0.9:0.1 ratio. In the final refinement cycles, the site occupation factors of the NCS⁻ and NO₃⁻ ligands were refined, but the sum of them was restrained to unity. Additionally, some geometrical restrains (SAME, SADI and FLAT instructions in SHELXL-97) and constraints on the fractional coordinates and anisotropic displacement parameters (EXYZ and EADP instructions) were applied in the refinement procedure of

the disordered regions in **1** and **2**. The structure plots were prepared with DIAMOND [23]. The crystal data and refinement parameters are presented in Table 1.

2.5. Experimental set up for catalytic oxidations

The liquid phase catalytic oxidations of alcohols were carried out under air (atmospheric pressure) in a 25 mL round bottom flask equipped with a magnetic stirrer. In a typical experiment, H_2O_2 was added to a flask containing the catalyst (1.45×10^{-3} mmol) and benzylalcohol (1 mmol) in a solvent (3 mL). The course of the reaction was monitored using a gas chromatograph equipped with a capillary column and a flame ionization detector. The oxidation products were identified by comparing their retention times with those of authentic samples or alternatively by TLC, ¹H NMR and GC–Mass analyses. Control reactions were carried out in the absence of catalyst, under the same conditions as the catalytic runs. No products were detected.

Table 1.

3. Results and discussion

3.1. Synthesis of the ligand and Mn complexes

The reaction of 2-(aminomethyl)pyridine with 2,4-di-*tert*-butylphenol in the presence formaldehyde gave the desired tetradentate bis(phenolate) ligand, H₂bp, in excellent yield and purity. The complex $[Mn(bp)(N_3)(CH_3OH)] \cdot 0.5CH_3OH$ (1) was synthesized by the reaction of H₂bp/Mn(NO₃)₂·4H₂O/NaN₃ with molar ratios 1.0:2.0:2.0 in methanol. Complex **2** was synthesized in a similar manner to **1**, with KSCN being used instead of NaN₃ and the molar ratios of the materials being constant. The formation of the

ligand H₂bp has been confirmed by elemental analysis, ¹H NMR (Fig. S1), mass (Fig. S2) and infrared spectroscopies. In the ¹H and ¹³C NMR spectra of the ligand, two CH₂ groups (those connected to the phenolic rings) are not equal and appear as two independent peaks. In the IR spectrum of the ligand (Fig. S5), the bands at 3100, 1597 and 1262 cm⁻¹ are due to O–H, C=N_{Py} and C–O_{phenolic} vibrations, respectively [24]. The elemental analysis is in good accordance with the proposed structure. Complexes 1 and 2 are slowly formed by the reaction of H₂bp with manganese in the presence of the pseudohalide ligand N_3^- or SCN⁻ as a co-ligand and methanol as the solvent. For both complexes 1 and 2, during the reaction manganese(II) is oxidized to manganese(III) by air. The IR spectrum of 1 was analyzed in comparison with that of the free ligand (Fig. S5). In both complexes, the change in the positions of the peaks in comparison to the free ligand indicates the coordination of the ligands to the metal core. In the IR spectrum of the complexes, the broad bands at about 3430 cm⁻¹ are due to the O-H_{methanol} vibration. In the IR spectrum of complex 1, a strong, well resolved peak at 2055 cm^{-1} was obtained, which was assigned to $v(N_3)$. In the IR spectrum of complex 2, an SCN peak is located at 2068 cm^{-1} .

The electronic spectra of complex 1 (purple), complex 2 (purple) and H₂bp (colorless) in methanol and acetonitrile solutions are shown in Fig. 1. The bis(phenolate) ligand displays strong bands at 228, 268 and 278 nm. Based on their extinction coefficients, these bands are assigned to intraligand $\pi \rightarrow \pi^*$ (228 nm) and $n \rightarrow \pi^*$ (268, 278 nm) transitions. The shifts of the bands in the complexes relative to the H₂bp bands indicate the coordination of the ligand to the Mn(III) ion. The UV-vis spectra of the complexes in methanol and acetonitrile solutions are approximately the same, and the

small differences in the shapes of the bands is due to solvent effects. For the complexes, the broad bands at higher energies of ~375 and ~520 nm are due to ligand to metal charge transfer (LMCT) transitions. The other higher energy intense transitions at about 225 and 260 nm are due to intraligand $\pi \to \pi^*$ and $n \to \pi^*$ charge transfer transitions. In these complexes, the d-d transitions are overlapped with the LMCT transitions and as a result their peaks are not visible.

Fig. 1.

