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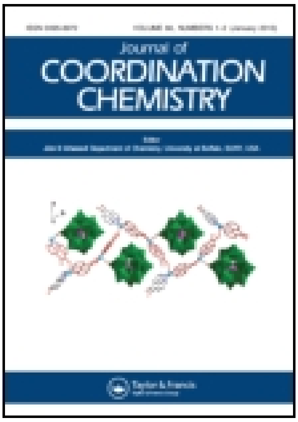

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Synthesis, crystal structures, and catalytic properties of phenoxo-bridged dinuclear manganese(III) complexes with bis-Schiff bases

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Synthesis, crystal structures, and catalytic properties of phenoxo-bridged dinuclear manganese(III) complexes with bis-Schiff bases

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Two structurally similar centrosymmetric phenoxo-bridged dinuclear manganese(III) complexes, $[Mn_2(L^1)_2(N_3)_2]$ (**1**) and $[Mn_2(L^2)_2(NCS)_2]$ (**2**), were prepared from the tetradentate bis-Schiff base ligands, *N,N'*-bis(salicylidene)propane-1,2-diamine (H_2L^1) and *N,N'*-bis(salicylidene)ethane-1,2-diamine (H_2L^2), respectively, in the presence of pseudohalides. The complexes have been characterized by FTIR, elemental analyses, and molar conductivity. Structures of the complexes have been confirmed by single-crystal X-ray determination. The bis-Schiff base ligands coordinate with Mn through their phenolate oxygen and imino nitrogen. Each Mn is an octahedral. The complexes showed that they exhibit high activity in catalytic olefin oxidation.

Keywords: bis-Schiff base; Manganese complex; Dinuclear complex; Crystal structure; Catalytic property

1. Introduction

Selective oxidation of organic molecules, under mild conditions, has attracted considerable attention [1–3]. The oxidation of hydrocarbons by transition metal complexes has been studied extensively [4–7]. Among the complexes, those derived from Schiff bases have received particular interest due to their effective catalytic properties in many oxidation and hydroxylation reactions [8–12]. A number of manganese complexes have been investigated as oxidation catalysts for organic substrates, particularly for epoxidation of olefins [13–15]. Manganese complexes with Schiff base ligands are often reported as good epoxidation catalysts under mild conditions due to their high activities and selectivities [8, 16]. As a further study of Schiff base manganese complexes and exploration of more effective catalysts for oxidation of olefins, in the present work, two new structurally similar centrosymmetric dinuclear manganese(III) complexes, $[Mn_2(L^1)_2(N_3)_2]$ (**1**) and $[Mn_2(L^2)_2(NCS)_2]$ (**2**), were prepared from the tetradentate bis-Schiff bases, *N,N'*-bis(salicylidene)propane-1,2-diamine (H_2L^1) and *N,N'*-bis(salicylidene)ethane-1,2-diamine (H_2L^2), respectively, in the presence of pseudohalides.

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2. Experimental

2.1. *Materials and methods*

All chemicals and solvents of analytical reagent grade were used as received. The Schiff bases were prepared according to the literature method [17, 18]. Microanalyses (C, H, and N) were performed using a Perkin-Elmer 2400 elemental analyzer. Infrared spectra were carried out using the JASCO FTIR model 420 spectrophotometer with KBr disks from 4000–200 cm^{-1}. GC analyses were carried out using a Shimadzu GC-2014C gas chromatograph. Molar conductivities were carried out using a DDS-11A digital conductivity meter.

