ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 2, pp. 142–148. © Pleiades Publishing, Ltd., 2015.

Synthesis, Structures, and Catalytic Property of Manganese(III) Complexes Derived from *N*,*N'*-Bis(5-Fluoro-2-Hydroxybenzylidene)ethane-1,2-Diamine[1]

G. S. Li* and H. L. Zhang

Key Laboratory of Surface & Interface Science of Henan, School of Material & Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou, 450002 P.R. China

**e-mail: gangsen_li@126.com*

Received June 19, 2014

Abstract—Two mononuclear manganese(III) complexes, [Mn(L)(NCS)] (**I**) and $[Mn(L)(OH_2)_2] \cdot$ Hfac $\cdot$ H_2O (**II**), where L is the deprotonated form of *N*,*N'*-bis(5-fluoro-2-hydroxybenzylidene)ethane-1,2-diamine, Hfac is hexafluoroacetylacetonate, were prepared and characterized by elemental analysis, IR spectra and single crystal X-ray determination (CIF files CCDC nos. 1008309 (**I**), 1008310 (**II**)). The Mn atoms in both complexes are in octahedral coordination. Complex **I** crystallized in orthorhombic space group *Pbca* with unit cell dimensions $a = 12.4090(4)$, $b = 13.5432(5)$, $c = 19.4637(7)$ Å, $V = 3271.0(2)$ Å^3, $Z = 8$, $R_1 = 0.0423$, $wR_2 = 0.0922$. Complex **II** crystallized in triclinic space group $P\bar{1}$ with unit cell dimensions $a = 7.6845(3)$, $b = 88.984(2)$, $c = 13.5522(7)$ Å, $\alpha = 78.369(1)°$, $\beta = 88.984(2)°$, $\gamma = 83.835(1)°$, $V = 1237.63(9)$ Å^3, $Z = 2$, $R_1 = 0.0526$, $wR_2 = 0.1421$. In the crystal structure of **I**, the complex molecules are stack via $\pi\cdots\pi$ interactions along the *y* axis. In the crystal structure of **II**, the molecules are linked through intermolecular O–H···O hydrogen bonds, to form chains along the *x* axis. The catalytic oxidation on olefins of the complexes was studied.

DOI: 10.1134/S1070328415020062

INTRODUCTION

Exploration of new and efficient catalysts is important for organic industry and related fields [1–4]. In recent years, much work indicated that metal complexes with various ligands have shown interesting catalytic properties on many organic reactions [5–10]. Schiff bases are readily coordinate to transition metal complexes. Manganese complexes with Schiff bases are effective catalysts for aerobic oxidation of olefins [11–13]. So as to explore new catalysts for the oxidation of olefins, in the present work, two new mononuclear manganese(III) complexes, [Mn(L)(NCS)] (**I**) and $[Mn(L)(OH_2)_2] \cdot$ Hfac $\cdot$ H_2O (**II**), where L is the deprotonated form of *N*,*N'*-bis(5-fluoro-2-hydroxybenzylidene)ethane-1,2-diamine (H_2L), Hfac is hexafluoroacetylacetonate, are presented.

EXPERIMENTAL

Materials and measurements. 5-Fluorosalicylaldehyde, ethylene-1,2-diamine, ammonium thiocyanate and bis(hexafluoroacetylacetonato)manganese were purchased from Fluka and used as received. Manganese perchlorate was prepared by the reaction of manganese carbon in water, followed by recrystallization. The solvents used were of reagent grade. The Schiff base H_2L was prepared according to the literature method [14, 15]. Elemental analyses were carried out using a PerkinElmer 2400 II elemental analyser. Infrared spectra were recorded on a PerkinElmer FT-IR spectrophotometer with a KBr disc. GC analyses were carried out using a Shimadzu GC-2014C gas chromatograph. The X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer at 298(2) K.

Synthesis of I. H_2L (3.04 g, 0.01 mol), ammonium thiocyanate (0.760 g, 0.01 mol) and manganese perchlorate (3.62 g, 0.01 mol) were dissolved and stirred in methanol (50 mL). The mixture was stirred at room temperature for 1 h and filtered. The filtrate was kept still at room temperature for several days to give deep brown block-like single crystals. The yield was 53%.

