

# First structurally characterized optically active mononuclear Mn(IV) complex: synthesis, crystal structure and properties of $[\text{Mn}^{\text{IV}}\text{L}_2]$ $\{\text{H}_2\text{L} = S(-)-2-[(2\text{-hydroxy-1-phenylethylimino)methyl]phenol}\}^\dagger$

Chullikkattil P. Pradeep, Tin Htwe, Panthapally S. Zacharias\* and Samar K. Das\*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India.

E-mail: skdsc@uohyd.ernet.in; Fax: +91 40-2301-2460

Received (in Montpellier, France) 1st December 2003, Accepted 12th February 2004

First published as an Advance Article on the web 17th May 2004

The reaction of  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  with  $\text{H}_2\text{L}$   $\{\text{H}_2\text{L} = S(-)-2-[(2\text{-hydroxy-1-phenylethylimino)methyl]phenol}\}$  in the presence of air afforded dark brown crystals of  $[\text{Mn}^{\text{IV}}\text{L}_2]$ , **1**. Compound **1** crystallizes in the monoclinic chiral  $C_2$  space group. Crystals of **1** were further characterized by elemental analysis, room temperature magnetic moment determination, IR, UV-visible and EPR spectroscopy, cyclic voltammetry and circular dichroism (CD) studies. Cyclic voltammetry reveals a quasi-reversible redox wave corresponding to the Mn(IV)/Mn(III) couple. The EPR spectrum at liquid nitrogen temperature consists of a strong signal at  $g \sim 4$  and a weak but resolved response at  $g \sim 2$ . The CD spectrum of **1** exhibits a negative band, such as shown by the enantiopure ligand  $\text{H}_2\text{L}$ . Complex **1** was found to catalyze the oxidation of olefins using iodosobenzene as the oxidant in acetonitrile solutions.

## Introduction

Besides the fact that high-valent manganese coordination complexes are relevant to the active site of the oxygen-evolving complex in photosystem II,<sup>1</sup> their catalytic activities towards organic transformations are equally recognized.<sup>2</sup> A major focus of manganese-catalyzed reactions has been to design catalysts that use chiral ligands for asymmetric oxidations. Manganese(III) complexes with chiral centres have attracted much interest over the past decade because of their unique catalytic activity, especially in the context of asymmetric olefin oxidation reactions.<sup>3</sup> Even though in most of these olefin oxidation reactions, Mn(III) compounds have been used as catalysts, Mn(IV) complexes (which are formed in these reactions) are found to be responsible for the radical-type epoxidation.<sup>4</sup> Therefore, monomeric Mn(IV) complexes that use chiral ligands are of considerable interest as they have potential to drive such asymmetric syntheses. Although the number of mononuclear Mn(IV) complexes, synthesized<sup>5</sup> and structurally characterized,<sup>6</sup> is no longer limited, optically active Mn(IV) monomers are still scarce. We herein describe the synthesis and crystal structure of a neutral mononuclear Mn(IV) complex  $[\text{Mn}^{\text{IV}}\text{L}_2]$ , **1**  $\{\text{H}_2\text{L} = S(-)-2-[(2\text{-hydroxy-1-phenylethylimino)methyl]phenol}\}$  that is chiral. To the best of our knowledge, this is the first report of a structurally characterized mononuclear Mn(IV) complex that is optically active. We also describe the oxidation of olefins, catalyzed by **1**, using iodosobenzene as the oxidant.

## Experimental

### Instrumentation

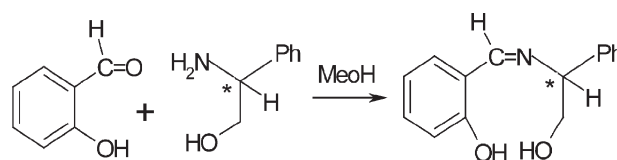
Microanalytical (C, H, N) data were obtained with a Perkin-Elmer Model 240C elemental analyzer. A Shimadzu 3101-PC UV/vis/NIR spectrophotometer was used to record the