55

3.2. X-ray structures of complexes 1 and 2

The molecular structures of complexes $[Mn(bp)(N_3)(CH_3OH)] \cdot 0.5CH_3OH (1)$ and $[Mn(bp)(NCS)_{0.9}(NO_3)_{0.1}(CH_3OH)] \cdot CH_3OH (2)$, determined by X-ray analysis, are shown in Figs. 2 and 3, respectively, and selected bond lengths and angles are tabulated in Table 2. In the asymmetric unit of complex 1, two crystallographically independent molecules (described as 1A and 1B) appear. An overlay of these two molecules shows that they are almost identical (Fig. S6). In the crystals of complex 2, which are of a solid solution type (see the *Experimental Part*), 10% of thiocyanate ligands are replaced by nitrate anions from the initial metal source, and only the molecule of the composition $[Mn(bp)(NCS)(CH_3OH)]$ will be discussed. X-ray analyses reveal that both 1 and 2 are neutral mononuclear complexes of Mn(III). The coordination environment around the Mn centers is best described as a distorted *mer*-[MnO_3N_3] octahedral geometry, with pyridinyl nitrogen, tertiary nitrogen and two oxygen atoms provided by the bis(phenolate) ligand, an oxygen atom from methanol and a nitrogen atom from the pseudohalide ligand (N₃⁻ in 1 and SCN/NO₃⁻ in 2).

In both complexes 1 and 2, two phenolate donor atoms, provided by the bis(phenolate) ligand, are located in a trans mode towards each other and their bond lengths are considerably shorter than the others, which can be attributed to their high σ donor ability and their negative charges (see Table 2). Also, two bonds (Mn-O_{methanol} and Mn-N_{pyridine}) are considerably elongated with respect to the other four, which is consistent with the Z-out Jahn-Teller effect, found in most octahedral Mn³⁺ complexes with HS-d⁴ electronic configuration [25]. The tertiary nitrogen and two phenolate oxygen atoms, together with nitrogen atom of the pseudohalide, form the basal plane, and the nitrogen atom of the pyridinyl moiety of the ligand scorpion-like tail entangles the metal core and coordinates to the axial position. The remaining axial position in both complexes is occupied by a methanol molecule. In complex 1, the terminal azide ligand shows asymmetric N–N distances (N3–N4/N4–N5) of 1.2004(18)/1.1506(19) Å and 1.2063(19)/1.142(2) Å for 1A and 1B, respectively, and the N3–N4–N5 angles are 177.62(15) and 176.56(17)°, which represent the typical shape of the azide ligand [26]. In complex 2, the Mn1–N3–C37 angle of 167.2(8)° is close to a linear coordination of NCS⁻ , which is the usual manner for an N-coordinated thiocyanate ligand [27].

Fig. 2. Fig. 3.

Having both coordinated and uncoordinated methanol molecules in the structures of **1** and **2**, it is not surprising that the crystal packing of these complexes is dominated by strong and directional hydrogen bonding. The acidic H from the coordinated methanol molecule forms a hydrogen bond with the oxygen atom of the uncoordinated methanol. In addition, the hydrogen atom of the uncoordinated methanol is involved in other hydrogen

bonding (O–H···O in **1** and O–H···S in **2**), and pseudo-dimeric units form by these interactions, as shown in Fig. 4. Geometric parameters characterizing the intermolecular interactions are collected in Table S1. In complex **1**, the pyridinyl rings of neighboring molecules from adjacent pseudo-dimeric units interact with each other *via* π ··· π stacking, with a centroid···centroid distance of 3.596(2) Å. In addition, the inter-dimeric contacts are assisted by C–H··· π interactions between pyridinyl C atoms and phenolate rings, as shown in Fig. S7 [28] (H···centroid = 2.46 and 2.65 Å). Similar inter-dimeric C–H··· π contacts, involving the same rings of the ligand, are also observed in the crystal structure of complex **2** (Fig. S8).

Fig. 4. Table 2.

