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Synthesis, Crystal Structures, and Catalytic Properties of Dinuclear Manganese(III) Complexes Derived from *N*,*N'*-Bis(5-Methylsalicylidene)propane-1,2-Diamine[1]

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Abstract—Two centrosymmetric dinuclear manganese(III) complexes, $[Mn_2L_2(N_3)_2]$ (**I**) and $[Mn_2L_2(NCS)_2]$ (**II**), where L is the deprotonated form of *N*,*N'*-bis(5-methylsalicylidene)propane-1,2-diamine (H_2L), have been prepared and structurally characterized by elemental analysis, IR and UV-Vis spectra and single crystal X-ray diffraction (CIF files CCDC nos. 1553014 (**I**), 1553015 (**II**)). The Mn atoms are in octahedral coordination. Catalytic properties for epoxidation of styrene by the complexes using PhIO and NaOCl as oxidant have been studied.

Keywords: crystal structures, Schiff base, dinuclear complex, manganese complex, catalytic oxidation

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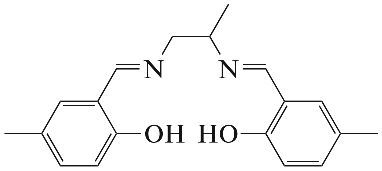
INTRODUCTION

Schiff bases are a kind of interesting and widely studied ligands in the construction of various metal complexes [1, 2]. Much attention has been focused on manganese(III) complexes with Schiff base ligands due to their important role in several metalloenzymes and catalytic properties in many organic reactions [3–5]. In addition, manganese complexes have interesting biological activities [6–8]. The involvement of manganese in many biological systems is well established. Manganese(III) complexes with salen-type ligands are among the most efficient catalysts for the epoxidation of various olefins with high selectivity and yield. Epoxidation of olefins catalyzed by manganese(III) salen complexes has been studied extensively since Kochi and coworkers described in 1986 that they are highly effective, chemoselective, and stereoselective catalysts [9]. Azide and thiocyanate are widely used because of their diverse binding modes which yield different types of molecules such as dimers, tetramers, one-, two-, or three-dimensional arrays [10–13]. We report herein the synthesis, characterization, crystal structures and catalytic oxidation property of two new complexes $[Mn_2L_2(N_3)_2]$ (**I**) and $[Mn_2L_2(NCS)_2]$ (**II**), where L is the deprotonated form of *N*,*N'*-bis(5-methylsalicylidene)propane-1,2-diamine (H_2L):



(H_2L)

EXPERIMENTAL

Materials and methods. 5-Methylsalicylaldehyde and *N*,*N'*-propane-1,2-diamine were purchased from Lancaster. The other chemicals were obtained from commercial sources. The Schiff base H_2L was prepared according to the literature method [14]. Iodosylbenzene (PhIO) was prepared by the hydrolysis of iodobenzenediacetate [15]. Styrene and styrene oxide were purchased from Aldrich and used in epoxidation experiment without further purification. The styrene oxide was used as standard sample in GC analysis. CHN elemental analyses were carried out with a Perkin-Elmer elemental analyzer. IR spectra were performed on a Nicolet 470 spectrometer with KBr pellets in the 4000–400 cm^{-1} region. The crystal determination was carried out on a Bruker Apex II CCD area diffractometer. GC experiments were performed with Agilent 5977A Network GC systems.

Synthesis of $[Mn_2L_2(N_3)_2]$ (I). The mixture of NaN_3 (0.065 g, 1.00 mmol) and $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.245 g, 1.00 mmol) in 30 mL methanol was

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stirred for 1 h at room temperature, then H_2L (0.310 g, 1.00 mmol) was added to the solution and the reaction continued to stirred for 1 h. After filtration, the brown filtrate was allowed to stand at room temperature for a few days to deposit brown crystals of the complex in 51% yield.

IR data (KBr; ν, cm^{-1}): 2038 s, 1619 s, 1542 m, 1460 m, 1380 w, 1288 m, 1163 m, 1078 s, 946 m, 861 m, 824 s, 527 m, 459 w.

For $C_{38}H_{40}N_{10}O_4Mn_2$

anal. calcd., %	C, 56.30	H, 4.97	N, 17.28
Found, %	C, 56.12	H, 4.88	N, 17.16

Synthesis of $[Mn_2L_2(NCS)_2]$ (II). The mixture of NH_4NCS (0.076 g, 1.0 mmol) and $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.245 g, 1.00 mmol) in 30 mL methanol was stirred for 1 h at room temperature, then H_2L (0.310 g, 1.00 mmol) was added to the solution and the reaction continued to stirred for 1 h. After filtration, the brown filtrate was allowed to stand at room temperature for a few days to deposit brown crystals of the complex in 62% yield.