For $C_{17}H_{12}N_3O_2F_2SMn$

anal. calcd., %:	C, 49.17;	H, 2.91;	N, 10.12.
Found, %:	C, 49.03;	H, 3.02;	N, 10.27.

IR (KBr; ν, cm^{-1}): 3020–2820 w (C–H of aliphatic and aromatic), 2033 s (NCS), 1613 s (C=N), 1580–1500 s (C=C), 1218 m (C–O).

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[1] The article is published in the original.

Table 1. Crystallographic data and experimental details for compound **I** and **II**

Parameters	Values	
	I	**II**
Fw	415.3	618.3
Crystal shape; color	Block; brown	Block; brown
Crystal size, mm	0.22 × 0.19 × 0.17	0.32 × 0.30 × 0.27
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
T, K	298(2)	298(2)
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	0.974	0.639
Unit cell dimensions:		
a, Å	12.4090(4)	7.6845(3)
b, Å	13.5432(5)	12.2039(5)
c, Å	19.4637(7)	13.5522(7)
α, deg	90	78.369(1)
β, deg	90	88.984(2)
γ, deg	90	83.835(1)
V, $Å^3$	3271.0(2)	1237.63(9)
Z	8	2
$T_{\min}/T_{\max}$	0.8143/0.8519	0.8217/0.8465
Number of measured reflections	31823	11580
Number of unique reflections (R_{int})	3749 (0.0388)	4557 (0.0185)
Number of observed reflections ($I > 2\sigma(I)$)	2853	3894
Data/restraints/parameters	3749/0/235	4557/9/370
F(000)	1680	624
Goodness of fit on F^2	1.053	1.020
R_1, wR_2 ($I > 2\sigma(I)$)	0.0423, 0.0922	0.0526, 0.1421
R_1, wR_2 (all data)	0.0649, 0.1009	0.0611, 0.1518
$\Delta\rho_{\max}/\Delta\rho_{\min}$), e $Å^{-3}$	0.493/–0.270	1.037/–0.618

Synthesis of II. H_2L (3.04 g, 0.01 mol) and bis(hexafluoroacetylacetonato)manganese (4.69 g, 0.01 mol) were dissolved and stirred in methanol (50 mL). The mixture was stirred at room temperature for 1 h and filtered. The filtrate was kept still at room temperature for several days to give deep brown block-like single crystals. The yield was 36%.

For $C_{21}H_{19}N_2O_7F_8Mn$

anal. calcd., %:	C, 40.79;	H, 3.10;	N, 4.53.
Found, %:	C, 40.96;	H, 3.22;	N, 4.40.

IR (KBr; ν, cm^{-1}): 3413 w (O–H), 3027–2812 w (C–H of aliphatic and aromatic), 1615 s (C=N), 1580–1500 s (C=C), 1215 m (C–O).

X-ray crystallography. Single crystals of the complexes were mounted on the top of glass fibers. Graphite-monochromatized $\mathrm{Mo}K_\alpha$ radiation (λ = 0.71073 Å) and the ω scan technique were used to collect the diffraction data. Absorption correction was applied with SADABS [16]. The structures of the complexes were solved with direct method and refined with a full-matrix least-squares technique with SHELXTL [17]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms of the water and methanol molecules were located from electronic density maps, with O–H and H···H distances restrained to 0.85(1) and 1.37(2) Å, respectively. The other hydrogen atoms were generated geometrically. The crystallographic data and the details of the data collection and refinement for the complex are listed in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonding information is given in Table 3. Crystallographic data for the complexes have been deposited with the Cam-

