

A Mononuclear Nickel(II) Complex and a Dinuclear Manganese(III) Complex Derived from *N,N'*-bis(5-methoxysalicylidene)-1,2-ethanediamine: Synthesis, Crystal Structures and Catalytic Epoxidation Property¹

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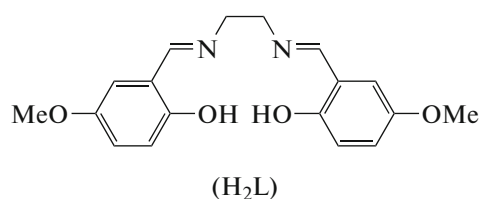
Abstract—Synthesis and characterization of a mononuclear nickel(II) complex $[\text{NiL}] \cdot \text{CH}_3\text{OH}$ (**I**) and a dinuclear manganese(III) complex $[\text{Mn}_2\text{L}_2(\text{NCS})_2]$ (**II**) derived from the bis-Schiff base *N,N'*-bis(5-methoxysalicylidene)-1,2-ethanediamine (H_2L) are reported. The complexes were characterized by elemental analyses, IR spectra and molar conductivity. Single crystal X-ray structures of the complexes have been determined (CIF files CCDC nos. 1056778 (**I**) and 1056688 (**II**)). The Ni atom in **I** is in a square planar coordination, and the Mn atom in **II** is in an octahedral coordination. Catalytic property for epoxidation of styrene by the complexes using PhIO and NaOCl as oxidant has been studied. As a result, complex **II** is efficient for the styrene epoxidation.

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INTRODUCTION

Schiff bases are very popular ligands because they efficiently act as chelates generating a rich variety of coordination compounds, ranging from mononuclear to polynuclear species. In recent years, a great number of complexes with Schiff bases have been reported, showing interesting structures and excellent properties, such as catalytic [1–3], magnetic [4–6], luminescent [7–9] and biological [10–12]. Manganese complexes with Schiff bases are often described as good epoxidation catalysts, due to their high activity and selectivity [13–15]. The method is mild and is an environment friendly process. 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 [16]. Numerous salen type ligands have been prepared and utilized to investigate steric, electronic, and overall structural effects on the catalytic activity of manganese(III) center. Thus, manganese(III) complexes derived from salen type ligands can be used as laboratory and industrial homogeneous catalysts in the epoxidation of unfunctionalised alkenes using iodosylbenzene, sodium hypochlorite, hydrogen peroxide and alkyl hydroperoxides as the oxygen source. The mechanism of the oxygen transfer from the intermedi-

ate oxo-metallic species to the olefin as well as the spin state of the intermediate oxo-metallic species, which exists possibly in a higher oxidation state, are still debatable issues [17]. Mohanta and coworkers reported the efficient catalyst for styrene epoxidation with Schiff base manganese(III) complexes and found that complexes with chloride ligand is better than those with methanol or azide ligand [18]. Pseudohalides, especially azide, thiocyanate or dicyanamide, have long been known for their versatile coordination modes. As a further study of the catalytic epoxidation of Schiff base complexes, in this study, the synthesis, characterization, and crystal structures of a new nickel(II) complex $[\text{NiL}] \cdot \text{CH}_3\text{OH}$ (**I**) and a dinuclear manganese(III) complex $[\text{Mn}_2\text{L}_2(\text{NCS})_2]$ (**II**), derived from the bis-Schiff base *N,N'*-bis(5-methoxysalicylidene)-1,2-ethanediamine (H_2L), are reported.



¹The article is published in the original.

EXPERIMENTAL

Material and measurements. All chemicals and solvents used for the synthesis were of analytical grade. 5-Methoxysalicylaldehyde, ethane-1,2-diamine, ammonium thiocyanate, styrene and styrene oxide were purchased from Aldrich and used without further purification. Iodosylbenzene (PhIO) was prepared by the hydrolysis of iodobenzene diacetate. Nickel perchlorate hexahydrate and manganese perchlorate hexahydrate were prepared by the treatment of perchloric acid with nickel carbonate and manganese carbonate, respectively, followed by slow evaporation on a steam bath. They were then filtered through a fine glass-frit and preserved in an anhydrous CaCl_2 desiccator. The Schiff base compound H_2L was prepared by 2 : 1 condensation of 5-methoxysalicylaldehyde and ethane-1,2-diamine in methanol, according to the literature method [19].