3.3. Catalytic activity studies

3.3.1. Oxidation of benzyl alcohol

The catalytic activity of complexes **1** and **2** were tested in the oxidation of alcohols. The catalytic oxidation of benzyl alcohol (scheme 2) as a representative substrate with hydrogen peroxide was studied in the presence of complexes **1** and **2**. Aqueous hydrogen peroxide (30%) was selected as the oxidant by considering its high selectivity, atom economy and environmentally benign properties. The results of control experiments revealed that the presence of catalyst and oxidant (H_2O_2) is essential for the oxidation. To achieve the maximum oxidation of alcohols, effective parameters for suitable reaction conditions, such as the oxidant concentration (moles of oxidant per moles of substrate), solvent and temperature of the reaction, were investigated. The results of the studies are summarized in Table 3. In all these reactions, benzyl alcohol

gave the benzaldehyde with 100% selectivity by catalyst and there was not any other product. The effect of oxidant concentration on the oxidation of benzyl alcohol by complex **1** is illustrated in Fig. 5. Different oxidant/substrate molar ratios (1:1, 2:1, 3:1 and 4:1) were considered, while the ratio of benzyl alcohol (1.0 mmol) to catalyst (1.5 μ mol, 0.001 g) in 3 mL of acetonitrile was constant. The conversion of benzyl alcohol increased on increasing the amount of hydrogen peroxide in the reaction mixture. When the H₂O₂/substrate molar ratio was 2:1, a maximum conversion of 42% was obtained at 60±1 °C.

Scheme 2.

In order to get the best reaction temperature, the oxidation of alcohols was studied at 25 (room temperature), 40, 60 and 80 °C, and the results are shown in Fig. 6. At room temperature the oxidation of benzyl alcohol was very low. Increasing the reaction temperature from 25 to 60 °C increased the conversion of benzyl alcohol, but a further increase of temperature to 80 °C lowered the conversion. The influence of the solvent nature in the catalytic oxidation of benzyl alcohol was tested and the results are presented in Table 3. Acetone, toluene, ethyl acetate, dichloromethane, chloroform, DMF, DMSO, THF and acetonitrile were used as solvents. Of the various solvents examined, acetonitrile was found to be the most suitable solvent for this catalytic reaction. It was observed that the catalytic activity of the catalyst decreased with respect to acetonitrile (dielectric constants e = 37.5 [29], donor number D = 14.1 [30]) > acetone (e = 20.7, D = 17) > toluene (e = 2.38, D = 0) > chloroform (e = 4.9, D = 0) > dichloromethane (e = 8.93, D = 0) > THF (e = 7.3, D = 20) > ethyl acetate (e = 6.02, D = 17.1) > DMF (e = 21,

D = 26.6 > DMSO (e = 46.7, D = 29.8). Overall, the reactivity of the catalyst in other solvents was very much lower than in acetonitrile. This may be due to the high relative dielectric constant and low coordination ability of this solvent. Solvents with a high donor ability decrease the reactivity of the catalyst, and the lowest conversion in DMSO is due to the highest coordinating ability of this solvent. High reactivity in toluene is due to the high solubility of the catalyst in this solvent.

The catalytic activity of complex **2** was examined under the optimized conditions for catalyst **1** (H_2O_2 /benzyl alcohol molar ratio = 2, acetonitrile, reaction temperature 60 °C). The reactivity of catalyst **2** is better than that of catalyst **1**, which may be due to the difference in the pseudohalide co-ligand.

Fig. 5. Fig. 6. Table 3.

3.3.2. Oxidation of various primary alcohols

Finally, in order to explore further the oxidation potential of the these complexes, the oxidation of various primary alcohols was performed under the same reaction conditions that proved to be the best for benzyl alcohol, and complex **2** was used as the catalyst due to its high reactivity in comparison with complex **1**. We have studied the effects of the substituents and nature of the aromatic rings on alcohol oxidation. The results are shown in Table 4 and indicate this catalytic system led to the oxidation of different primary alcohols to the corresponding aldehydes with 100% selectivity. It seems that the efficiency of the oxidation in this catalytic system is dependent on the electronic and steric demands of the substrate.

It was observed that the presence of an electron-donating (–OMe, –OH) group at the *para* position of benzyl alcohol enhanced the conversion in comparison with a molecule having no substituent on the ring (entries 1, 2 and 3). In addition, electronwithdrawing -Cl and especially -NO₂ groups on the phenyl ring decelerated the oxidation reaction (entries 4 and 5). This behavior is in agreement with the Hammett plot which has been studied for the oxidation of benzyl alcohols under different conditions in detail [31]. Moreover, the influence of steric factors in this catalytic system is also notable. The lower conversion of ortho-substituted alcohols, such as 2-Cl- and 2-NO₂benzyl alcohol (entries 7 and 8), in comparison with the corresponding non-hindered alcohols after similar reaction times may be related to the steric hindrance at the vicinity of the active Mn center. It is worth noting that the oxidation of 2-OH-benzyl alcohol is the same as 4-OH-benzyl alcohol (entries 2 and 6), and this may be due to the formation of hydrogen bonding through the O-H phenol group at the ortho position to the alcoholic group of the substrate, which may help the substrate to approach near to the Mn center. The conversion of 4-pyridylmethanol and 3-pyridylmethanol is abnormally low. This may due to the electron withdrawing nature of the pyridine ring together with the high donor ability of these substrates, which can coordinate to the Mn center through the Npyridine group. Perhaps, coordination of the pyridine group to the active site of the catalyst inactivates the catalyst. This is also in agreement with the low activity of catalysts in solvents that have a high donor ability (DMSO, DMF). The behavior of catalyst 1 is similar to 2, so UV-vis spectroscopy was employed to find evidence for coordination of these substrates to the metals centers (Fig. 7). After addition of these substrates (3- or 4-pyridylmethanol) to catalyst 1, the band at 515 nm shifted to a higher