IR data (KBr; ν, cm^{-1}): 2056 s, 1619 s, 1540 m, 1462 m, 1380 w, 1300 m, 1275 w, 1163 m, 1141 w, 1123 w, 1046 w, 1021 w, 946 w, 824 s, 567 m, 532 m, 455 w.

For $C_{40}H_{40}N_6O_4S_2Mn_2$

anal. calcd., %	C, 57.00	H, 4.78	N, 9.97
Found, %	C, 57.17	H, 4.87	N, 9.85

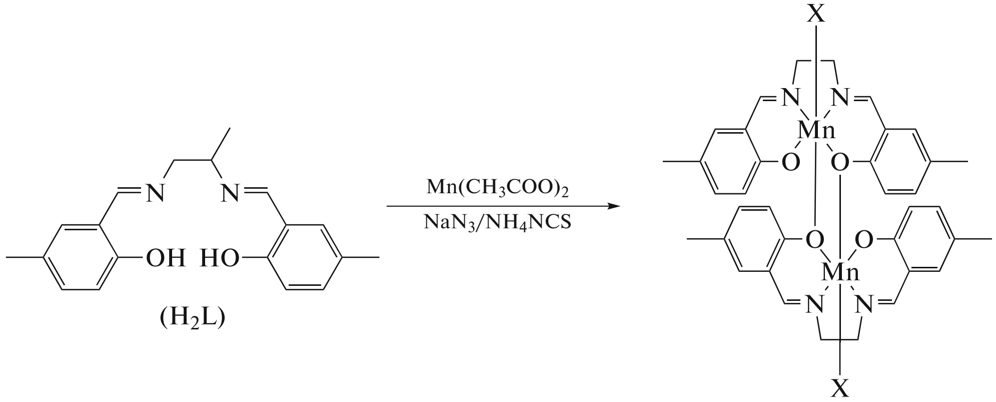
X-ray crystallography.. Suitable single crystals of the complexes were mounted at the top of glass fibres and scanned on a Bruker SMART 1000 CCD area diffractometer with a MoK_α radiation (λ = 0.71073 Å) at 298(2) K. The unit cell dimensions were obtained with the least-squares refinements and the structures were solved and refined by direct methods with SHELXTL-97 program [16]. Multi-scan absorption correction was applied by using the SADABS program [17]. The final refinement was performed by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms on F^2. The hydrogen atoms were placed geometrically, with $U_{iso}(H)$ restrained to 1.2 $U_{eq}(C)$ and 1.5 $U_{eq}(C_{methyl})$. The propane groups in both structures are disordered over two sites, with occupancies of 0.698(2) and 0.302(2) for **I** and 0.441(2) and 0.559(2) for **II**. Crystallographic data are summarized in Table 1.

Supplementary material for the structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1553014 (**I**), 1553015 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam. ac.uk).

General method for styrene oxidation. The oxidation reactions were carried out at room temperature in acetonitrile under nitrogen atmosphere with constant stirring. The composition of the reaction mixture was 2.00 mmol of styrene, 2.00 mmol of chlorobenzene (internal standard), 0.10 mmol of Mn(III) complex (catalyst) and 2.00 mmol iodosylbenzene or sodium hypochlorite (oxidant) in 5.00 mL freshly distilled acetonitrile. When the oxidant was sodium hypochlorite, the solution was buffered to pH 11.2 with NaH_2PO_4 and NaOH [18]. The composition of reaction medium was determined by GC with styrene and styrene epoxide quantified by the internal standard method (chlorobenzene). All other products detected by GC were mentioned as others. For each complex the reaction time for maximum epoxide yield was determined by withdrawing periodically 0.1 mL aliquots from the reaction mixture and this time was used to monitor the efficiency of the catalyst on performing at least two independent experiments. Blank experiments with each oxidant and using the same experimental conditions except catalyst were also performed.

