Journal of the Chinese Chemical Society, **2003**, *50*, 41-46

Mononuclear Iron(III) and Manganese(III) Complexes with Substituted Salicylaldimine Ligands: Structure, Magnetic Properties, and Catalytic Activity of Olefins-Epoxidation

Sheng-Chuan Cheng[a] (鄭勝權), Cheng-Wei Chang[a] (張振偉), Ho-Hsiang Wei[a]* (魏和祥),
Gene-Hsiang Lee[b] (李錦祥) and Yu Wang[b] (王　瑜)
[a]*Department of Chemistry, Tamkang University, Tamsui, Taiwan, R.O.C.*
[b]*Instrumentation Center College of Science, National Taiwan University, Taipei, Taiwan, R.O.C.*

Two mononuclear manganese(III) and iron(III) complexes with substituted salicylaldimine ligands, $[MnL(H_2O)_2]Cl\cdot H_2O$ (**1**) and $[FeL(H_2O)(Cl)]CH_3CN$ (**2**) [H_2L = N,N′-(1,1-cyclohexane)bis(3-methoxysalicylaldimine)] were prepared and characterized. The X-ray crystal structure shows that **1** and **2** centers are six-coordinate with distorted octahedral geometry. In **1**, the hydrogen bonding of water molecules form a quasi one-dimensional chain structure. The temperature dependence of magnetic susceptibility measurements for complexes of **1** and **2** was analyzed in terms of the zero-field splitting (D) spin-Hamiltonian formula with $D = 2.0\ cm^{-1}$ for **1** and $J = 7.5\ cm^{-1}$, and $D = 0.01\ cm^{-1}$ for **2**, respectively. The complexes of **1** and **2** activate the epoxidation of *cis*-stilbene or α-methylstyrene by NaOCl. With **1** the epoxides were produced in 75% yield with *cis*:*trans* = 12:88 from *cis*-stilbene and 82% from α-methylstyrene, and with **2** the epoxides were produced in 43% with *cis*:*trans* = 30:70 from *cis*-stilbene and 71% from α-methylstyrene.

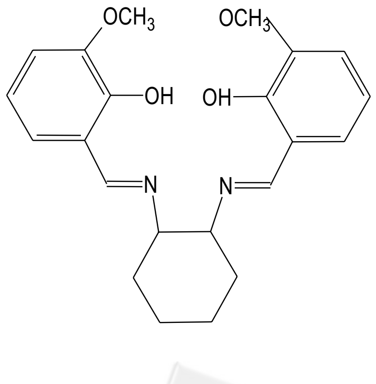
Keywords: Manganese complex; Iron complex; Magnetic properties; Epoxidation of olefins.

INTRODUCTION

Groves and co-workers have reported that iron(III) and manganese(III) porphyrins are good models for the reaction site of cytochrome P-450[1] and have been found to be efficient catalysts for the epoxidation of olefins.[2] The use of manganese(III) complexes of substituted salen ligands [salen = N,N-(ethylene)bis(salicylideneaminate)] as a catalyst for the epoxidation of olefins has been widely investigated.[2-5] An increase in the enantioselectivities for these substrates has been achieved by modulating the steric and electronic properties of the catalyst through varying the substitution pattern at the salicylidene moiety and the diamine fragment.[6-10] Recently, asymmetric catalysis of epoxide ring-opening reaction with cobalt(III)(salen) and chromium(III)(salen) complexes has been reported.[11] However, very little attention has been paid to studies on the epoxidation of olefins using salen-iron(III) complexes. Recently, we reported the first catalytic activity in the epoxidation of *cis*-stilbene with NaOCl of mononuclear iron(III) complexes with substituted salen ligands and found that the iron(III)(salen) complexes having OCH_3 group in positions C(2) of salen moiety make excellent catalysts for the epoxidation of *cis*-olefins.[12]

In this context, we present herewith the preparation, characterization, and comparison of the mononuclear manganese(III) and iron(III) complexes with substituted salicylaldimine ligands catalyzed epoxidation of *cis*-stilbene and α-methylstylene. For the present study, the cyclohexyl and CH_3O groups substituted salicylaldimine ligands (Scheme I) with Mn(III) and Fe(III) ions were chosen to assess the structural and electronic factors that influence their magnetic properties and catalytic activities of olefins epoxidation.