energy (blue shift), which may due to the coordination of the N-pyridine group to the Mn(III) center.

Fig. 7.

Table 4.

The interaction of H_2O_2 with catalyst **1** was monitored in methanol by UV-vis spectroscopy. Fig. 8 shows the UV-vis spectra of the complex after the addition of 1, 2 and 3 drops of H_2O_2 to the methanol (Fig. 8a) and acetonirile (Fig. 8b) solutions of **1** (1 drop per 10 minutes). After the addition of one drop of H_2O_2 to a solution of **1** (3 mL, 2.5 $\times 10^{-5}$ mol L⁻¹), the intensity of the bands between 200 and 270 nm increases and undergo a blue shift, together with a change in intensity and shape of the bands in the region 300-520 nm. All this suggests the interaction of the peroxo group with the Mn(III) center during the catalytic reactions.

Fig. 8.

4. Conclusion

Two new manganese(III) complexes of a tetradentate bis(phenolate) ligand were synthesized and characterized by spectroscopic and single crystal X-ray analyses. The catalytic abilities of these complexes were investigated using the environmentally benign and clean oxidant H_2O_2 for the oxidation of primary alcohols. The effects of various parameters, including the molar ratio of oxidant to substrate, the temperature and the solvent, have been studied and optimized conditions were obtained. These complexes are selective catalysts for the oxidation of primary alcohols to the corresponding aldehydes. The influence of the presence of electron-withdrawing and electron-donating groups on

the phenyl ring of benzyl alcohol on the reactivity of the catalysts has been investigated. Excellent conversions were obtained for the oxidation of alcohols containing electrondonating groups at the *para*-position.

Acknowledgements

We acknowledge the University of Zanjan for funding this research work.

Appendix A. Supplementary material

CCDC 935112 and 935113 contain the supplementary crystallographic data for complexes **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* <u>www.ccdc.cam.ac.uk/data_request/cif</u>. Supplementary data associated with this article can be found, in the online version.

References

- [1] (a) R.A. Sheldon, J.K. Kochi, Metal Catalayzed Oxidation of Organic Compounds, Academic Press: New York, (1981).
- (b) M. Hudlicky, Oxidation in Organic Chemistry, American Chemical Society: Washington, D.C., (1990).
- [2] (a) R.C. Larock, Comprehensive Organic Transformations, VCH: New York (1989) 604–834.
- (b) M. Hudlicky, Oxidations in Organic Chemistry, ACS Monograph Ser. 186, American Chemical Society, Washington, D.C., (1990) 114.
- [3] (a) A.-K. C. Schmidt, C.B.W. Stark, Org. Lett. 13 (2011) 4164-4167.
- (b) M.M. Zhao, J. Li, E. Mano, Z.J. Song, D.M. Tschaen, Org. Syn. 81 (2005) 195-203.