Infrared spectra were recorded as KBr pellets on a JASCO FT-IR 4100 spectrophotometer. Elemental analyses (C, H, N) were carried out using a Perkin-Elmer 2400 II elemental analyser. GC analysis was performed with Agilent 6890N Network GC systems. Molar conductivity of the complexes in acetonitrile was measured with a DDS-11A molar conductivity meter.

Caution! Although no problem was encountered in this work, perchlorate salts are potentially explosive and should be used in small quantity with much care.

Synthesis of complex I. The appropriate quantity of solid Schiff base ligand H_2L (0.328 g, 1 mmol) was dissolved in dry methanol (20 mL). A solution of nickel(II) perchlorate hexahydrate (0.366 g, 1 mmol) in dry methanol (10 mL) was added to this solution followed by the addition of ammonium thiocyanate (0.076 g, 1.00 mmol) in dry methanol (10 mL). The mixture was refluxed for 1 h. The resulting red solution was then filtered off and the filtrate was left undisturbed. After a week fine red needle shaped X-ray diffraction quality single crystals separated out. They were filtered, washed with methanol and dried in vacuo over anhydrous CaCl_2 .

For $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_5\text{Ni}$

anal. calcd., %: C, 54.7; H, 5.3; N, 6.7.
Found, %: C, 54.5; H, 5.4; N, 6.9.

Synthesis of complex II. The appropriate quantity of solid Schiff base ligand H_2L (0.328 g, 1 mmol) was dissolved in dry methanol (20 mL). A solution of manganese(II) perchlorate hexahydrate (0.362 g, 1 mmol) in dry methanol (10 mL) was added to this solution followed by the addition of ammonium thiocyanate (0.076 g, 1.00 mmol) in dry methanol (10 mL). The mixture was refluxed for 1 h. The resulting brown solution was then filtered off and the filtrate was left undisturbed. After a week fine deep brown block

shaped X-ray diffraction quality single crystals separated out. They were filtered, washed with methanol and dried in vacuo over anhydrous CaCl_2 .

For $\text{C}_{38}\text{H}_{36}\text{N}_6\text{O}_8\text{S}_2\text{Mn}_2$

anal. calcd., %: C, 51.9; H, 4.1; N, 9.6.
Found, %: C, 51.7; H, 4.2; N, 9.5.

X-ray structure determination. Intensity data of the complexes were collected at 298(2) K on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). Suitable crystals were affixed to the end of glass fibers using silicone grease and transferred to the goniostat. The unit cell parameters were obtained from SAINT; absorption corrections were performed with SADABS [20]. Structures of the complexes were solved by direct method and refined by full-matrix least-squares method on F^2 using SHELXTL crystallographic software package [21]. All the non-hydrogen atoms are refined anisotropically. All hydrogen atoms were included in fixed calculated positions. Crystal data for the complexes are summarized in Table 1. Selected bond lengths and angles of the complexes are given in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1056778 (**I**) and 1056688 (**II**); deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

General method for styrene epoxidation. The epoxidation 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 the complexes (catalyst) and 2.00 mmol of sodium hypochlorite (oxidant) in 5.00 mL acetonitrile. When the oxidant was sodium hypochlorite, the solution was buffered to pH 11.2 with NaH_2PO_4 and NaOH . The composition of reaction medium was determined by GC with styrene and styrene epoxide quantified by the internal standard method (chlorobenzene). Styrene oxide was used as standard sample in GC analysis. All other products detected by GC were mentioned as others. For the complexes the reaction time for maximum epoxide yield was determined by withdrawing periodically 0.10 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

The tetradentate bis-Schiff base H_2L was easily prepared from the reaction between 5-methoxysalicy-