Scheme I



Dedicated to Professor Fa-Ching Chen on the occasion of his ninetieth birthday.

EXPERIMENTAL SECTION

Syntheses of [MnL(H_2O)$_2$]Cl·H_2O (1) and [FeL(H_2O)(Cl)]CH_3CN (2)

The Schiff base H_2L was obtained from the reaction of 3-methoxy-salicyaldehyde and 1,2-diaminocyclohexane in methanol.

The manganese(III) and iron(III) complexes with H_2L were prepared according to the standard methods. A methanol solution (30 mL) containing $MnCl_2 \cdot 4H_2O$ (1.97 g, 10 mmol) or $FeCl_3 \cdot 4H_2O$ (2.97 g, 10 mmol) and the ligand was refluxed 3-4 h in air, and the desired powder manganese(III) complex **1** or iron(III) complex **2** were filtered. Single crystals of **1** and **2** were grown from CH_3OH/CH_3CN solution. In addition, it found that only complex **1** exhibited a white precipitate in a silver nitrate solution, this implies that the chloride atom as an anion exists in **1**. Anal. found: C, 52.86; H, 5.09; N, 5.06. Calc. for $C_{22}H_{30}ClMnN_2O_7$ (**1**): C, 52.23; H, 4.83; N, 4.93%. Found: C, 54.61; H, 5.17; N, 6.31%. IR (KBr) ν(CN)/cm^{-1}: 1623. Calc. for $C_{24}H_{29}ClFeN_3O_5$ (**2**): C, 52.76; H, 5.31; N, 5.47%. Found: C, 52.64; H, 5.39; N, 5.52%. IR (KBr) ν(CN)/cm^{-1}: 1617.

Physical Measurements

IR spectra were recorded on a Bio-Rad FTS-40 FTIR spectrophotometer as KBr pellets in the 4000-400 cm^{-1} regions. The temperature dependence of the magnetic susceptibility of polycrystalline samples was measured between 2 and 300 K in a field 1 T on a MPMS quantum design SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants.[13]

Table 1. Crystallographic Data for Complexes **1** and **2**

	1	**2**
Formula	$C_{22}H_{30}ClMnN_2O_7$	$C_{24}H_{29}ClFeN_3O_5$
M	524.87	530.80
Space group	*C*2/c	*P*2$_1$/n
a (Å)	18.131(4)	14.3706(6)
b (Å)	17.732(3)	13.5500(5)
c (Å)	7.869(2)	14.9261(5)
α (^{o})	90	90
β (^{o})	111.30(2)	118.644(1)
γ (^{o})	90	90
V (Å^3)	2357.3(8)	2550.7(2)
Z	4	4
T (K)	293(2)	295(2)
D_{calc} (mg m^{-3})	1.479	1.382
N	2709	10896
N_o	2709	4458
R_1	0.0444	0.0518
wR_2 (F^2)	0.0986	0.1104

X-ray Crystal Structure Analysis

Crystallographic data were collected for compounds of **1** and **2** on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo K_α radiation (λ = 0.7107 Å), 2θ - θ scan mode at 293 K. *N* independent reflections and N_o with $I > 2.0\ \sigma(I)$ were observed. The structures were solved by direct method and refined (based on F^2) by a full-matrix least-squares method using the SHELXTL software package;[14] the function minimized was $\sum w(|F_o| - |F_c|)^2$ and unit weights were used. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters: $R_1 = \sum|F_o - F_c| / \sum|F_o|$ and $wR_2 = (\sum(w|F_o^2 - F_c^2|)^2 / |\sum w|F_o^2|^2)^{1/2}$. The summary of the crystal and diffraction data is given in Table 1, and the selected bond distances and angles are given in Table 2.

