**Synthesis, Crystal Structures and Catalytic Oxidation of Manganese(III) Complexes Derived from Salen-Type Schiff Base *N,N’*-Bis(5-nitrosalicylidene)ethane-1,2-diamine**

**Qing-Bin Li, Yong-Jun Han, Gan-Qing Zhao, Ling-Wei Xue\***

*College of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan Henan 467000, P.R. China*

*\* Corresponding author. E-mail: pdsuchemistry@163.com*

**Abstract**

Two mononuclear Schiff base manganese(III) complexes, [MnL(N3)(OH2)]·CH3OH (**1**) and [MnL(NCS)(OH2)]·H2O (**2**), where L is the dianionic form of *N,N’*-bis(5-nitrosalicylidene)ethane-1,2-diamine, have been prepared and structurally characterized by elemental analysis, IR and UV-Vis spectra and single crystal X-ray diffraction. The Mn atom in each complex is in an octahedral coordination. Molecules in the complexes are linked through intermolecular hydrogen bonds. Catalytic properties for epoxidation of styrene by the complexes using PhIO and NaOCl as oxidant have been studied.

**Keywords:** Synthesis, Crystal structure, Schiff base, Manganese complex, Catalytic oxidation

**1. Introduction**

Schiff bases with salen-type are a kind of versatile ligands in coordination chemistry.1 In recent years extensive studies have been made on the chemistry of manganese(III) complexes derived from Schiff bases due to their important role in several metalloenzymes and to understand their catalytic activities in many organic reactions.2 Manganese complexes have interesting biological activities.3 The involvement of manganese in many biological systems is well established. Manganese(III) salen complexes 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.4 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.5 In order to investigate the influence of the azide and thiocyanate ligands on manganese(III) complexes with tetradentate Schiff base ligands, as well as the catalytic oxidation property, we report here the synthesis, characterization, crystal structures and catalytic oxidation property of two new complexes [MnL(N3)(OH2)]·CH3OH (**1**) and [MnL(NCS)(OH2)]·H2O (**2**), where L is the dianionic form of *N,N’*-bis(5-nitrosalicylidene)ethane-1,2-diamine.

**2. Experimental**

**2.1. Materials and methods**

Manganese perchlorate, sodium azide and ammonium thiocyanate obtained from commercial sources were of analytical grade and used without further purification. 5-Nitrosalicylaldehyde and *N,N'*-ethane-1,2-diamine were purchased from Aldrich. The Schiff base H2L was prepared according to the literature method.6 Iodosylbenzene (PhIO) was prepared by the hydrolysis of iodobenzenediacetate.7 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 Finnigan EA 1112 elemental analyzer. IR spectra were performed on a Nicolet 470 spectrometer with KBr pellets in the 4000–400 cm–1 region. UV-Vis spectra were recorded on a Lambda 35 spectrometer. The crystal determination was carried out on a Bruker SMART 1000 CCD area diffractometer. GC experiments were performed with Agilent 5977A Network GC systems. 1H and 13C NMR data were recorded on a Bruker 300 MHz instrument.

*Caution!* Perchlorate and azide complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

**2.2. Synthesis of [MnL(N3)(OH2)]∙CH3OH**

The mixture of NaN3 (0.065 g, 1.00 mmol) and Mn(ClO4)2·6H2O (0.362 g, 1.00 mmol) in 50 mL methanol was stirred for half an hour with heating, then H2L (0.358 g, 1.00 mmol) was added to the solution and the reaction continued to stirred for 1 h. After filtration, the deep brown filtrate was allowed to stand at room temperature for a week to deposit brown crystals of the complex in 37.2% yield. *Anal.* Calc. for C17H18MnN7O8: C, 40.57; H, 3.60; N, 19.48. Found: C, 40.38; H, 3.72; N, 19.35%. IR data (KBr; ν, cm–1): 3450 (m, br), 2041 (s), 1634 (s), 1601 (s), 1559 (w), 1501 (m), 1451 (s), 1343 (w), 1301 (m), 1093 (s), 948 (m), 853 (s), 799 (w), 693 (w), 545 (s). UV-Vis data in acetonitrile [λmax (nm)]: 298, 343.