- [4] J. March, Advanced Organic Chemistry; Reaction, Mechanisms, and Structure, 4th edn., John Wiley & Sons, New York, 1992.
- [5] (a) J.M. Hoover, S.S. Stahl, J. Am. Chem. Soc. 133 (2011) 16901-16910.
- (b) R. Kawahara, K. Fujita, R. Yamaguchi, J. Am. Chem. Soc. 134 (2012) 3643-3646.
- (c) N. Jiang, A.J. Ragauskas, J. Org. Chem. 72 (2007) 7030-7033.
- (d) C. Parmeggiani, F. Cardona, Green Chem.14 (2012) 547-564.
- (e) S.E. Davis, M.S. Ide, R.J. Davis, Green Chem. 15 (2013) 17-45.
- [6] B.S. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457-2474.
- [7] (a) S.M. Islam, A.S. Roy, P. Mondal, N. Salam, J. Mol. Catal. A: Chem. 358 (2012) 38-48.
- (b) R.R. Fernandes, J. Lasri, M.F.C. Guedes da Silva, J.A.L. da Silva, J.J.R. Frausto da
- Silva, A.J.L. Pombeiro, App. Catal. A 402 (2011) 110-120.
- (c) G. Romanowski, J. Mol. Catal. A: Chem. 368–369 (2013) 137-144.
- [8] (a) P. Pattanayak, J.L. Pratihar, D. Patra, P. Brandão, D. Mal, V. Felix, Polyhedron 59 (2013) 23-28
- (b) A.M. Kirillov, M.V. Kirillova, L.S. Shulpina, P.J. Figiel, K.R. Gruenwald, M.F.C. Guedes da Silva, M. Haukka, A.J.L. Pombeiro, G.B. Shulpin, J. Mol. Catal. A: Chem. 350 (2011) 26-34.
- [9] S. Chakravorty, B.K. Das, Polyhedron 29 (2010) 2006-2013.
- [10] M.M. Najafpour, M. Hołyńska, M. Amini, S.H. Kazemi, T. Lis, M. Bagherzadeh, Polyhedron 29 (2010) 2837-2843.
- [11] (a) M. Herbert, F. Montilla, A. Galindo, Polyhedron 29 (2010) 3287-3293.
- (b) M.N. Missaghi, J.M. Galloway, H.H. Kung, App. Catal. A 391 (2011) 297-304.
- [12] B. Machura, J. Palion, J. Mroziński, B. Kalińska, M. Amini, M.M. Najafpour, R. Kruszynski, Polyhedron 53 (2013) 132-143.
- [13] (a) A.K. Ghosh, D. Ghoshal, E. Zangrando, J. Ribas, N.R. Chaudhuri, Dalton Trans.(2006) 1554-1563.
- (b) C. Lampropoulos, M. Murugesu, K.A. Abboud, G. Christou, Polyhedron 26 (2007) 2129-2134.
- (c) J.D. McCall, S. Vaddypally, S.K. Kondaveeti, M.J. Zdilla, Inorg. Chem. Commun. 37 (2013) 225-227.

[14] (a) W.H. Armstrong, Manganese Redox Enzymes, (Ed.: V. L. Pecoraro), VCH, New York, 1992.

(b) G.C. Dismukes, Chem. Rev. 96 (1996) 2909-2926.

(c) M.Y. Chae, G.A. Omburo, P. Lindahl, F.M. Raushel, J. Am. Chem. Soc. 115 (1993) 12173-12174.

[15] (a) T. Katsuki, Coord. Chem. Rev. 140 (1995) 189-214.

(b) J.N. Armor, Catal. Today 163 (2011) 3-9.

[16] S. Dharmarathna, C.K. Kingondu, L. Pahalagedara, C.-H. Kuo, Y. Zhang, S.L. Suib,

Appl. Catal. B: Environ. 147 (2014) 124-131.

[17] E.M. McGarrigle, D.G. Gilheany, Chem. Rev. 105 (2005) 1563-1602.

[18] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189-214.

[19] A. Gaquere, S. Liang, F.-L. Hsu, X.R. Bu, Tetrahedron: Asymmetry, 13 (2002) 2089-2093.

[20] (a) J.U. Ahmad, P.J. Figiel, M.T. Raisanen, M. Leskela, T. Repo, App. Catal. A 371 (2009) 17-21

(b) R.E. Key, K. Venkatasubbaiah, C.W. Jones, J. Mol. Catal. A: Chem. 366 (2013) 1-7.

(c) C. Li, J. Zhao, R. Tan, Z. Peng, R. Luo, M. Peng, D. Yin, Catal. Commun. 15 (2011) 27-31.

[21] CrysAlis^{Pro} in Xcalibur R software. Agilent Technologies, Inc., Yarnton, Oxfordshire, UK

[22] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112-122.

[23] K. Brandenburg, Diamond (Version 3.2d), Crystal, Molecular Structure Visualization, Crystal Impact – K. Brandenburg & H. Putz Gbr, Bonn (Germany), 2009.

[24] (a) H. Adams, D.E. Fenton, G. Minardi, E. Mura, A.M. Pistuddi, C. Solinas, Inorg. Chem. Commun. 3 (2000) 24-28.

(b) H. Hosseini Monfared, R. Bikas, P. Mayer, Inorg. Chim. Acta 363 (2010) 2574-2583.