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II**

Bond	*d* , Å	Bond	*d* , Å
		I	
Mn(1)–O(1)	1.8874(17)	Mn(1)–O(2)	1.8652(16)
Mn(1)–N(1)	1.9924(19)	Mn(1)–N(2)	1.9706(19)
Mn(1)–N(3)	2.133(2)		
		II	
Mn(1)–O(1)	1.876(2)	Mn(1)–O(2)	1.876(2)
Mn(1)–N(1)	1.973(3)	Mn(1)–N(2)	1.987(3)
Mn(1)–O(3)	2.245(2)	Mn(1)–O(4)	2.241(2)
Angle	ω, deg	Angle	ω, deg
		I	
O(2)Mn(1)O(1)	93.89(7)	O(2)Mn(1)N(2)	91.47(7)
O(1)Mn(1)N(2)	164.92(8)	O(2)Mn(1)N(1)	167.97(8)
O(1)Mn(1)N(1)	89.60(8)	N(2)Mn(1)N(1)	82.45(8)
O(2)Mn(1)N(3)	100.54(9)	O(1)Mn(1)N(3)	99.10(9)
N(2)Mn(1)N(3)	93.75(9)	N(1)Mn(1)N(3)	90.25(9)
		II	
O(2)Mn(1)O(1)	93.25(9)	O(2)Mn(1)N(1)	175.11(10)
O(1)Mn(1)N(1)	91.60(10)	O(2)Mn(1)N(2)	92.52(10)
O(1)Mn(1)N(2)	174.23(10)	N(1)Mn(1)N(2)	82.64(11)
O(2)Mn(1)O(4)	89.78(9)	O(1)Mn(1)O(4)	94.45(10)
N(1)Mn(1)O(4)	90.51(10)	N(2)Mn(1)O(4)	85.41(10)
O(2)Mn(1)O(3)	92.12(10)	O(1)Mn(1)O(3)	90.08(10)
N(1)Mn(1)O(3)	87.20(10)	N(2)Mn(1)O(3)	89.87(10)
O(4)Mn(1)O(3)	174.99(8)		

Table 3. Geometric parameters of hydrogen bonds for **II***

D–H···A	Distance, Å			Angle
	D–H	H···A	D···A	D–H···A, deg
O(7)–H(7*B*)···O(5)$^{\rm i}$	0.89(2)	1.99(3)	2.875(3)	175(15)
O(3)–H(3*A*)···O(7)$^{\rm ii}$	0.88(3)	1.92(3)	2.774(3)	163(16)
O(4)–H(4*A*)···O(7)	0.85(1)	2.07(6)	2.881(3)	160(15)
O(4)–H(4*B*)···O(1)$^{\rm iii}$	0.85(1)	1.96(4)	2.784(3)	163(15)
O(3)–H(3*B*)···O(2)$^{\rm iv}$	0.87(2)	1.93(3)	2.794(3)	174(15)
O(7)–H(7*A*)···O(6)$^{\rm v}$	0.92(4)	1.92(8)	2.752(4)	150(13)
O(7)–H(7*A*)···O(5)$^{\rm v}$	0.92(4)	2.51(11)	3.144(3)	127(11)

* Symmetry codes: $^{\rm i}\,1 + x, y, z$; $^{\rm ii}\,-1 + x, y, z$; $^{\rm iii}\,1 - x, 1 - y, 1 - z$; $^{\rm iv}\,-x, 1 - y, 1 - z$; $^{\rm v}\,1 - x, -y, 1 - z$.

bridge Crystallographic Data Centre (CCDC nos. 1008309 (**I**) and 1008310 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Catalytic epoxidation of olefins. H_2O_2 (1.1 mmol, 30% H_2O solution) as oxidant was added to a solution of olefins (0.28 mmol), $NaHCO_3$ (0.11 mmol) and catalyst (9.4×10^{-4} mmol) in MeCN (0.5 mL). After the reaction was over, for the products analysis, the solution was subjected to multiple ether extraction, and the extract was also concentrated down to 0.5 cm^3 by distillation in a rotary evaporator at room temperature and then a sample (2 μL) was taken from the solution and analyzed by GC. The retention times of the peaks were compared with those of commercial stan-