**2.3. Synthesis of [MnL(NCS)(OH2)]·H2O**

The mixture of NH4NCS (0.076 g, 1.0 mmol) and Mn(ClO4)2·6H2O (0.362 g, 1.00 mmol) in 50 mL methanol was stirred for half an hour with heating, then H2L (0.358 g, 1.00 mmol) was added to the solution and the reaction continued to stirred for 1 h. After filtration, the deep brown filtrate was allowed to stand at room temperature for a week to deposit brown crystals of the complex in 45.0% yield. *Anal.* Calc. for C17H16MnN5O8S: C, 40.40; H, 3.19; N, 13.86. Found: C, 40.53; H, 3.33; N, 13.70%. IR data (cm–1): 3445 (m, br), 2067 (s), 1634 (s), 1601 (s), 1561 (w), 1500 (m), 1446 (s), 1345 (w), 1298 (w), 1102 (s), 993 (m), 951 (m), 855 (s), 799 (w), 696 (w), 547 (s). UV-Vis data in acetonitrile [λmax (nm)]: 298, 343.

**2.4. X-ray diffraction**

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 Mo*Kα* 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.8 The final refinement was performed by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms on *F*2. The water and hydroxyl hydrogen atoms (O3 and O8 for **1** and **2**) were located from difference Fourier maps, with O–H and H···H distances restrained to 0.85(1) and 1.37(2) Å, respectively. The remaining hydrogen atoms were placed geometrically, with *U*iso(H) restrained to 1.2 *U*eq(C) and 1.5 *U*eq(Cmethyl). Multi-scan absorption correction was applied by using the SADABS program.9 Crystallographic data are summarized in Table 1.

**Table 1.** Crystal and structure refinement data for the complexes

|  |  |  |
| --- | --- | --- |
|  | **1** | **2** |
| Formula | C17H18MnN7O8 | C17H16MnN5O8S |
| FW | 503.32 | 505.35 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *P*21/*n* | *P*21/*c* |
| *a* /Å | 13.8160(9) | 13.936(2) |
| *b* /Å | 12.2649(8) | 12.707(2) |
| *c* /Å | 13.8286(9) | 13.067(2) |
| *β* /° | 117.280(1) | 116.187(2) |
| *V* /Å3 | 2082.7(2) | 2076.5(5) |
| *Z* | 4 | 4 |
| *μ* /mm-1 (Mo-K*α*) | 0.696 | 0.793 |
| Reflections/parameters | 11921/308 | 11814/301 |
| Independent reflections | 4529 | 4516 |
| Observed reflections [*I* ≥ 2*σ*(*I*)] | 3836 | 3623 |
| Restraints | 4 | 6 |
| *F*(000) | 1032 | 1032 |
| Goodness of fit on *F2* | 1.081 | 1.050 |
| *R*1, *wR*2 [*I* ≥ 2*σ*(*I*)]*a* | 0.0297, 0.0816 | 0.0411, 0.1148 |
| *R*1, *wR*2 (all data)*a* | 0.0380, 0.0890 | 0.0538, 0.1294 |

a *R*1 = ∑||*Fo*|-|*Fc*||/∑|*Fo*|, *wR*2 = [∑*w*(*Fo*2-*Fc*2)2/∑*w*(*Fo*2)2]1/2

**2.5. 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 NaH2PO4 and NaOH.10 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.

**3. Results and Discussion**

Complexes **1** and **2** were synthesized according to the procedure as described in Scheme 1.



**Scheme 1**. The synthetic procedure for the complexes

**3.1. Crystal structure description of the dioxomolybdenum complexes**

The structures of complexes **1** and **2** are shown in Figs. 1 and 2, respectively. Selected bond lengths and bond angles are listed in Table 2. The distances and angles related to the hydrogen bonding are listed in Table 3.