RESULTS AND DISCUSSION

Complexes **I** and **II** were prepared according to the procedure as described below:



X = N_3 for **I**, NCS for **II**

Table 1. Crystallographic data and structure refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
Fw	810.68	842.78
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	8.829(1)	8.716(2)
b, Å	14.973(2)	15.308(3)
c, Å	14.493(2)	15.208(3)
β, deg	105.301(2)	105.939(3)
V, Å^3	1848.0(4)	1951.1(6)
Z	2	2
F(000)	840	872
$\mu(MoK_\alpha)$, mm^{-1}	0.739	0.803
Collcted reflections	10372	11052
Independent reflections	3441	3636
Observed reflections ($I \geq 2\sigma(I)$)	2500	2151
Restraints/parameters	20/265	37/264
Goodness of fit on F^2	1.109	1.040
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0690, 0.1789	0.0693, 0.1952
R_1, wR_2 (all data)*	0.0945, 0.1962	0.1163, 0.2276

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

The structures of complexes **I** and **II** are shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2.

Single crystal X-ray structural analysis revealed that both complexes are similar centrosymmetric phenolate bridged dinuclear manganese compounds. The Mn···Mn distances are 3.562(2) Å for **I** and 3.464(2) Å for **II**. The merely difference is the secondary ligands, viz. N_3 for **I** and NCS for **II**. The Mn atoms in the complexes are in octahedral environment consisting of the N_2O_2 donor set of the Schiff base ligands, and the terminal nitrogen donor of the azide or thiocyanate ligand. The equatorial plane of the octahedral coordination is defined by the phenolate oxygen and imino nitrogen of the Schiff base ligands with the Mn atoms deviate from the least-squares planes by 0.220(2) Å for **I** and 0.169(2) Å for **II**. The Mn–N and Mn–O bond lengths are comparable to the corresponding values observed in manganese complexes with Schiff base ligands [19–24]. The axial Mn(1)–N(3) and Mn(1)–O(2*A*) bond lengths are longer than the equatorial bonds, which is caused by Jahn–Teller effects expected for d^4 high spin manganese(III) systems [25]. The azide and thiocyanate ligands are quasi-linear with angles of 177.6(9)° for **I** and 179.1(6)° for **II**.

IR spectra of the manganese(III) complexes are very similar. The strong bands indicative of ν(C=N) are located at 1619 cm^{-1}. The shift of the strong bands towards lower frequencies, compared to the spectrum of the free Schiff base, is consistent with the imino nitrogen coordination. The intense absorption for the stretching vibrations of the azide ligand in **I** and the thiocyanate ligand in **II** are observed at 2038 and 2056 cm^{-1}, respectively.

Oxidation of styrene was carried out at room temperature with the complexes as the catalysts and PhIO and NaOCl as oxidants. The brown color of the solutions containing the complexes and the substrate was intensified after the addition of oxidant indicating the formation of oxo-metallic intermediates of the catalysts [26]. After completion of oxidation reaction of the alkene, the solution regains its initial color which suggests that the regeneration of the catalysts takes place.