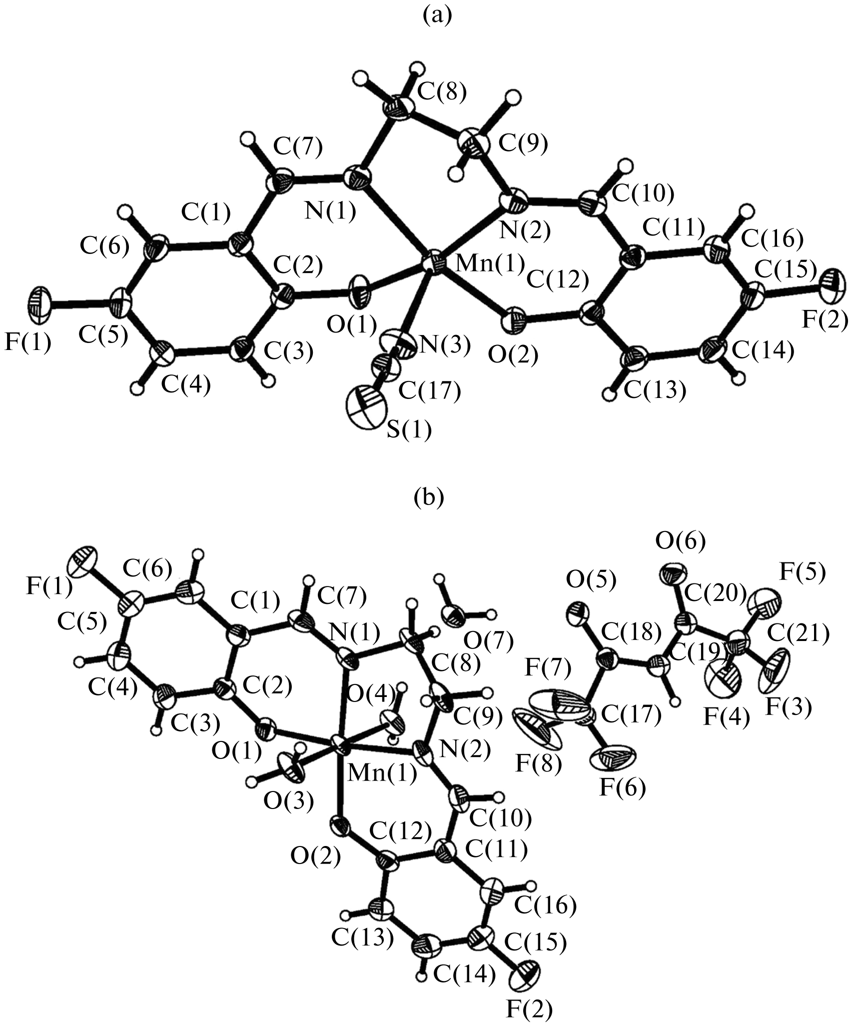


Fig. 1. Molecular structure of complex **I** (a) and **II** (b) with 30% probability level.

dards, and chlorobenzene was used as an internal standard for GC yield calculation.

RESULTS AND DISCUSSION

The two complexes were readily prepared by the reaction of equimolar quantities of the Schiff base ligand with manganese salts in methanol. It should be noted that even though no problem occurred, perchlorate salts are potential explosive. Only small quantities of such chemicals should be handled and with great care. Elemental analyses of the complexes are in good agreement with expected values.

The medium and broad absorption centered at 3413 cm^{-1} for **II** can be assigned to the O–H stretching vibrations of the water molecules. The weak absorptions in the region 3030–2810 cm^{-1} are resulted from the C–H vibrations of the aliphatic and aromatic groups. The intense absorptions at 1613 cm^{-1} for **I** and 1615 cm^{-1} for **II** can be assigned to the vibration of C=N groups. The intense absorption indicative of the thiocyanate ligand is observed at 2033 cm^{-1}.

The molecular structure of complex **I** is shown in Fig. 1a. The Mn atom in complex **I** is in a square pyramidal coordination with two imino N and two phenolate O atoms of the Schiff base ligand defining the basal plane and with one thiocyanate N atom located at the apical position. The Mn atom deviates from the least-squares plane defined by the basal donor atoms by 0.206(2) Å. The distortion of the coordination can be observed from the bond angles related to the Mn atoms. Due to the strain created from the five-membered chelated ring Mn(1)–N(1)–C(8)–C(9)–N(2), the angle N(1)Mn(1)N(2) is much small. The Mn–O and Mn–N bond lengths in the present complex are comparable to those observed in similar manganese complexes [18, 19]. The dihedral angles between the two benzene rings of the Schiff base ligand is 2.9(5) Å. In the crystal structure of complex **I**, the molecules are stack along the *y* axis by π···π interactions (Fig. 2a, Table 4).

