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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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# Synthesis, X-Ray Structural Characterization, and Catalytic Property of a Manganese (II) Complex With 2-Bromo-6-[(3cyclohexylammoniopropylimino)methyl]phenolate and Thiocyanate Ligands

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**Thiocyanate Ligands** 

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A new manganese(II) complex  $[MnL_2(NCS)_2]$ -2H<sub>2</sub>O with the Schiff base ligand derived from 3-bromosalicylaldehyde with *N*-cyclohexylpropane-1,3-diamine has been synthesized and structurally characterized by physicochemical methods and single-crystal X-ray determination. The crystal of the complex crystallizes in monoclinic space group C2/c, with a = 24.749(2), b = 7.2957(7), c = 26.183(4) Å,  $\beta = 118.70(2)^{\circ}$ , V = 4171.6(8) Å<sup>3</sup>, Z = 4,  $R_1 = 0.0893$ ,  $wR_2 = 0.2305$ , GOOF = 1.084. X-ray analysis indicates that the complex is a mononuclear manganese species, which possesses crystallographic inversion center symmetry. The Mn atom, lying on the inversion center, is coordinated in an octahedral coordination by two phenolate O and two imine N atoms from two Schiff base ligands, and two thiocyanate N atoms. The catalytic property for epoxidation of styrene by the complex has also been tested.

Keywords catalytic property, crystal structure, manganese complex, Schiff base ligand, thiocyanate ligand

# **INTRODUCTION**

Schiff base compounds represent one of the most attractive series of ligands in coordination chemistry. The ligands bearing typical C=N groups and suitable O, N, or S donor atoms are capable of binding various transition and rare earth metal atoms to form complexes with versatile structures and properties.<sup>[1-3]</sup> To date, most Schiff base complexes have been reported to have interesting catalytic properties, such as asymmetric epoxidation, oxidation of sulfides, and various type of polymerization.<sup>[4–8]</sup> Among the Schiff base complexes, those with Mn centers are of particular interest for their epoxidation of olefins.<sup>[9–11]</sup> Herein we report the synthesis, X-ray crystal structure, and catalytic property of a new manganese complex, [MnL<sub>2</sub>(NCS)<sub>2</sub>]·2H<sub>2</sub>O, where L is 2-bromo-6-[(3-cyclohexylammoniopropylimino)methyl]phenolate.

#### **EXPERIMENTAL**

#### Materials

Manganese chloride, 3-bromosalicylaldehyde, and *N*-cyclohexylpropane-1,3-diamine were purchased from Aldrich. All other reagents with AR grade were used as received without further purification.

#### **Physical Measurements**

Infrared spectra (4000–400 cm<sup>-1</sup>) were recorded as KBr discs with a FTS-40 BioRad FT-IR spectrophotometer. Microanalyses (C, H, N) of the complex were carried out on a Carlo-Erba 1106 elemental analyzer. Solution electrical conductivity was measured at 298 K using a DDS-11 conductivity meter. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph.

#### X-Ray Crystallography

Crystallographic data of the complex were collected on a Bruker SMART CCD area diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298(2) K. Absorption corrections were applied by using the multiscan program.<sup>[12]</sup> The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97), and anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least-squares procedure against  $F^2$  (SHELXL-97).<sup>[12]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode, with a common thermal parameter. The crystallographic data and experimental details



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 TABLE 1

 Crystallographic data for the single crystal of the complex

| Empirical formula                         | $C_{34}H_{50}Br_2MnN_6O_4S_2$ |  |
|---|-------------------------------|--|
| Formula weight                            | 885.7                         |  |
| Temperature (K)                           | 298(2)                        |  |
| Crystal system                            | Monoclinic                    |  |
| Space group                               | C2/c                          |  |
| <i>a</i> (Å)                              | 24.749(2)                     |  |
| b (Å)                                     | 7.2957(7)                     |  |
| <i>c</i> (Å)                              | 26.183(4)                     |  |
| $\beta$ (°)                               | 118.070(2)                    |  |
| V (Å <sup>3</sup> )                       | 4171.6(8)                     |  |
| Z   | 4                             |  |
| <i>F</i> (000)                            | 1820                          |  |
| Data/restraints/parameters                | 3701/6/223                    |  |
| Goodness-of-fit on $F^2$                  | 1.084                         |  |
| Final <i>R</i> indices $[I > 2\sigma(I)]$ | $R_1 = 0.0893, wR_2 = 0.2305$ |  |

for the structure analysis are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