Reaction of NaOCl with *cis*-Stilbene and α-Methylstyrene Catalyzed by [MnL(H_2O)$_2$]Cl·H_2O (1) and [FeL(H_2O)Cl]CH_3CN (2)

An unbuffered, undiluted solution of commercial sodium hypochloride (13% w/w, 0.40 mL, 0.56 mmol) was slowly added to a solution of *cis*-stilbene (0.101 g, 0.56 mmol) or α-methylstyrene, and complex **1** (0.01 g, 0.02

Table 2. Selected Bond Distances (Å) and Bond Angles (Å) of **1** and **2**

Compound **1**			
Bond lengths			
Mn-O(1)	1.885(2)	Mn-O(3)	2.214(2)
Mn-N(1)	1.987(2)		
Bond angles			
O(1)-Mn-N(1a)	173.84(9)	O(1a)-Mn-N(1)	173.85(9)
O(3)-Mn-O(3a)	177.4(2)	O(1)-Mn-O(1a)	93.98(12)
O(1)-Mn-N(1)	92.16(9)	O(1a)-Mn-N(1a)	92.17(9)
N(1a)-Mn-N(1)	81.69(13)	O(1a)-Mn-O(3a)	89.47(10)
O(1)-Mn-O(3a)	92.32(10)	N(1)-Mn-O(3a)	89.94(11)
N(1a)-Mn-O(3)	89.46(10)	N(1)-Mn-O(3)	88.07(10)
Compound **2**			
Bond lengths			
Fe-O(1)	1.908(2)	Fe-O(2)	1.918(2)
Fe-O(5)	2.242(3)	Fe-N(1)	2.105(3)
Fe-N(2)	2.094(3)		
Bond angles			
O(1)-Fe-N(2)	164.51(12)	O(2)-Fe-N(1)	166.28(11)
O(5)-Fe-Cl(1)	177.18(9)	O(1)-Fe-O(2)	100.87(10)
O(2)-Fe-N(2)	88.99(11)	O(1)-Fe-N(1)	89.36(11)
O(1)-Fe-O(5)	85.02(12)	N(2)-Fe-N(1)	79.20(12)
N(2)-Fe-O(5)	83.67(13)	O(2)-Fe-O(5)	86.55(11)
O(1)-Fe-Cl(1)	96.26(8)	N(1)-Fe-O(5)	85.25(12)
N(2)-Fe-Cl(1)	94.60(10)	O(2)-Fe-Cl(1)	95.66(8)

mmol) or complex **2** were dissolved in methylene chloride (10 mL). After complete addition, the mixture was stirred at 25 °C for 10 h under an atmosphere of nitrogen. The methylene chloride was removed under reduced pressure. The organic products were extracted with diethyl ether, dried with Na_2SO_4 and filtered. The products analysis by ^1H NMR spectroscopy, 1,4-dibromo-benzene in $CDCl_3$ as an internal standard, showed the presence of *cis*-stilbene oxide (single δ 4.25) and a *trans*-stilbene oxide (single δ 3.85) or α-methylstyrene oxide.

RESULTS AND DISCUSSION

Crystal Structure Description of Complexes 1 and 2

The X-ray crystal structures and atom numbering schemes for complexes **1** with Cl^- and H_2O, and **2** without CH_3CN are illustrated in Figs. 1-2, respectively. The selected bond distances and angles relevant to the metal coordination sphere are listed in Table 2.