2.2. *Synthesis of the complexes*

2.2.1. $[Mn_2(L^1)_2(N_3)_2]$ (1). A methanolic solution (20 mL) of $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.245 g, 1 mM) was added to a methanolic solution (20 mL) of H_2L^1 (0.310 g, 1 mM) and sodium azide (0.065 g, 1 mM). The resulting brown solution was stirred for 20 min at reflux and then cooled to ambient temperature. Single crystals of **1** suitable for X-ray diffraction were formed by slow evaporation of a methanolic solution of the complex in air for several days. Yield: 45%. Anal. Calcd for $C_{38}H_{40}Mn_2N_{10}O_4$: C, 56.3; H, 5.0; N, 17.3%. Found: C, 56.5; H, 4.9; N, 17.1. IR data (KBr, cm^{-1}): 3436 (w), 2036 (vs), 1623 (s), 1537 (m), 1462 (w), 1376 (w), 1285 (m), 1222 (w), 1158 (w), 1130 (w),1050 (w), 820 (m), 568 (w), 528 (w), 458 (w). $\Lambda_M = 17\,\Omega^{-1}\,cm^2\,M^{-1}$.

2.2.2. $[Mn_2(L^2)_2(NCS)_2]$ (2). A methanolic solution (20 mL) of $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.245 g, 1 mM) was added to a methanolic solution (20 mL) of H_2L^2 (0.296 g, 1 mM) and ammonium thiocyanate (0.076 g, 1 mM). The resulting brown solution was stirred for 20 min at reflux and then cooled to ambient temperature. Single crystals of **2** suitable for X-ray diffraction were formed by slow evaporation of a methanolic solution of the complex in air for several days. Yield: 37%. Anal. Calcd for $C_{38}H_{36}Mn_2N_6O_4S_2$: C, 56.0; H, 4.5; N, 10.3%. Found: C, 55.9; H, 4.4; N, 10.5%. IR data (KBr, cm^{-1}): 3427 (w), 2054 (vs), 1623 (s), 1536 (m), 1465 (w), 1378 (w), 1285 (m), 1221 (w), 1163 (w), 1125 (w),1052 (w), 820 (m), 554 (w), 535 (w), 443 (w). $\Lambda_M = 25\,\Omega^{-1}\,cm^2\,M^{-1}$.

2.3. *X-ray structure determination*

X-ray measurements were performed using a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the ω-scan technique. Determination of the Laue class, orientation matrix, and cell dimensions were performed according to established procedures where Lorentz polarization and absorption corrections were applied. Absorption corrections were applied by fitting a pseudoellipsoid to the ψ-scan data of selected strong reflections over a wide range of 2θ angles [19]. The positions of almost all non-hydrogen atoms were located with direct methods. Subsequent Fourier syntheses were used to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. All hydrogens were placed in calculated positions and constrained to ride on their parent atoms. The analysis was performed with the aid of the SHELXS-97 and

Table 1. Crystallographic data for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{38}H_{40}Mn_2N_{10}O_4$	$C_{38}H_{36}Mn_2N_6O_4S_2$
Formula weight	810.7	814.7
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.811(2)	8.8424(5)
b (Å)	14.940(2)	15.2051(7)
c (Å)	14.510(2)	14.3968(7)
β (°)	105.623(3)	107.458(2)
V (Å^3)	1839.5(5)	1846.5(2)
Z	2	2
λ (Å)	0.71073	0.71073
μ (MoKα) (mm^{-1})	0.742	0.846
ρ_{Calcd} (g cm^{-3})	1.464	1.465
T (K)	298(2)	298(2)
F (000)	840	840
Crystal size (mm)	0.17 × 0.15 × 0.15	0.27 × 0.23 × 0.22
θ range (°)	2.73–25.78	2.68–25.50
$h/k/l$	−10, 10/−18, 18/−17, 17	−10, 10/−18, 18/−17, 15
T (min)	0.8842	0.8038
T (max)	0.8968	0.8357
Reflections collected	14,978	18,248
Unique reflections	3509	3420
Observed reflections [$I > 2\sigma(I)$]	2343	3094
Data/restraints/parameters	3509/14/256	3420/0/237
Goodness-of-fit on F^2	1.090	1.067
R_{int}	0.0535	0.0174
Final R indices [$I > 2\sigma(I)$]	0.0705, 0.1595	0.0299, 0.0805
R indices (all data)	0.1152, 0.1799	0.0339, 0.0840
Largest peak and hole (eÅ^{-3})	0.838, −0.364	0.241, −0.196

SHELXL-97 suite of codes [20, 21]. The crystallographic data for the complexes are summarized in table 1. Selected bond lengths and angles are given in table 2.