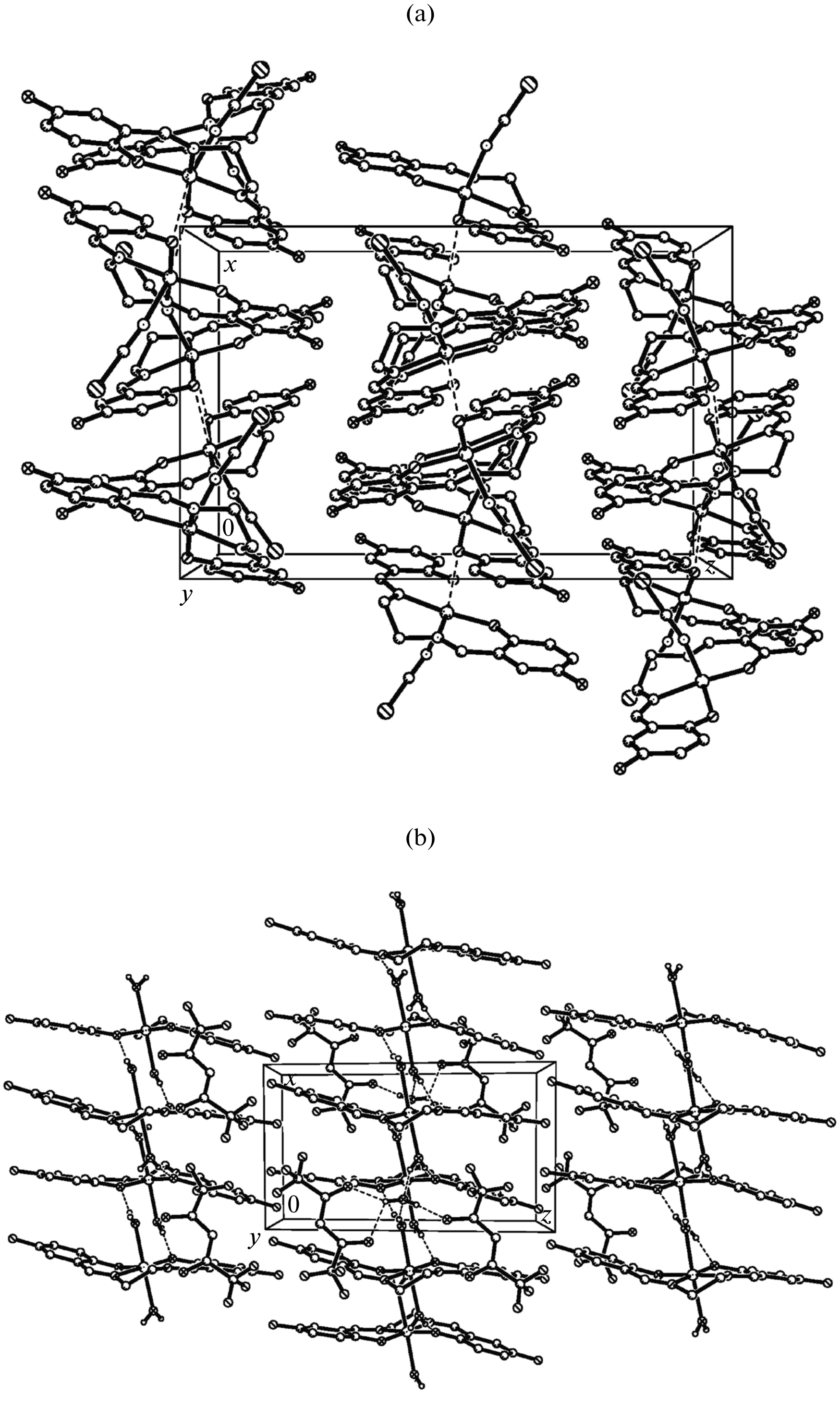


Fig. 2. Molecular packing of complex **I** (a) and **II** (b), viewed along the *y* axis. Hydrogen bonds are shown as dashed lines.