All of the structures illustrated the coordination geometry around each metal atom and can be described as a distorted octahedral for **1** and **2**. In compound **1** the equatorial sites are occupied by the N_2O_2 donor atoms of the ligand L with the bond distances of Mn-N = 1.987(2) Å and Mn-O = 1.885(2) Å, and the apical oxygen atom of H_2O with Mn-O = 2.214(2) Å. The displacements of the Mn(III) ions from O(1), O(1a), N(1), and N(1a) equatorial planes of **1** are zero. This zero displacement of Mn(III) ion from the N_2O_2 plane in **1** may be due to the two apical water ligands, which make hydrogen bonds between the hydrogen atoms of coordinated H_2O and the oxygen atoms of two free crystalline water molecule with O(4)···H-O(3) = O(4a)···H′-O(3a) = 2.079 Å, thus then to form a quasi polymeric chain (Fig. 3).

In compound **2**, the carbon atoms of the cyclohexyl ring, C(8)-C(13), are in disorder. Two apical sites are occupied by the chloride and oxygen of water with Fe-Cl(1) = 2.3504(12) Å and Fe-O(5) = 2.242(3) Å, and the basal coordination plane consists of the N_2O_2 donor atoms of the L ligand with the average bond distances of Fe-N = 2.0995(10) Å and Fe-O = 1.913(2) Å. The displacement of the Fe(III) ions from O(1), O(2), N(2), and N(1) equatorial planes of complexes **1** is 0.167 Å which is smaller than that of 0.46 Å observed for Fe(salen)Cl.[12,15-16] The displacement of metal ion from N_2O_2 plane reflects the strain exerted by the ligand structure.

Studies of the iron(III)-salen systems have shown that the metal to imine nitrogen bond distance is sensitive to the electronic spin state of the metal ion. The metal to imine nitrogen distances are in the range 2.00 ~ 2.10 Å for the high-spin state and in the range 1.93 ~ 1.96 Å for the low-spin case.[17] In the structure of complex reported here the mean Fe-N bond distances of 2.0995(10) Å for **2**, suggest that the

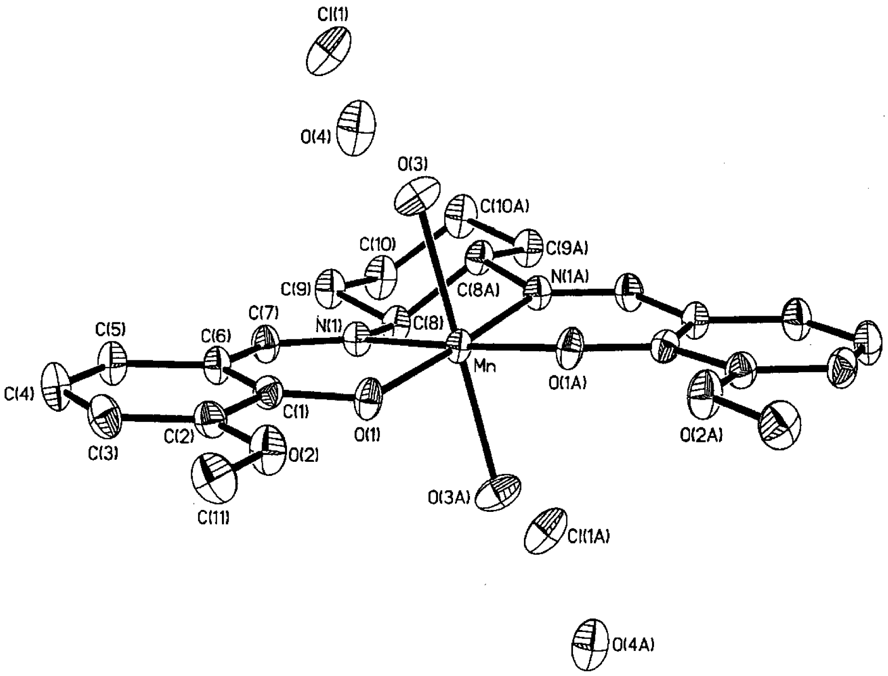


Fig. 1. Perspective view of complex **1** with the atom numbering scheme. Thermal ellipsoids are drawn at 30% probability level.

iron(III) ion in **2** is in the high-spin state (S = 5/2), which is consistent with the results of room temperature magnetic susceptibility measurements (see below).