(c) H. Hosseini-Monfared, R. Bikas, P. Mahboubi-Anarjan, A.J. Blake, V. Lippolis, N.B. Arslan, C. Kazak, Polyhedron 69 (2014) 90-102.

[25] I.B. Bersuker, The Jahn-Teller Effect, Cambridge University Press, 2006.

[26] (a) R. Bikas, H. Hosseini-Monfared, T. Lis, M. Siczek, Inorg. Chem. Commun. 15 (2012) 151-155.

(b) H. Hosseini-Monfared, R. Bikas, J. Sanchiz, T. Lis, M. Siczek, J. Tucek, R. Zboril, P. Mayer, Polyhedron 61 (2013) 45-55.

(c) R. Bikas, H. Hosseini-Monfared, M. Siczek, A. Gutiérrez, M.S. Krawczyk, T. Lis, Polyhedron 67 (2014) 396-404.

[27] S. Biswas, S. Naiya, C.J. Gómez-García, A. Ghosh, Dalton Trans. 41 (2012) 462-473.

[28] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885-3896.

[29] Y. Marcus, J. Rydberg, C. Musikas, Choppin GR Principles and practices of solvent

extraction, Marcel Dekker, New York, (1992) p23.

[30] J.E. Huheey, Inorganic Chemistry, third ed., Harper International SI Edition,

Cambridge, 1983. p340.

[31] (a) P.D. Sharma, P. Panchariya, P. Purohit, P.K. Sharma, Eur. Chem. Bull. 2 (2013) 816-824.

(b) P.D. Sharma, P. Panchariya, P. Purohit, PK. Sharma, Indian J. Chem. 47 (2008) 669-676.

(c) K.G. Sekar1, C.L. Edison Raj, J. Chem. Pharm. Res. 3 (2011) 596-601.

(d) B. Ramkumar, V.S. Kumar, M. Rukmangathan, International Journal of Research in Physical Chem. 3 (2013) 14-17.

Schemes/Figures/Tables caption

Scheme 1. a) Structure of the ligand used for the most widely active metal complexes in selective oxidation reactions; b) The structure of the ligand H_2 bp used in this study

Scheme 2. Catalytic oxidation of alcohols in the presence of Mn(III) complexes

Fig. 1. The electronic spectra of H_2 bp, complex 1 and complex 2 in methanol and acetonitrile

Fig. 2. The molecular structure of one of two crystallographically independent complex molecules present in **1**. Displacement ellipsoids are drawn at the 50% probability level

Fig. 3. The molecular structure of one of two complex molecules present in $2 (NO_3^-)$ and the disorder of the NCS⁻ ligand are omitted for clarity). Displacement ellipsoids are drawn at the 30% probability level

Fig. 4. Pseudo-dimeric units observed in **1** (left) and **2** (right), formed by methanolmediated hydrogen bonds (dashed lines) between complex molecules. Alternative positions of the disordered MeOH molecule in **1** are shown with different colors. Ligand H atoms are omitted for clarity. Symmetry code is given in Table S1

Fig. 5. Effect of H_2O_2 concentration on the oxidation of benzyl alcohol by **1**. *Reaction conditions*: Catalyst, complex **1**, 1.45 µmol (0.001 g); CH₃CN, 3 mL; benzyl alcohol, 1 mmol; temperature, 60 ± 1 °C

Fig. 6. Effect of the reaction temperature on the oxidation of benzyl alcohol by **1**. *Reaction conditions*: Catalyst, complex **1**, 1.45 μ mol (0.001 g); CH₃CN, 3 mL; benzyl alcohol, 1 mmol; H₂O₂, 2 mmol

Fig. 7. UV-vis spectra of 1 after the addition of a) 4-pyridylmethanol b) 3-pyridylmethanol

Fig. 8. UV-vis spectra of 1 after the addition of H_2O_2 (a) in methanol (b) in acetonitrile

Table 1. Crystallographic data of 1 and 2

Table 2. Selected geometric parameters (Å, °) for 1 and 2

Table 3. Comparison the catalytic activities of catalysts **1** and **2** in the oxidation of benzyl alcohol with hydrogen peroxide under different conditions

Table 4. Oxidation of various primary alcohols by complex 2 / H₂O₂ /CH₃CN /60 °C





Scheme 1.

ACCERTIFIC





Scheme 2.