# Preparation of 2-bromo-6-[(3cyclohexylaminopropylimino)methyl]phenol

Hot methanol solutions of 3-bromosalicylaldehyde and *N*-cyclohexylpropane-1,3-diamine (1:1, v/v) were stirred under reflux for 1 h, and cooled to room temperature. The yellow precipitate was collected by filtration and dried *in vacuo*. Yield: 83%. Anal. Calcd. for  $C_{16}H_{23}BrN_2O$  (%): C, 56.6; H, 6.8; N, 8.3. Found (%): C, 56.4; H, 6.9; N, 8.2.

# Preparation of the Complex [MnL<sub>2</sub>(NCS)<sub>2</sub>]·2H<sub>2</sub>O

To a stirred solution of 2-bromo-6-[(3-cyclohexylaminopropylimino)methyl]phenol (0.34 g, 1 mmol) and ammonium thiocyanate (0.076 g, 1 mmol) in 20 mL methanol was added  $MnCl_2 \cdot 4H_2O$  (0.20 g, 1 mmol). The resulting mixture was

 TABLE 2

 Selected bond distances (Å) and bond angles (°) for the complex

| (1)           |          |            |          |
|---------------|----------|------------|----------|
| Bond distance |          |            |          |
| Mn1-O1        | 1.883(6) | Mn1-N1     | 2.054(6) |
| Mn1-N3        | 2.288(8) |            |          |
| Bond angle    |          |            |          |
| O1-Mn1-O1A    | 180      | O1-Mn1-N1A | 88.9(2)  |
| O1-Mn1-N1     | 91.1(2)  | N1-Mn1-N1A | 180      |
| O1-Mn1-N3     | 90.4(3)  | O1-Mn1-N3A | 89.6(3)  |
| N1-Mn1-N3A    | 90.4(2)  | N1-Mn1-N3  | 89.6(2)  |
| N3-Mn1-N3A    | 180      |            |          |

refluxed for 1 h. The deep brown reaction solution was filtered and the solvent removed under reduced pressure, yielding brown solid of the complex. Yield: 43%. Well-shaped single crystals suitable for X-ray diffraction were obtained by recrystallization of the solid from methanol. Anal. Calcd. for  $C_{34}H_{50}Br_2MnN_6O_4S_2$  (%): C, 46.1; H, 5.7; N, 9.5. Found (%): C, 46.2; H, 5.7; N, 9.4.

# **Styrene Epoxidation**

The epoxidation reactions were carried out at room temperature in acetonitrile under N2 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 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<sub>2</sub>PO<sub>4</sub> and NaOH. 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**

#### Synthesis

The Schiff base ligand was readily prepared by condensation reaction of 3-bromosalicylaldehyde with *N*-cyclohexylpropane-1,3-diamine in methanol (see Scheme 1). The stoichiometric reaction of the Schiff base ligand and ammonium thiocyanate with manganese chloride in refluxing methanol yielded the corresponding manganese complex (see Scheme 2). The reaction progress is accompanied by an immediate color change of the solution from yellow to deep brown. We have attempted to prepare and grow diffraction quality crystals of the complexes from various solvents; yet, only methanol is suitable. The molar conductivity ( $\Lambda_{\rm M} = 30 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}$ ) is consistent with the values expected for non-electrolytes.<sup>[13]</sup>

# Description of the Structure of the Complex

Single-crystal X-ray analysis reveals that the complex consists of a centrosymmetric mononuclear manganese complex



SCH. 1. The preparation of the Schiff base ligand.