Single-crystal X-ray structural analysis revealed that both complexes are similar. The asymmetric unit of each complex contains a mononuclear manganese complex molecule and a solvent molecule, *viz.* methanol for **1** and water for **2**. The Mn atoms in the complexes are in octahedral environment consisting of the N2O2 donor set of the Schiff base ligands, the oxygen donor of water 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 0.061(2) Å for **1** and 0.089(2) Å for **2**. The Ni–N and Ni–O bond lengths are comparable to the corresponding values observed in manganese complexes with Schiff base ligands.11 The axial Mn1–N5 and Mn1–O3 bond lengths are longer than the equatorial bonds, which is caused by Jahn-Teller effects expected for d4 high spin manganese(III) systems.12 The azide and thiocyanate ligands are quasi-linear, with angles of 178.8(2)° for **1** and 177.8(3)° for **2**. The plane defined by N1–N2–O1–O2 forms dihedral angles of 17.9(3)° and 13.1(3)° for **1**, and 14.8(3)° and 16.7(3)° for **2**, with C1–C6 and C11–C16 benzene rings, respectively.

In the crystal structure of **1**, the manganese complex molecules are linked by water molecules through intermolecular hydrogen bonds of O–H∙∙∙O to form dimers. The dimers are then connected *via* O–H∙∙∙N hydrogen bonds to form 2D layers (Fig. 3). In the crystal structure of **2**, the manganese complex molecules are linked by water molecules through intermolecular hydrogen bonds of O–H∙∙∙O to form dimers. The dimers are then connected by water molecules to form 2D layers (Fig. 4).

**Table 2.** Selected bond lengths (Å) and angles (°) for the complexes

|  |  |  |  |
| --- | --- | --- | --- |
| **1** |  |  |  |
| Mn1–O1 | 1.8745(12) | Mn1–O2 | 1.8844(12) |
| Mn1–N1 | 1.9737(14) | Mn1–N2 | 1.9766(13) |
| Mn1–O3 | 2.3031(15) | Mn1–N5 | 2.2288(17) |
| O1–Mn1–O2 | 91.61(5) | O1–Mn1–N1 | 91.80(6) |
| O2–Mn1–N1 | 174.92(6) | O1–Mn1–N2 | 174.25(6) |
| O2–Mn1–N2 | 92.72(6) | N1–Mn1–N2 | 83.63(6) |
| O1–Mn1–N5 | 95.91(6) | O2–Mn1–N5 | 93.58(6) |
| N1–Mn1–N5 | 89.82(7) | N2–Mn1–N5 | 87.60(6) |
| O1–Mn1–O3 | 89.72(6) | O2–Mn1–O3 | 90.32(6) |
| N1–Mn1–O3 | 85.93(6) | N2–Mn1–O3 | 86.47(6) |
| N5–Mn1–O3 | 173.05(6) |  |  |
| **2** |  |  |  |
| Mn1–O1 | 1.8830(16) | Mn1–O2 | 1.9107(16) |
| Mn1–N1 | 1.981(2) | Mn1–N2 | 1.979(2) |
| Mn1–O3 | 2.297(2) | Mn1–N5 | 2.205(3) |
| O1–Mn1–O2 | 93.49(7) | O1–Mn1–N2 | 172.49(9) |
| O2–Mn1–N2 | 91.63(8) | O1–Mn1–N1 | 91.36(8) |
| O2–Mn1–N1 | 172.62(8) | N2–Mn1–N1 | 83.04(9) |
| O1–Mn1–N5 | 92.31(9) | O2–Mn1–N5 | 94.78(9) |
| N2–Mn1–N5 | 92.74(10) | N1–Mn1–N5 | 90.58(10) |
| O1–Mn1–O3 | 91.55(8) | O2–Mn1–O3 | 89.49(8) |
| N2–Mn1–O3 | 83.00(8) | N1–Mn1–O3 | 84.81(8) |
| N5–Mn1–O3 | 174.06(9) |  |  |