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

Parameter	Value	
	I	II
Formula weight	417.1	878.7
Crystal size, mm	0.17 × 0.15 × 0.12	0.23 × 0.22 × 0.18
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a , Å	11.406(1)	7.856(2)
b , Å	7.413(1)	9.577(2)
c , Å	21.622(2)	13.989(2)
α , deg	90	92.008(2)
β , deg	92.079(2)	102.001(2)
γ , deg	90	105.989(2)
V , Å ³	1827.0(3)	984.9(3)
Z	4	1
ρ_{calcd} , g cm ⁻³	1.516	1.482
$\mu(\text{MoK}\alpha)$, mm ⁻¹	1.096	0.806
$F(000)$	872	452
Number of measured reflections	16048	4884
Number of observations ($I > 2\sigma(I)$)	3390	2766
Unique reflections	2658	2160
Parameters	246	255
Number of restraints	13	0
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0512, 0.1366	0.0642, 0.1323
R_1, wR_2 (all data)*	0.0688, 0.1492	0.0866, 0.1487
Goodness of fit of F^2	1.046	1.105
Largest difference peak/hole, e Å ⁻³	0.905/−0.645	0.511/−0.485

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

laldehyde and ethane-1,2-diamine in methanol with 2 : 1 stoichiometric ratio. Reaction of H₂L and ammonium thiocyanate with nickel perchlorate hexahydrate and manganese perchlorate hexahydrate, respectively, in a molar ratio of 1 : 1 : 1 in methanol, followed by slow evaporation, afforded the single crystals of complexes **I** and **II**, respectively. The thiocyanate ligand coordinated to the Mn atom of the manganese complex, while not coordinated to the Ni atom of the nickel complex. During the synthesis performed under aerobic conditions, the reaction system of complex **II** exhibited an obvious color change from light to deep brown. This suggest the occurrence of oxidation process (Mn(II) → Mn(III)) induced by the oxygen in air. Crystals of the complexes are stable in air. The molar conductivities of the complexes **I** and **II** in acetonitrile are 25 and 18 Ω⁻¹ cm² mol⁻¹, respectively, indicating the non-electronic nature [22]. The infrared spectra of the complexes were recorded within the 4000–

400 cm⁻¹ region. The strong sharp bands around 1615–1623 cm⁻¹ in the spectra of the complexes are characteristic of $\nu(\text{C}=\text{N})$. The band centered at 3327 cm⁻¹ in the spectrum of complex **I** is due to the methanol molecule of crystallization. The intense absorption at 2113 cm⁻¹ is due to the thiocyanate ligand in **II**.

An ORTEP representation of complex **I** with atom numbering scheme is depicted in Fig. 1. The complex contains a mononuclear [NiL] complex molecule and a methanol molecule of crystallization. The Ni centre is four coordinated by four donor atoms (N₂O₂) of the coordinated Schiff base ligand L. The coordination environment of the Ni atom is slightly distorted, as evidenced from the bond lengths and angles. The metal–ligand bond distances involving the imine nitrogens (Ni(1)–N(1) 1.846(3), Ni(1)–N(2) 1.851(3) Å) are comparable to the bond lengths involving phenolate oxygens (Ni(1)–O(1) 1.847(3), Ni(1)–O(2) 1.848(3) Å). The *trans* angles (178.9(1)° and

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

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
I			
Ni(1)–O(1)	1.847(3)	Ni(1)–O(2)	1.848(3)
Ni(1)–N(1)	1.846(3)	Ni(1)–N(2)	1.851(3)
II			
Mn(1)–O(1)	1.873(3)	Mn(1)–O(2)	1.905(3)
Mn(1)–N(1)	1.989(4)	Mn(1)–N(2)	1.977(4)
Mn(1)–N(3)	2.193(6)	Mn(1)–O(2) ⁱ	2.594(6)
Angle	ω, deg	Angle	ω, deg
I			
O(1)Mn(1)O(2)	95.9(1)	O(1)Mn(1)N(2)	169.8(2)
O(2)Mn(1)N(2)	88.8(2)	O(1)Mn(1)N(1)	91.4(2)
O(2)Mn(1)N(1)	165.0(2)	N(2)Mn(1)N(1)	82.0(2)
O(1)Mn(1)N(3)	95.3(2)	O(2)Mn(1)N(3)	97.0(2)
N(2)Mn(1)N(3)	93.0(2)	N(1)Mn(1)N(3)	95.3(2)
O(1)Mn(1)O(2) ⁱ	89.6(2)	O(2)Mn(1)O(2) ⁱ	81.5(2)
N(1)Mn(1)O(2) ⁱ	85.4(2)	N(2)Mn(1)O(2) ⁱ	82.2(2)
N(3)Mn(1)O(2) ⁱ	175.0(2)		
II			
N(1)Ni(1)O(1)	94.5(1)	N(1)Ni(1)O(2)	178.9(1)
O(1)Ni(1)O(2)	84.9(1)	N(1)Ni(1)N(2)	86.1(2)
O(1)Ni(1)N(2)	178.6(1)	O(2)Ni(1)N(2)	94.5(1)

* Symmetry code: ⁱ $-x, 1-y, -z$.