Magnetic Susceptibility

Variable-temperature magnetic studies were performed on dried, powder samples of Mn(III) complex **1** and Fe(III) complex **2** in the temperature range 2-300 K. Plots of $\chi_m T$ versus T for **1** and **2** are shown in Fig. 4. The value $\chi_m T$ of **1** decreases from a value of 2.87 $cm^3 mol^{-1}$ K at 300 K rapidly with decreasing temperature until it reaches a value of 0.015 $cm^3 mol^{-1}$ K, which is characteristic of an antiferromagnetic exchange interaction. The analysis of the magnetic susceptibility of **1** was constructed by the combination of the anisotropic zero-field splitting and the Heisenberg one-dimensional isotropic spin exchanging chain, using expression (1) derived by Fisher.[18-19]

$$\chi_m(\text{chain}) = \chi_o(\text{chain}) + \Delta\chi_{ZFS} \qquad (1)$$

where $\chi_o(\text{chain}) = [Ng^2\mu_B^2S(S+1)/3kT][(1+u)/(1-u)]$
with

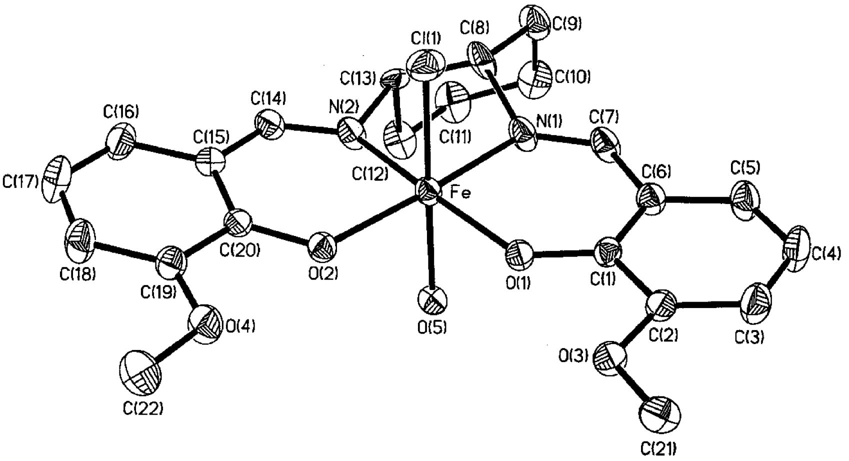


Fig. 2. Perspective view of complex **2** with the atom numbering scheme. The solvent $CHCN_3$ is omitted for clarity. Thermal ellipsoids are drawn at 30% probability level.