**Table 3.** Distances (Å) and angles (°) involving hydrogen bonding of the complexes.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *D*–H∙∙∙*A* | *d*(*D*–H) | *d*(H∙∙∙*A*) | *d*(*D*∙∙∙*A*) | Angle(*D*–H∙∙∙*A*) |
| **1** |  |  |  |  |
| O3–H3A∙∙∙O8 | 0.85(1) | 1.88(1) | 2.716(2) | 168(3) |
| O3–H3B∙∙∙O2i | 0.84(1) | 2.16(1) | 2.967(2) | 163(3) |
| O3–H3B∙∙∙O1i | 0.84(1) | 2.60(2) | 3.188(2) | 128(2) |
| O8–H8∙∙∙N5ii | 0.87(1) | 1.96(1) | 2.185(3) | 167(3) |
| O8–H8∙∙∙N6ii | 0.87(1) | 2.61(1) | 3.461(3) | 167(3) |
| **2** |  |  |  |  |
| O3–H3A∙∙∙O8 | 0.85(1) | 1.88(1) | 2.696(30 | 162(3) |
| O3–H3B∙∙∙O2iii | 0.85(1) | 1.99(1) | 2.819(3) | 164(3) |

Symmetry codes: (i) 1 – *x*, – *y*, – *z*; (ii) 3/2 – *x*, ½ + *y*, ½ – *z*; (iii) – *x*, 2 – *y*, 1 – *z*.

**fig1**

**Figure 1.** Molecular structure of **1** at 30% probability thermal ellipsoids.

**fig1**

**Figure 2.** Molecular structure of **2** at 30% probability thermal ellipsoids.

fig2

**Figure 3.** Molecular packing of **1**. Intermolecular hydrogen bonds are shown as dashed lines.

fig2

**Figure 4.** Molecular packing of **2**. Intermolecular hydrogen bonds are shown as dashed lines.

**3.2. Infrared and electronic spectra**

IR spectra of the manganese(III) complexes are very similar. The complexes exhibit broad bands centered at *ca.* 3450 cm–1, indicative of the presence of coordinated and/or lattice water or methanol molecules. The strong bands indicative of *ν*(C=N) are located at 1601 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 asymmetric and symmetric vibrations of the nitro groups are located at about 1451 and 1301 cm–1, respectively. The intense absorption for the stretching vibrations of the azide ligand in **1** and the thiocyanate ligand in **2** are observed at 2041 cm–1 and 2067 cm–1, respectively.

UV-Vis spectra for diluted acetonitrile solutions of the complexes were registered. The absorption at 298 nm and 343 nm are due to the benzene and azomethine chromophore π→π\* transitions, respectively.

**3.3. Oxidation of styrene by the complexes**

Oxidation of styrene was carried out at room temperature with the complexes as the catalysts and PhIO and NaOCl as oxidants. The deep 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.13 After completion of oxidation reaction of the alkene, the solution regains its initial color which suggests that the regeneration of the catalysts takes place. The percentage of conversion of styrene, selectivity for styrene oxide, yield of styrene oxide for each complex and reaction time to obtain maximum yield using both the oxidants are given in Table 4.

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 89% and 87% for **1** and **2**, respectively. When the reactions were carried out with NaOCl, styrene conversions are 75% and 76% for **1** and **2**, respectively. 1H NMR data for the product (*δ*, ppm, CDCl3): 2.76 (t, 1H), 3.09 (t, 1H), 3.82 (t, 1H), 7.28 (m, 5H). 13C NMR data for the product (*δ*, ppm, CDCl3): 51.0, 52.3, 125.5, 128.1, 128.5, 137.7. The catalytic properies of the complexes are comparable to those of the molybdenum complexes.14

**Table 4.** Catalytic results.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Time (h) | Oxidant | Conversion (%) | Epoxide yield (%) | Selectivity (%) | |
| Epoxide | Other |
| 1 | 2.0 | PhIO | 89 | 77 | 83 | 17 |
|  | 3.0 | NaOCl | 75 | 62 | 80 | 20 |
| 2 | 2.0 | PhIO | 87 | 79 | 85 | 15 |
|  | 3.0 | NaOCl | 76 | 65 | 78 | 22 |

**4. Supplementary Mateiral**

1060283 for **1**, and 1060284 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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