178.6(1)° and the *cis* angles (84.9(1)–94.5(1)°) deviate slightly from the ideal values. The coordinate bond values are in agreement with those observed in nickel(II) complexes with Schiff bases [23, 24]. The average deviation (0.017(1) Å) of the donor atoms and the displacement (0.003(1) Å) of the metal center from the least-squares plane defined by the donor atoms indicates that the N₂O₂ cavity affords an almost perfect plane to the metal center. The Schiff base ligand is approximate planar with dihedral angle between the two benzene rings of 2.6(3)°. The methanol molecule is linked to the [NiL] complex molecule through intermolecular O(5)–H(5A)⋯O(2) hydrogen bond (O(5)–H(5A) 0.82, H(5A)⋯O(2) 2.00(2) Å, O(5)⋯O(2) 2.819(7) Å, O(5)–H(5A)⋯O(2) = 178(3)°).

An ORTEP representation of complex **II** with atom numbering scheme is depicted in Fig. 2. The dinuclear manganese complex possesses a crystallographic inversion center symmetry, with the Mn⋯Mn separation of 3.437(2) Å. The Mn centre is six coordinated by

four donor atoms (N₂O₂) of the coordinated Schiff base ligand L, one phenolate oxygen atom of another Schiff base ligand, and one thiocyanate nitrogen atom. In the octahedral coordination, O(2A) and N(3) are the axial ligand atoms, and O(1), O(2), N(1) and N(2) form the equatorial plane. The coordination environment of the Mn atom is slightly distorted, as evidenced from the bond lengths and angles. In the equatorial plane, the metal–ligand bond distances involving the imine nitrogens (Mn(1)–N(1) 1.989(4), Mn(1)–N(2) 1.977(4) Å) are slightly longer than the bond lengths involving phenolate oxygens (Mn(1)–O(1) 1.877(3), Mn(1)–O(2) 1.905(3) Å). As expected due to Jahn–Teller distortion of high spin manganese(III), the bond distances involving the axial donor atoms (Mn(1)–O(2A) 2.594(6), Mn(1)–N(3) 2.193(6) Å) significantly longer than the bond lengths involving the equatorial atoms. The *trans* angles (169.8(2)°, 165.0(2)°, and 175.0(2)°) and the *cis* angles (81.5(2)°–97.0(2)°) deviate slightly from the ideal values. The coordinate bond values are in agreement with those

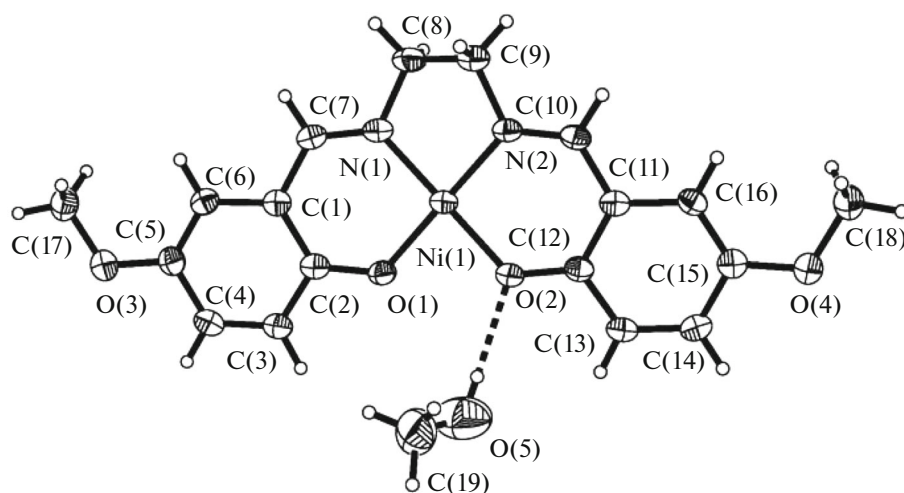


Fig. 1. A perspective view of the molecular structure of complex **I** with atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen bond is shown as a dashed line.