Acception

















	Complex 1	Complex 2
Formula	$\underline{C_{37}H_{54}MnN_5O_3} \cdot 0.5(CH_4O)$	$\underline{C_{37.9}H_{54}MnN_{3}O_{3.3}S_{0.9}\cdot CH_{4}O}$
$M_{\rm r}/{ m g}~{ m mol}^{-1}$	687.81	720.28
Crystal size/mm	$0.38 \times 0.15 \times 0.15$	$\underline{0.47} \times \underline{0.22} \times \underline{0.02}$
Crystal shape, color	Block, dark purple	Plate, dark purple
T/K	100(2)	100(2)
Radiation	<u>MoKa</u> ($\lambda = 0.71073$ Å)	$\underline{MoK\alpha} \ (\lambda = \underline{0.71073} \ \text{\AA})$
Crystal system, space group	Monoclinic, <u>P2₁/n</u>	<u>Triclinic</u> , <u>P</u> ī
a/Å	15.088(5)	<u>10.856 (4)</u>
b/Å	18.945(5)	<u>12.354 (3)</u>
c/Å	26.629(7)	<u>16.202 (6)</u>
α/°		<u>104.75 (3)</u>
β/°	98.39(3)	<u>103.62 (3)</u>
γ/°		<u>91.96 (3)</u>
V/Å ³	7530(4)	2032.0 (12)
Ζ	8	2
Calc. density/g cm^{-3}	<u>1.213</u>	<u>1.177</u>
μ/mm^{-1}	<u>0.39</u>	0.41
Absorption correction	analytical	empirical (multi-scan)
T_{\min}, T_{\max}	0.874, 0.955	0.921, 1.000
Measured reflections	<u>51656</u>	<u>68187</u>
R _{int}	<u>0.035</u>	<u>0.064</u>
h, k, l	<u>-21</u> →21, <u>-</u> 26→25, <u>-</u> 23→37	$\underline{-14} \rightarrow 14, \underline{-16} \rightarrow 16, \underline{-21} \rightarrow 21$
Θ range	2.15–30.07	2.71-28.86
Independent reflections	21359	<u>10035</u>
Observed refls. $(I > 2\sigma(I))$	<u>15969</u>	<u>7952</u>
Data/Parameters/Restraints	<u>21359/909/</u> 9	<u>10035/473</u> /13
<i>F</i> (000)	<u>2952</u>	772
$R1(F_{obs})$	0.042^{a}	0.061^{a}
$wR2(F^2)$	0.103^{a}	0.158^{a}
GooF = S	<u>1.02</u>	<u>1.05</u>
Shift/error _{max}	0.002	<u>0.001</u>
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min} / e {\rm \AA}^{-3}$	<u>0.44/_0.</u> 36	0.90/-0.42

Table 1.	Crystallog	anhic data	of 1	and 2
Lanc L.	CI ystanogi	aprile uata		and Z

PC

^a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]}$; Detailed information on the weighting scheme (w) are given in the crystallographic information files (CIFs).

	Complex 1 – 1A	Complex 1 – 1B	Complex 2
Mn1–O1	1.8601(11)	1.8589(11)	1.8498(18)
Mn1–O2	1.8886(11)	1.8947(12)	1.8761(18)
Mn1–N1	2.1359(14)	2.1318(13)	2.104(2)
Mn1–N2	2.2234(14)	2.2198(15)	2.2703(19)
Mn1–N3	2.0198(14)	1.9981(14)	2.045(5)
Mn1-O1M/O2M	2.2364(14)	2.2725(14)	2.2118(17)
O1-Mn1-O2	169.52(5)	172.97(5)	174.85(7)
O1–Mn1–N1	91.07(5)	92.57(4)	89.12(8)
O1-Mn1-N2	100.19(5)	95.57(5)	95.43(8)
O1-Mn1-N3	88.88(5)	90.48(5)	89.6(2)
O2-Mn1-N1	92.82(5)	90.42(4)	92.61(8)
O2-Mn1-N2	90.13(5)	91.25(5)	89.66(8)
O2-Mn1-N3	88.37(5)	86.92(5)	89.5(2)
N1-Mn1-N2	78.03(5)	78.71(5)	79.09(7)
N1-Mn1-N3	173.36(5)	175.54(5)	170.3(3)
N2-Mn1-N3	95.44(6)	97.75(6)	91.5(3)
O1-Mn1-O1 <i>M</i> /O2 <i>M</i>	85.03(5)	85.41(5)	89.39(8)
O2–Mn1–O1 <i>M</i> /O2 <i>M</i>	85.07(5)	88.34(5)	85.72(8)
N1-Mn1-O1 <i>M</i> /O2M	92.63(5)	88.06(5)	91.69(7)
N2-Mn1-O1 <i>M</i> /O2M	169.30(4)	166.77(5)	169.50(7)
N3-Mn1-O1 <i>M</i> /O2 <i>M</i>	93.99(5)	95.43(6)	97.9(3)