2.4. *Catalytic epoxidation of olefins*

The catalytic reaction was carried out according to literature methods [22, 23]. To a solution of olefins (0.28 mM), $NaHCO_3$ (0.11 mM) and a catalyst (9.4×10^{-4} mM) in MeCN (0.5 mL) were added to H_2O_2 (1.1 mM, 30% H_2O solution) as the oxidant. After the reaction was over, for the product 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 standards and chlorobenzene was used as an internal standard for GC yield calculation.

3. Results and discussion

3.1. *Synthesis*

The two complexes were readily prepared by reacting manganese acetate with the Schiff base ligands and sodium azide or ammonium thiocyanate in methanol. The reaction

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.[a]

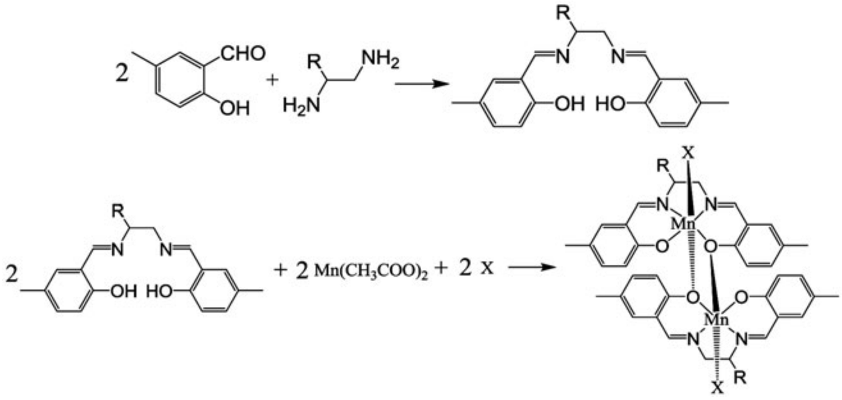
1			
Bond lengths			
Mn1–O1	1.897(3)	Mn1–O2	1.859(3)
Mn1–N1	1.988(4)	Mn1–N2	1.976(4)
Mn1–N3	2.130(5)	Mn1–O1A	2.737(5)
Bond angles			
O2–Mn1–O1	94.33(14)	O2–Mn1–N2	92.01(15)
O1–Mn1–N2	161.12(18)	O2–Mn1–N1	170.07(17)
O1–Mn1–N1	88.39(16)	N2–Mn1–N1	82.56(17)
O2–Mn1–N3	97.98(19)	O1–Mn1–N3	97.61(19)
N2–Mn1–N3	99.1(2)	N1–Mn1–N3	91.11(19)
N1–Mn1–O1A	80.8(2)	N2–Mn1–O1A	80.8(2)
O1–Mn1–O1A	81.4(2)	O2–Mn1–O1A	90.2(2)
N3–Mn1–O1A	171.8(2)		
2			
Bond lengths			
Mn1–O1	1.8646(12)	Mn1–O2	1.9038(12)
Mn1–N1	1.9799(14)	Mn1–N2	1.9927(14)
Mn1–N3	2.1728(19)	Mn1–O2B	2.5228(13)
Bond angles			
O1–Mn1–O2	96.36(5)	O1–Mn1–N1	91.66(6)
O2–Mn1–N1	164.14(6)	O1–Mn1–N2	172.35(6)
O2–Mn1–N2	88.83(6)	N1–Mn1–N2	82.00(6)
O1–Mn1–N3	93.92(7)	O2–Mn1–N3	94.77(6)
N1–Mn1–N3	98.32(7)	N2–Mn1–N3	91.25(7)
O1–Mn1–O2B	92.25(5)	O2–Mn1–O2B	80.08(5)
N1–Mn1–O2B	85.97(5)	N2–Mn1–O2B	83.07(5)
N3–Mn1–O2B	172.37(5)		