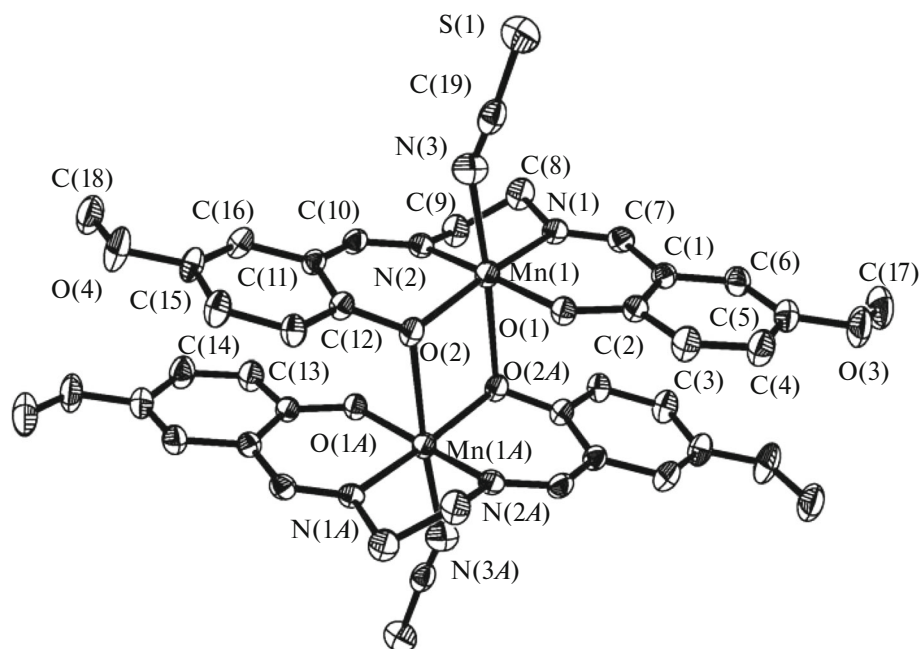


Fig. 2. A perspective view of the molecular structure of complex **II** with atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Atoms with the suffix *A* are at the symmetry position $-x, 1-y, -z$.

observed in manganese(III) complexes with Schiff bases [25, 26]. The average deviation ($0.036(2)$ Å) of the equatorial donor atoms and the displacement ($0.176(2)$ Å) of the metal center from the least-squares plane defined by the equatorial donor atoms indicates that the N_2O_2 cavity affords an almost perfect plane to the metal center. The Schiff base ligand is approximate planar with dihedral angle between the two benzene rings of $9.1(3)^\circ$.

Epoxidation of styrene was carried out at room temperature with the complexes as the catalyst and PhIO or NaOCl as the oxidant. For the reaction system with complex **I** as the catalyst, the red color was not changed. While the brown solution containing complex **II** and the substrate was intensified after the addition of oxidant indicating the formation of oxo-metallic intermediates of the catalyst. After completion of oxidation reaction of the alkene, the solution with complex **II** as the catalyst regains its initial color

which suggests that the regeneration of the catalyst takes place. Epoxidation of styrene catalyzed by the manganese complex are below:

Time, h	Oxidant	Conversion, %	Epoxide yield, %	Selectivity, %	
				epoxide	other
2.5	PhIO	94	81	85	15
3.0	NaOCl	79	62	78	22

The data reveal that complex **II** as a catalyst converts styrene efficiently in the presence of both oxidants. The catalyst is selective towards the formation of styrene epoxide despite of the formation of by-products which have been identified by GC-MS as benzaldehyde, phenylacetaldehyde, styrene epoxide derivative, alcohols, etc. When the reactions were carried out with PhIO, styrene conversions are 94%. With NaOCl as oxidant, styrene conversion dropped to 79%. It is evident that PhIO acts as a better oxidant with respect to both styrene conversion and styrene epoxide selectivity.

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