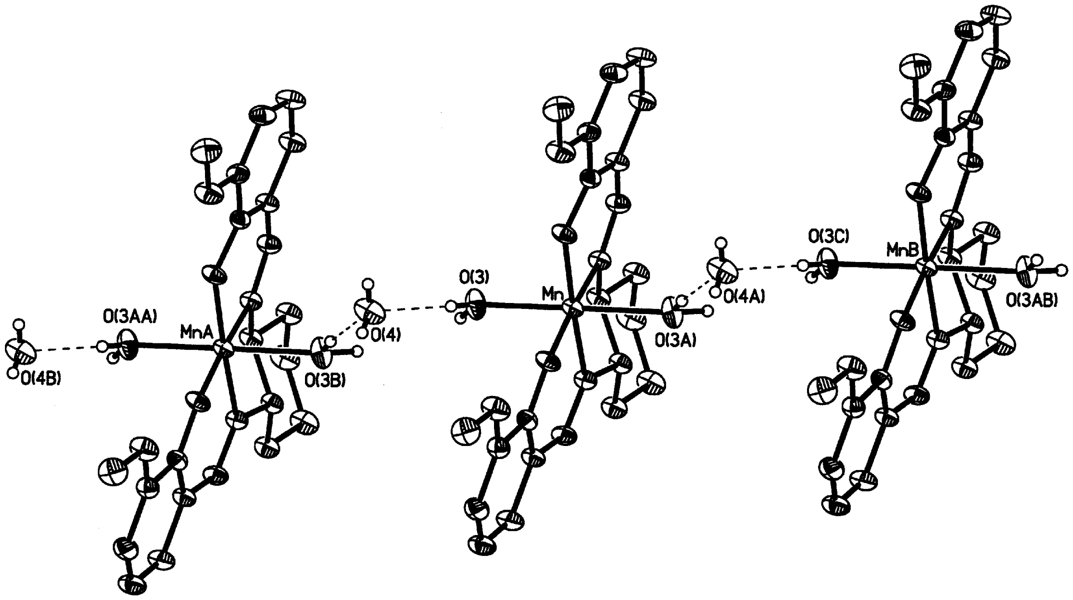


Fig. 3. View of the formation of one-dimensional molecular chain in complex **1**. Weak intermolecular hydrogen bonds are shown by dotted lines.

$$u = \coth[JS(S+1)/kT] - [kT/JS(S+1)]$$
$$\Delta\chi_{ZFS} = (\chi_{\parallel} - \chi_{\perp})$$
$$= [2Ng^2\mu_B^2 S(S+1)/15kT][DS(S+1)F/kT]]$$
$$F = [(1+u)(1+\nu)/(1-u)(1-\nu)] + 2u/(1-u)$$

and ν defined by

$$\nu = 1 - [3ukT/JS(S+1)]$$

Careful variation of D and J then gave a best fit with $J = -7.50$ cm^{-1}, $D = 0.01$ cm^{-1}, and $g = 2.10$ shown in Fig. 4. The antiferromagnetic interactions are the result of super-exchange operating via hydrogen bonding water molecules in the structure.

The plot of χ_mT *vs* T for **2** is illustrated in Fig. 4. Above ca. 50 K the χ_mT value is 4.32 cm^3 mol^{-1} K and is independent of temperature. Below 50 K it begins to decrease quite rapidly, with a marked curvature in the plot, reaching a value of 2.12 cm^3 mol^{-1} K at 2 K. This behaviour is generally reminiscent of a $^6A_1$ state of Fe(III), having considered zero-field splitting and weak intermolecular magnetic interactions.[12,19-21]

The observed magnetic data were analysed with the axial symmetry spin Hamiltonian,[20,21] $H = g_i\mu_B HS_i + D[S_{iz}^2 - (1/3)S(S+1)]$, let $g_{\parallel} = g_{\perp} = g$ and derived the equation (2)

$$\chi_m = (\chi_{\parallel} + 2\,\chi_{\perp})/3 \qquad (2)$$

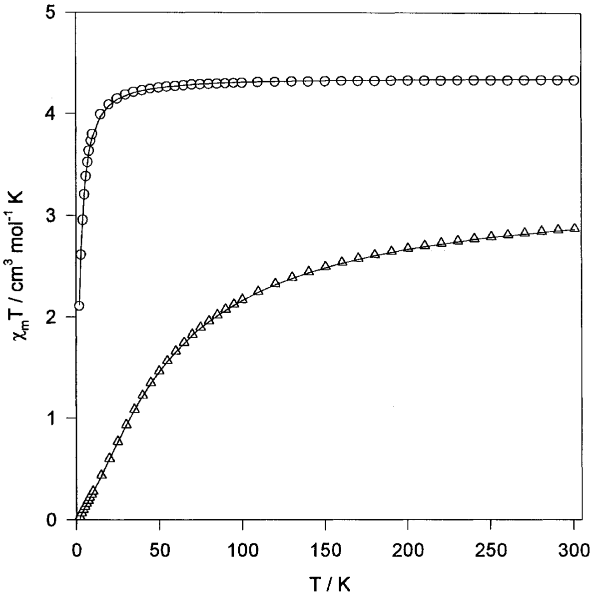


Fig. 4. Temperature dependence of χ_mT for complexes **1** (- Δ -) and **2** (- o -). The solid line is calculated with the fitted parameters reported in the text.