[a] A and B denote $2-x$, $2-x$, and $1-z$ and $1-x$, $-x$, and $2-z$, respectively.

process of the Schiff bases and the complexes is shown as scheme 1. As expected, $\mathrm{Mn^{II}}$ underwent aerial oxidation to $\mathrm{Mn^{III}}$ during the synthesis and crystallization. The crystals of the complexes are stable in air at room temperature and soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. The molar conductance values of **1** and **2** in methanol at 10^{-3} M are 17 and 25 Ω^{-1} cm^{2} M^{-1}, indicating they are nonelectrolytes [24].

3.2. *Crystal structure description*

The molecular structures of **1** and **2** are shown in figures 1 and 2, respectively. The molecular structures of the complexes are similar. Both complexes crystallize as centrosymmetric dinuclear structures, with Mn···Mn distances of 3.555(1) Å for **1** and 3.412(1) Å for **2**. Each molecule of the complexes is a dimer of two [MnLX] units connected through phenolate oxygen bridges. Mn in the complexes has distorted octahedral coordination. The equatorial plane of each octahedron is formed by two phenolate oxygens and two imino nitrogens of a Schiff base ligand. One axial position of each octahedron is occupied by a phenolate oxygen of the other Schiff base ligand and the other axial position is occupied by one nitrogen of a pseudohalide ligand, viz. azide for **1** and thiocyanate for **2**. Mn deviates from the mean plane is defined by the four equatorial donors by 0.220(2) Å for **1** and 0.154(2) Å for **2**, toward the direction of the pseudohalide. Axial bonds are much longer than the equatorial ones, caused by Jahn–Teller effects in octahedral complexes. The



Scheme 1. The preparation of the Schiff bases and the complexes. For **1**, R = CH_3, X = N_3; For **2**, R = H, X = NCS.

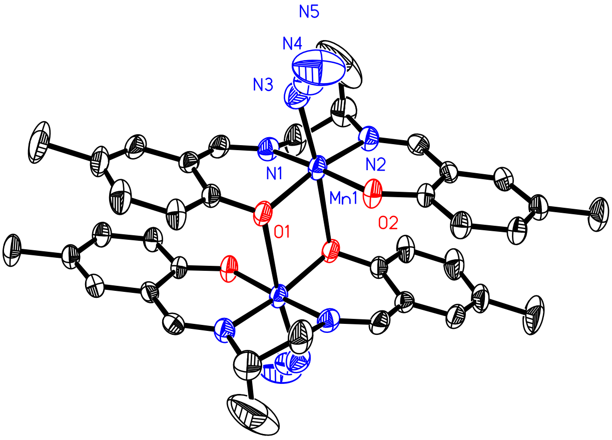


Figure 1. An ORTEP diagram of **1** with atom labeling scheme and 30% probability thermal ellipsoids for all non-hydrogen atoms. Unlabeled atoms are related to the symmetry operation $2 - x$, $2 - x$, and $1 - z$.

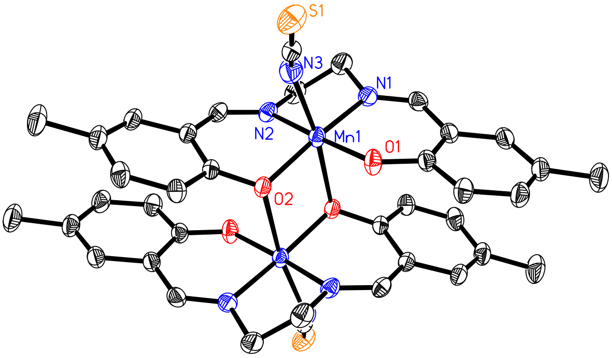


Figure 2. An ORTEP diagram of **2** with atom labeling scheme and 30% probability thermal ellipsoids for all non-hydrogen atoms. Unlabeled atoms are related to the symmetry operation $1 - x$, $-x$, and $2 - z$.

corresponding Mn–O and Mn–N bond lengths in the two complexes are similar to each other and also comparable with those observed in similar manganese(III) complexes with Schiff base ligands [25–27]. The dihedral angles between the two substituted benzene rings of the Schiff base ligands are 9.1(3)° for **1** and 9.6(3)° for **2**.