Table 2. Selected geometric parameters (Å, °) for 1 and 2

ο.0.07(5) 92.63(5) ...02M 169.30(4) 93.99(5)

		, 0	1				
Entry	Catalyst	H_2O_2	Solvent	Temp.	Yield	Selectivity	TON(TOF/h ⁻¹)
		(mmol))		$(^{\circ}C)^{a}$	(%)	
1	1	1	CH ₃ CN	60	15	100	103(26)
2	1	2	CH ₃ CN	60	42	100	290(72)
3	1	3	CH ₃ CN	60	39	100	269(67)
4	1	4	CH ₃ CN	60	40	100	276(69)
5	1	2	CH ₃ CN	25	5	100	35(9)
6	1	2	CH ₃ CN	40	18	100	124(31)
7	1	2	CH ₃ CN	80	40	100	276(69)
8	1	2	$(CH_3)_2CO$	60	37	100	255(64)
9	1	2	Toluene	60	31	100	214(54)
10	1	2	CHCl ₃	60	25	100	172(43)
11	1	2	CH_2Cl_2	60	22	100	152(76)
12	1	2	THF	60	17	100	117(29)
13	1	2	EtOAc	60	11	100	76(19)
14	1	2	DMF	60	4	100	28(7)
15	1	2	DMSO	60	0	100	0(0)
16	2	2	CH ₃ CN	60	46	100	317 (79)

Table 3. Comparison of the catalytic activities of catalysts **1** and **2** in the oxidation of benzyl alcohol with hydrogen peroxide under different conditions

Reaction conditions: catalyst, 1.45 µmol; benzyl alcohol, 1 mmol; solvent, 3 mL; time, 4 hours ^a Yields are based on the starting benzyl alcohol

Entry	Substrate	Product	Yield (Selectivity)	TON (TOF/h ⁻¹)
1	Me0		54 (100)	372 (93)
2	HO CH-OH	HO	49 (100)	338 (84.5)
3	СН;ОН		46 (100)	317 (79)
4	СІ		41 (100)	283 (71)
5	O ₂ N CH ₂ OH	O ₂ N O	30 (100)	207 (52)
6	он сн ₂ он	он	49 (100)	338 (84.5)
7	Cl Cl		39 (100)	269 (67)
8	CH ₂ OH		25 (100)	172 (43)
9	CH ₂ OH	N N N N N N N N N N N N N N N N N N N	7 (100)	48 (12)
10		N Y	4 (100)	27.5 (7)

Table 4. Oxidation of various primary alcohols by complex 2 / H_2O_2 /CH₃CN /60 °C.

Reaction conditions: catalyst, 1.45 µmol; substrate, 1 mmol; H₂O₂, 2mmol; solvent, CH₃CN, 3 mL; time, 4

hours

Acceleration

Synthesis, characterization and catalytic reactivity of Mn(III) complexes with a Scorpion-like bis(phenolate) ligand: Selective oxidation of primary alcohols to aldehydes

Nader Noshiranzadeh,^{a,*} Marzieh Emami, Rahman Bikas,^a Katarzyna Ślepokura,^b and Tadeusz Lis^b

Highlights

- ✓ The synthesis and structures of two Mn(III) complexes containing a scorpionlike bis(phenolate) ligand and pseudohalides is reported.
- ✓ The catalytic behavior of the Mn(III) complexes in the selective oxidation of primary alcohols is demonstrated.
- ✓ The effect of substitution on the aromatic ring in the oxidation reactions has been surveyed.

Graphical abstract

Synthesis, characterization and catalytic reactivity of Mn(III) complexes with a Scorpion-like bis(phenolate) ligand: Selective oxidation of primary alcohols to aldehydes

Nader Noshiranzadeh,^{a,1} Marzieh Emami, Rahman Bikas,^a Katarzyna Ślepokura,^b and Tadeusz Lis^b



The structure of bp²⁻

 $MnCl_2 4H_2O + H_2pb + NaN_3$ (or KSCN) $-CH_3OH$ Catalyst 1-2



¹ Corresponding author. Tel.: +98 241 5152583; fax: +98 241 2283203. *E-mail address:* <u>nadernoshiranzadeh@znu.ac.ir</u> (Nader Noshiranzadeh).