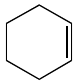
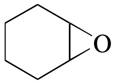
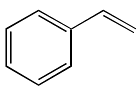
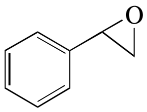
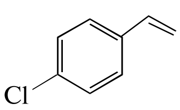
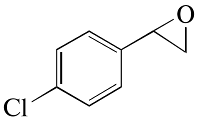
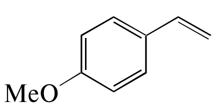
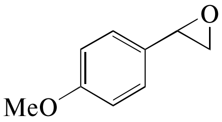
The molecular structure of complex **II** is shown in Fig. 1b. The asymmetric unit of complex **II** contains a mononuclear manganese(III) complex cation, a hexafluoroacetylacetate anion, and a water molecule. The Mn atom in the complex cation is in octahedral coordination with two imino N and two phenolate O atoms defining the equatorial plane and with two water O atoms located at the axial positions. The distortion of the coordination can be observed from the bond angles related to the Mn atoms. Due to the strain created from the five-membered chelated ring Mn(1)–N(1)–C(8)–C(9)–N(2), the angle N(1)Mn(1)N(2) is

Table 4. Parameters between the planes for complexes **I** and **II***

Cg	Distance between ring centroids, Å	Dihedral angle, deg	Perpendicular distance of *Cg*(*I*) on *Cg*(*J*) (Å)	Perpendicular distance of *Cg*(*J*) on *Cg*(*I*) (Å)
		I		
Cg(1)–*Cg*(3)	3.876	86	–1.079	2.020
Cg(1)–*Cg*(4)	4.888	87	–2.026	–3.558
Cg(2)–*Cg*(1)$^{\text{vi}}$	2.997	90	1.223	–1.755
Cg(2)–*Cg*(3)$^{\text{vi}}$	3.507	8	–3.141	–3.314
Cg(3)–*Cg*(v)$^{\text{vi}}$	3.560	3	–3.283	–3.277
		II		
Cg(5)–*Cg*(6)$^{\text{iv}}$	3.896	10	–3.712	–3.485
Cg(5)–*Cg*(6)$^{\text{iii}}$	4.233	10	3.854	3.869

* Symmetry codes: $^{\text{vi}}$ $-x, -y, -z$. For **I**: *Cg*(1), *Cg*(2), *Cg*(3) and *Cg*(4) are the centroids of Mn(1)–O(1)–Mn(1*A*)–O(1*A*), Mn(1)–O(2)–C(12)–C(11)–C(10)–N(2), C(1)–C(2)–C(3)–C(4)–C(5)–C(6), and C(11)–C(12)–C(13)–C(14)–C(15)–C(16), respectively. For **II**: *Cg*(5) and *Cg*(6) are the centroids of C(1)–C(2)–C(3)–C(4)–C(5)–C(6) and C(11)–C(12)–C(13)–C(14)–C(15)–C(16), respectively.

Table 5. Catalytic oxidation results*

Substrate	Product	Conversion, % (TON) **	Conversion, % ***
		77 (165) (**I**) 72 (154) (**II**)	27 25
		83 (202) (**I**) 87 (195) (**II**)	32 29
		92 (190) (**I**) 95 (213) (**II**)	35 31
		67 (177) (**I**) 73 (163) (**II**)	18 23

* The molar ratios for catalyst : substrate : $NaHCO_3$: H_2O_2 are 1 : 300 : 120 : 1200. The reactions were performed in (80 : 20) mixture of $CH_3OH–CH_2Cl_2$ at ambient conditions.

** The GC conversion was measured relative to the starting olefin after 75 min. TON = (mmol of product)/mmol of catalyst.

*** The conversion without the addition of sodium bicarbonate.

much small. The *cis* and *trans* angles are range from 82.6(1)° to 94.4(1)°, and 174.2(1)° to 175.1(1)°. The Mn–O and Mn–N bond lengths in the present complex are comparable to those observed in similar manganese complexes [20–22]. The dihedral angle among the benzene rings of the Schiff base ligand is 9.4(3)°. In the crystal structure of complex **II**, the molecules are linked through intermolecular O–H···O hydrogen bonds to form chains along the *x* axis (Fig. 2b). In addition, there are also π···π interactions among the molecules (Table 4).

The catalytic oxidation results are listed in Table 5. The complexes have good catalytic capability in the oxidation of selected olefins to the corresponding epoxides. Both complexes have similar catalytic property. When H_2O_2 was used as a sole oxidant the catalytic efficiency is not good, but when $NaHCO_3$ was added as a co-catalyst the efficiency of the system increases sharply. The H_2O_2 and hydrogen carbonate may react in an equilibrium process to produce peroxymonocarbonate, HCO_4^-, which is a more reactive nucleophile than H_2O_2 and speeds up the epoxidation reaction.

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