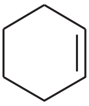
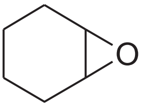
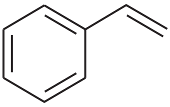
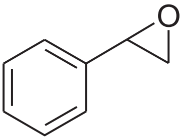
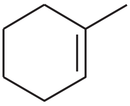
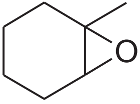
3.3. *IR spectra*

Infrared spectra of the complexes are consistent with the structural data presented in this article. Broad bands for the free Schiff bases are centered at 3430–3550 cm^{-1} due to O–H of the phenol. Absence of the phenolic O–H vibration in spectra of the complexes indicates that the Schiff bases are deprotonated during coordination. IR spectra of the complexes exhibit strong absorptions at 1625 cm^{-1}, attributed to the stretch of C=N of the Schiff base. The intense and sharp absorptions at 2039 cm^{-1} for **1** and 2088 cm^{-1} for **2** are attributed to the stretch of the terminal azide and thiocyanate, respectively. The phenolic C–O stretches are at 1285 cm^{-1} in both complexes [28]. Ligand coordination to manganese is substantiated by weak bands at 450–570 cm^{-1}, attributable to ν(Mn–N) and ν(Mn–O) [29]. IR spectra of the two complexes are similar, indicating that the complexes are of similar structures, as evidenced by the single-crystal X-ray determination.

3.4. *Catalytic properties*

Both complexes showed effective catalysis in oxidation of various olefins to their corresponding epoxides. The details of catalytic properties with respect to epoxidation of olefins with **1** and **2** as catalysts are given in table 3. Generally, high epoxide yields were observed for all substrates. The catalytic studies reveal that the efficiency of catalysts toward all the substrates is similar with maximum conversion and TON. When H_2O_2 was

Table 3. Details of the catalytic oxidation of olefins catalyzed by **1** and **2**[a].

Substrate	Product		Conversion (%)[b] (TON)[c]		Conversion (%)[d]
		**1**	92 (191)	**1**	33
		2	87 (180)	**2**	30
		**1**	95 (203)	**1**	19
		2	90 (187)	**2**	21
		**1**	87 (165)	**1**	23
		2	89 (173)	**2**	18

[a] The molar ratios for catalyst: substrate: $NaHCO_3 : H_2O_2$ are 1 : 298 : 117 : 1170. The reactions were performed in (70 : 30) mixture of CH_3OH/CH_2Cl_2 (1.2 mL) under air at room temperature.

[b] The GC conversion are measured relative to the starting olefin after 74.5 min.

[c] TON = (mM of product)/mM of catalyst.

[d] The conversion without the addition of sodium bicarbonate.

used as a sole oxidant, the catalytic efficiency is not high, but when $NaHCO_3$ was added as a co-catalyst, the efficiency of the system increases many-fold. The key aspect of such a reaction is that H_2O_2 and hydrogen carbonate 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 [13].

4. Conclusions

Synthesis and characterization of two new centrosymmetric phenoxo-bridged dinuclear manganese(III) complexes with bis-Schiff base ligands and terminal pseudohalides have been described in this article. The complexes showed effective catalytic properties in the oxidation of various olefins to their corresponding epoxides.

Supplementary material

CCDC reference numbers 914979 for **1** and 914980 for **2** contain the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk, or from Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk.

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