where

$$\chi_{\parallel} = [Ng^2\mu_B^2/4k(T-\theta)][\{1 + 9\exp(-2x) + 25\exp(-6x)\}/\{1 + \exp(-2x) + \exp(-6x)\}]$$
$$\chi_{\perp} = [Ng^2\mu_B^2/4k(T-\theta))[\{(9 + 8/x) - (11\exp(-2x)/2x) - (5\exp(-6x)/2x)\}/\{1 + \exp(-2x) + \exp(-6x)\}]$$

with $x = D/kT$

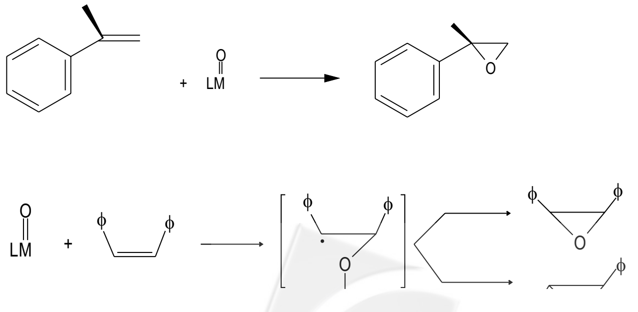
A least-squares fitting of the data to Eq. 2 gave g = 2.00, $D = 2.50$ cm^{-1}, and θ = -1.20 cm^{-1}, here the θ value of -1.20 cm^{-1} indicative of a weak intermolecular antiferromagnetic interaction.

Epoxidation of *cis*-Stilbene and α-Methylstyrene

An unbuffered, undiluted solution of NaOCl at 25 °C under N_2 atmosphere was found to react readily with $[MnL(H_2O)_2]Cl$ (**1**) and $[FeL(H_2O)(Cl)]$ (**2**) complexes in the presence of *cis*-stilbene or α-methylstyrene to produce *cis*-stilbene oxide and *trans*-stilbene oxide or α-methylstyrene oxide.

With **1** the epoxides were produced in 75% yield with *cis*:*trans* = 12:88 from *cis*-stilbene and 82% from α-methylstyrene, and with **2** the epoxides were produced in 43% with *cis*:*trans* = 30:70 from *cis*-stilbene and α-methylstyrene oxide 71% from α-methylstyrene. These data clearly show that the *cis*-stilbene produced higher yields of *trans*-epoxide, and the relative reactivity of epoxidation by using Mn(III) complex is higher than that of Fe(III) complex as catalyst. It has been observed that *cis*-stilbene reacts with iron-porphyrin complexes to give high yields of *cis*-stilbene oxide containing a minor amount of the corresponding trans isomer.[1-5] Nevertheless, the epoxidation *cis*-olefins catalyzed by Mn(salen) derivatives essentially favors the production of *trans*-epoxide products.[7-9] We propose at this moment that the mechanism accounts for the selective formation of *trans*-epoxides from *cis*-olefins by using complex Mn(III) (salen)[8,22-24] (as shown in Scheme II) including a radical inter-

Scheme II



mediate with rotational collapse could explain the present results. That the relative yields of epoxidation by using Mn-complex are higher than those of Fe-complex as catalyst could be explained by saying that the radical intermediate of **1** is more stable than that of **2**.

ACKNOWLEDGMENT

The authors would like to thank the National Science Council of Taiwan for financial support via grant NSC-90-2113-M-032-020.

Received July 5, 2002.