SCH. 2. The preparation of the complex.

subunit and two water molecules of crystallization. The OR-TEP plot of the complex is shown in Figure 1. The manganese atom is in a distorted octahedral geometry, which is coordinated by the N<sub>2</sub>O<sub>2</sub> donor atoms from two zwitterionic Schiff base ligands in the equatorial mode and two N donor atoms from two thiocyanate ligands in the axial positions. The distortion of the octahedral coordination of the structure can be observed from the bond angles (Table 2) related to the Mn atoms. The O1-Mn1-N1A and O1-Mn1-N1 bond angles are 88.9(2)° and  $91.1(2)^{\circ}$ , respectively, which are slightly distorted from the ideal value of 90°. The bond lengths of Mn–O and Mn–N (Table 2) are close to those in other Mn-Salen complexes.<sup>[14,15]</sup> As expected, the bond lengths in the axial positions are elongated due to a Jahn-Teller distortion effect. The space packing of the complex along the c axis is shown in Figure 2, in which hydrogen bonds link the manganese complex subunits and the water molecules into a one-dimensional supramolecular aggregation.

#### Spectral Characterization

In the IR spectrum of the complex exhibits strong absorption at 2060 cm<sup>-1</sup>, assignable to the asymmetric stretching vibration of the thiocyanate ligand. Also, the strong characteristic absorption of the CH=N group is detected at 1619 cm<sup>-1</sup>.<sup>[16]</sup>

The medium band centered at 3370 cm<sup>-1</sup> can be attributed to the  $v_{OH}$  vibrations of the water molecules.

#### Catalytic epoxidation results

The percentage of conversion of styrene, selectivity for styrene oxide, yield of styrene oxide, and reaction time to obtain maximum yield using both the oxidants are given in Table 3. The data reveal that the complex as a catalyst converts styrene most efficiently in the presence of both oxidants. Nevertheless, the catalyst is selective towards the formation of styrene epoxides despite of the formation of by-products, which have been identified by GC-MS as benzaldehyde, phenylacetaldehyde, styrene epoxides derivative, and alcohols. From the data it is also clear that the complex exhibits excellent efficiency for styrene epoxide yield. When the reactions are carried out with PhIO and NaOCl, styrene conversions were about 80% and 67%, respectively. It is evident that between PhIO and NaOCl, the former acts as a better oxidant with respect to both styrene conversion and styrene epoxide selectivity. The epoxide yields for the complex are 72% using PhIO as an oxidant and 55% using NaOCl as an oxidant.



FIG. 1. ORTEP diagram of the complex (30% thermal ellipsoid).



FIG. 2. The molecular packing structure of the complex linked by hydrogen bonds.

| Time<br>(h) | Oxidant | Conversion<br>(%) | Epoxide<br>yield<br>(%) | Selectivity<br>(%) |
|-------------|---------|-------------------|-------------------------|--------------------|
| 2           | PhIO    | 80                | 72                      | 83                 |
| 3           | NaOCl   | 67                | 55                      | 79                 |

TABLE 3Catalytic epoxidation results

# CONCLUSION

A new Mn-Schiff base coordination complex has been prepared and structurally characterized in this study. Structural analysis shows that the complex consists of a centrosymmetric mononuclear manganese complex subunit and two water molecules of crystallization. The thiocyanate groups act as terminal ligands. The Schiff base ligands are zwitterionic, with the phenol hydrogen transferred to the amino group. The complex shows effective catalytic epoxidation on styrene.

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#### SUPPLEMENTAL MATERIAL

Supplementary data are available from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; or via www.ccdc.cam.ac.uk/conts/retrieving.html) on request, quoting the deposition numbers: CCDC 933127.

#### REFERENCES

- Cukurovali, A.; Yilmaz, I.; Gur, S.; Kazaz, C. Synthesis, antibacterial and antifungal activity of some new thiazolylhydrazone derivatives containing 3-substituted cyclobutane ring. *Eur. J. Med. Chem.* 2006, *41*, 201–207.
- Basak, S.; Sen, S.; Marschner, C.; Baumgartner, J.; Batten, S.R.; Turner, D.R.; Mitra, S. Synthesis, crystal structures and fluorescence properties of

two new di- and polynuclear Cd(II) complexes with N<sub>2</sub>O donor set of a tridentate Schiff base ligand. *Polyhedron* **2008**, *27*, 1193–1200.