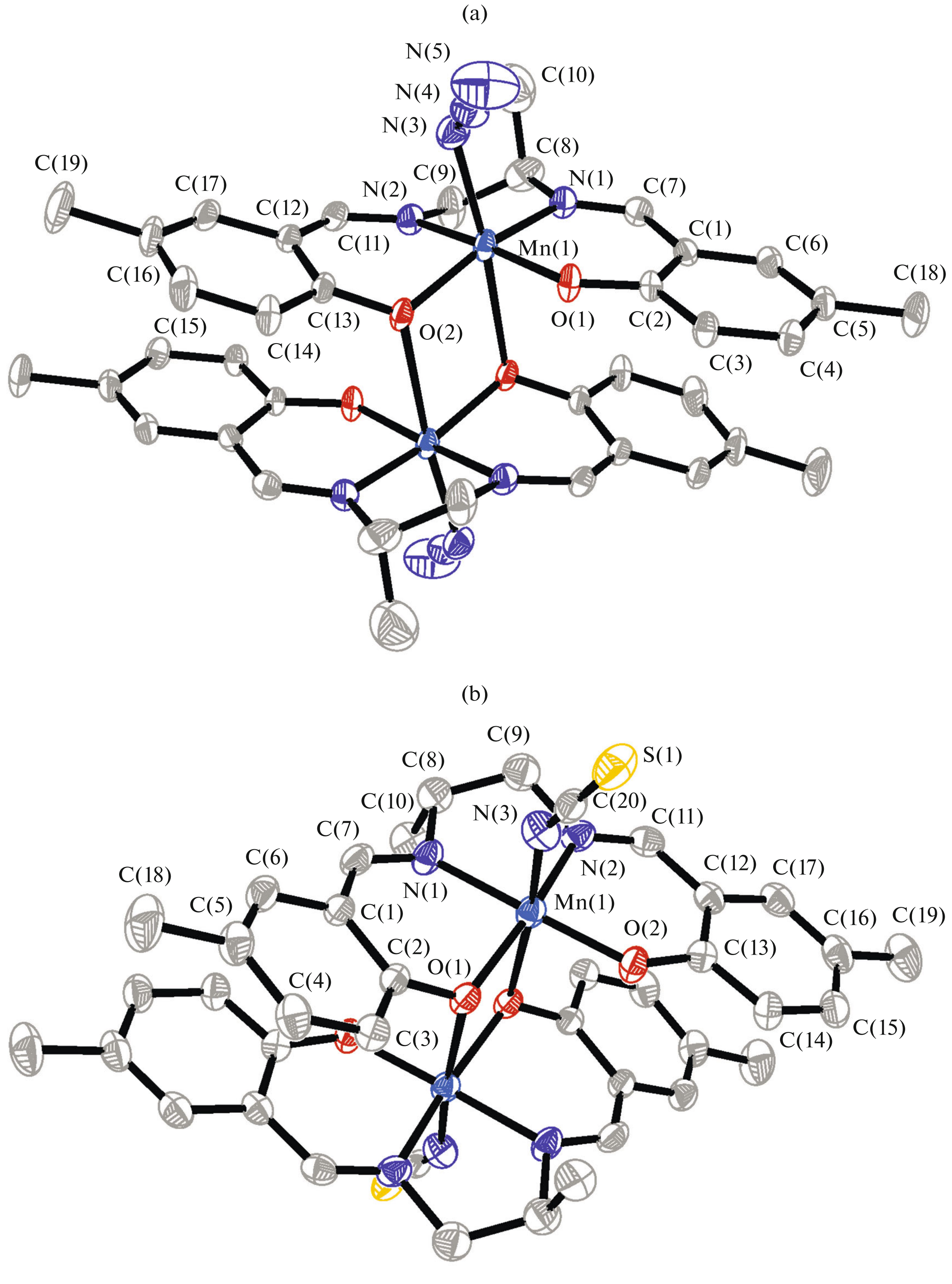


Fig. 1. Molecular structure of **I** (a) and **II** (b) at 30% probability thermal ellipsoids. Unlabelled atoms are at the symmetry position $2 - x$, $2 - y$, $1 - z$.

The two complexes as catalysts convert styrene most efficiently in the presence of PhIO or NaOCl. It is easily observed that there is no obvious difference for the catalytic properties between the two complexes, as a result of similar structures. The complexes are selective towards the formation of styrene epoxide. When the reactions were carried out with PhIO, styrene conversions are 83 and 85% for **I** and **II**, respec-

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)	1.861(3)	Mn(1)–O(2)	1.899(3)
Mn(1)–N(1)	1.975(4)	Mn(1)–N(2)	1.991(4)
Mn(1)–N(3)	2.141(6)		
II			
Mn(1)–O(1)	1.899(4)	Mn(1)–O(2)	1.855(4)
Mn(1)–N(1)	1.979(5)	Mn(1)–N(2)	1.975(5)
Mn(1)–N(3)	2.163(7)		
Angle	**ω, deg**	**Angle**	**ω, deg**
I			
O(1)Mn(1)O(2)	94.20(14)	O(1)Mn(1)N(1)	92.20(16)
O(2)Mn(1)N(1)	161.05(19)	O(1)Mn(1)N(2)	170.09(18)
O(2)Mn(1)N(2)	88.55(17)	N(1)Mn(1)N(2)	82.34(18)
O(1)Mn(1)N(3)	98.08(19)	O(2)Mn(1)N(3)	97.49(19)
N(1)Mn(1)N(3)	99.2(2)	N(2)Mn(1)N(3)	91.0(2)
II			
O(2)Mn(1)O(1)	95.30(16)	O(2)Mn(1)N(2)	92.0(2)
O(1)Mn(1)N(2)	163.6(2)	O(2)Mn(1)N(1)	172.3(2)
O(1)Mn(1)N(1)	89.09(19)	N(2)Mn(1)N(1)	82.2(2)
O(2)Mn(1)N(3)	94.3(2)	O(1)Mn(1)N(3)	95.4(2)
N(2)Mn(1)N(3)	98.7(2)	N(1)Mn(1)N(3)	91.6(2)

tively. When the reactions were carried out with NaOCl, styrene conversions are 72 and 75% for **I** and **II**, respectively.

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