REFERENCES

1. (a) Groves, J. T.; Nemo,T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (b) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc*. **1983**, *105*, 5786. (c) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc*. **1988**, *110*, 8443.
2. Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc*. **1983**, *105*, 5791. (b) Groves, J. T.; Visiki, P. *J. Org. Chem*. **1990**, *55*, 3628.
3. O'Malley, S.; Kdadek, T. *J. Am. Chem. Soc*. **1989**, *111*, 9116.
4. Naruta, Y.; Tani, F.; Ishihara, N.; Maruyama, K. *J. Am. Chem. Soc*. **1991**, *113*, 6865.
5. Yang, S. J.; Nam, W. *Inorg. Chem*. **1998**, *37*, 606.
6. Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc*. **1986**, *108*, 2309.
7. (a) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobson, E. N. *J. Am. Chem. Soc*. **1990**, *112*, 2801. (b) Jacobson, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VHC, New York, 1993, pp. 386-436. (c) Finney, N. S.; Posisil, P. J.; Chang, S.; Palucki, M.; Konsler, R. G.; Hansen, K. B.; Jacobson, E. N. *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 1720. (d) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobson, E. N. *Science*. **1997**, *277*, 936. (e) Waldemar, A.; Rainer, T. F.; Veit, R. S.; Chantu, R. S-M. *J. Am. Chem. Soc.* **1998**, *120*, 708. (f) Sigman, M. S.; Jacobson, E. N. *J. Am.. Chem. Soc.* **1998**, *120*, 85.
8. (a) Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189. (b) Linker, T. *Angew. Chem Int. Ed. Engl.* **1997**, *36*, 2060. (c) Ito, Y. N.; Katsuki, T. *Bull. Chem. Soc. Jpn*. **1999**, *72*, 603. (d) Canali, L.; Sherrington, D. C. *Chem. Soc. Rev.* **1999**, *28*, 85.
9. Norrby, P. O. *J. Am. Chem. Soc.* **1995**, *117*, 10356.
10. Bernardo, K.; Leopard, S.; Robert, A.; Commenges, G., Dahan, F.; Meunier, B. *Inorg. Chem.* **1996**, *35*, 387.
11. (a) Annis, D. A.; Jacobson, E. N. *J. Am. Chem. Soc.* **1999**, *121*, 4147. (b) Jacobson, E. N. *Acct. Chem. Res*. **2000**, *33*, 421.
12. Shyu, H. L.; Wei, H. H.; Lee, G. H.; Wang, Yu. *J. Chem. Soc., Dalton Trans.* **2000**, 915.
13. Kahn, O. In *Molecular Magnetism*; VCH, Weiheim, 1993; pp 3-4.
14. Sheldrick, G. M. *SHELXL-93. Program for the Refinement of Crystal Structures*; University of Göttingen, Germany, 1993.
15. Gerloch, M.; Mabbs, F. E. *J. Chem. Soc. A*. **1967**, 1598.
16. Preut, H.; Ruther, R.; Huber, F. *Acta Crystallogr.*, *Sect. C.* **1986**, *42*, 1154.
17. (a) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385. (b) Haris, N. J.; Beattie, J. K. *Inorg. Chem.* **1977**, *16*, 245. (c) Oosterhuis, W. T. *Struct. Bonding (Berlin)*. **1974**, *16*, 245. (d) Ref. 13. p 257-258.
18. Fisher, M. E. *Am. J. Phys*. **1964**, *32*, 343.
19. Marathe, V. R.; Mitra, S. *J. Chem. Phys*. **1983**, *78*, 915.
20. (a) Kennedy, B.; Brain, G.; Horn, E.; Murray, K. S.; Snow, M. R. *Inorg. Chem.* **1985**, *24*, 1647. (b) Kennedy, B. J.; McGrath, A. C.; Murray, K. S.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1987**, *26*, 483.
21. Berry, K. J.; Clark, P. E.; Murray, K. S.; Ralston, C. L.; White, A. H. *Inorg. Chem*. **1983**, *22*, 3928.
22. Groves, J. T.; Stern, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 3812.
23. Zhang, W.; Lee, N. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 425.
24. Jacobsen, E. N.; Zhang, W.; Muci, L. C.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc*. **1991**, *113*, 7063.