- Boskovic, C.; Bircher, R.; Tregenna-Piggott, P.L.W.; Gudel, H.U.; Paulsen, C.; Wernsdorfer, W.; Barra, A.-L.; Khatsko, E.; Neels, A.; Stoeckli-Evans, H. Ferromagnetic and antiferromagnetic intermolecular interactions in a new family of Mn<sub>4</sub> complexes with an energy barrier to magnetization reversal. J. Am. Chem. Soc. 2003, 125, 14046–14058.
- Pouralimardan, O.; Chamayou, A.-C.; Janiak, C.; Hosseini-Monfared, H. Hydrazone Schiff base-manganese(II) complexes: synthesis, crystal structure and catalytic reactivity. *Inorg. Chim. Acta* 2007, *360*, 1599–1608.
- Monfared, H. H.; Sadighian, S.; Kamyabi, M.-A.; Mayer, P. Iron(III) aroylhydrazone complexes: Structure, electrochemical studies and catalytic activity in oxidation of olefins. *J. Mol. Catal. A: Chem.* 2009, 304, 139–146.
- Monfared, H.H.; Bikas, R.; Mayer, P. Homogeneous green catalysts for olefin oxidation by mono oxovanadium(V) complexes of hydrazone Schiff base ligands. *Inorg. Chim. Acta* 2010, *363*, 2574–2583.
- Bagherzadeh, M.; Amini, M. Synthesis, characterization and catalytic study of a novel iron(III)-tridentate Schiff base complex in sulfide oxidation by UHP. *Inorg. Chem. Commun.* 2009, 12, 21–25.
- Roy, P.; Manassero, M. Tetranuclear copper(II)-Schiff-base complexes as active catalysts for oxidation of cyclohexane and toluene. *Dalton Trans.* 2010, *39*, 1539–1545.
- Patel, R.V.; Panchal, J.G.; Mistry, B.R.; Menon, S.K. Synthesis and study of binuclear calyx[4]arene Schiff base Mn(II) complexes as catalyst in the presence of PhIO for the catalytic oxidation of olefin. *J. Incl. Phenom. Macrocycl. Chem.* 2012, *74*, 473–480.
- Majumder, S.; Hazra, S.; Dutta, S.; Biswas, P.; Mohanta, S. Syntheses, structures and electrochemistry of manganese(III) complexes derived from *N*,*N*'-*o*-phenylenebis(3-ethoxysalicylaldimine): Efficient catalyst for styrene epoxidation. *Polyhedron* 2009, *28*, 2473–2479.
- Bagherzadeh, M.; Tahsini, L.; Latifi, R. Efficient oxidation of olefins and sulfides catalyzed by manganese(III)-tridentate Schiff base complex using UHP as oxidant. *Catal. Commun.* 2008, 9, 1600–1606.
- 12. Sheldrick, G. M. SHELXTL97, Program for Refining Crystal Structure Refinement; University of Göttingen, Germany, 1997.
- Geary, W. J. Use of conductivity measurements in organic solvents for characterization of coordination compounds. *Coord. Chem. Rev.* 1971, 7, 81–122.
- Chakraborty, J.; Samanta, B.; Pilet, G.; Mitra, S. Synthesis, structure and spectral characterization of a hydrogen-bonded polymeric manganese(III) Schiff base complex. *Struct. Chem.* 2006, *17*, 585–593.
- Dinda, R.; Sengupta, P.; Ghosh, S.; Mayer-Figge, H.; Sheldrick, W.S. A family of mononuclear molybdenum-(VI), and –(IV) oxo complexes with a tridentate (ONO) ligand. J. Chem. Soc. Dalton Trans. 2002, 4434–4439.
- Zhang, N.; Huang, C.-Y.; Shi, D.-H.; You, Z.-L. Unprecedented preparation of *bis*-Schiff bases and their manganese(III) complexes with urease inhibitory activity. *Inorg. Chem. Commun.* **2011**, *14*, 1636–1639.