† Electronic supplementary information (ESI) available: GC analysis of the styrene epoxidation; <sup>1</sup>H NMR spectrum of (*E*)-stilbene oxide produced by the epoxidation of (*E*)-stilbene. See <http://www.rsc.org/suppdata/nj/b3/b315658c/>

electronic spectra. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra of the ligand in CDCl<sub>3</sub> solution were recorded on a Bruker 200 MHz spectrometer using Si(CH<sub>3</sub>)<sub>4</sub> as an internal standard. The room temperature solid state magnetic susceptibility was measured by using a Sherwood Scientific magnetic susceptibility balance. Solution electrical conductivity was measured with a Digisun DI-909 conductivity meter. A CH-Instruments model 620A electrochemical analyzer was used for cyclic voltammetric experiments on an acetonitrile solution of the complex containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The three-electrode measurement was carried out at 298 K under a dinitrogen atmosphere with a platinum disc working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE). Optical rotation was measured with an AUTOPOL-II automatic polarimeter (readability  $\pm 0.01^\circ$ ). The CD spectra were measured with a Jasco J-810 spectropolarimeter. EPR spectra were recorded on a Joel JES-FA200 spectrometer. Gas chromatographic analyses were carried out in a Shimadzu GC 14B instrument equipped with a stainless steel packed column (5 m, 5% SE 30) and a flame ionization detector.

### Syntheses

**Enantiopure ligand  $\text{H}_2\text{L}$ .** (*S*)-(+)-2-Phenylglycinol (0.137 g, 1 mmol) and salicylaldehyde (0.122 g, 1 mmol) were stirred together in methanol (15 mL) for 1 h at room temperature (see Scheme 1 below). The resulting yellow solution was



Scheme 1

filtered and the filtrate was kept for 2 days in an open beaker for slow evaporation. Yellow, needle-shaped crystals, precipitated during this time, were collected by filtration, washed with hexane and dried at room temperature. Yield: 0.233 g (97%). Anal calcd (found): C, 74.67 (75.02); H, 6.27 (6.16); N, 5.81 (5.79)%. Mp: 115–116° C. IR (KBr,  $\text{cm}^{-1}$ ): 3214, 1626, 1577, 1491, 1458, 1383, 1273, 1211, 1153, 1118, 1062, 916, 857, 806, 754, 692, 636, 520, 457. UV/Vis [ $\text{CH}_3\text{CN}$ ;  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ): 214 (29060), 255 (14180), 315 (4290).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.95 (d,  $J = 6.12$  Hz, 2H,  $\text{CH}_2$ ), 4.49 (t,  $J = 6.49$  Hz, 1H, CH), 6.864–7.008 (m, 2H, Ar), 7.269–7.403 (m, 7H, Ar), 8.5 (s, 1H).  $^{13}\text{C}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  67.62, 75.69, 117.08, 118.89, 127.16, 127.90, 128.86, 131.82, 132.72, 139.39, 166.27.  $[\alpha]_{\text{D}}^{25} = -122$  ( $c$  0.04, MeOH).

**1.** To a methanolic solution (15 mL) of ligand  $\text{H}_2\text{L}$  (0.241 g, 1 mmol) was added  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.245 g, 1 mmol). The mixture was allowed to stir at room temperature in air for 3 h. The resulting dark brown solution was evaporated to dryness using rotary vapor and vacuum pump. The solid, thus obtained, was dissolved in dichloromethane, washed twice with water, once with brine solution (using a separating funnel) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The resulting dark brown solution, on slow evaporation, gave a brown microcrystalline solid of **1**. Yield: 0.198 g (74.15%). X-Ray quality crystals of **1** were grown from ethanol by the slow evaporation method. Anal calcd (found): C, 67.54 (67.16); H, 4.91 (4.83); N, 5.25 (5.33)%. IR (KBr,  $\text{cm}^{-1}$ ): 1616, 1535, 1440, 1312, 1200, 1148, 1022, 943, 897, 802, 756, 700, 640, 611, 579, 540, 457. UV/Vis [ $\text{CH}_3\text{CN}$ ;  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ): 210 sh, 240 (44640), 340 sh, 410 sh, 550 sh. FAB-MS (3-nitrobenzyl alcohol)  $m/z$ : 535. Conductivity ( $\text{CH}_3\text{CN}$ ,  $10^{-3}$  M solution): 1.7 mho  $\text{cm}^2 \text{mol}^{-1}$ , consistent with a neutral compound.

### Epoxidation studies

**(E)-Stilbene catalyzed by 1.** (*E*)-Stilbene (0.1 g, 0.55 mmol) and iodobenzene (0.244 g, 1.1 mmol) were added to a solution of **1** (0.016 g, 30  $\mu\text{mol}$ ) in acetonitrile (5 mL) at room temperature. After stirring for 12 h, the mixture was concentrated under vacuum and purified with column chromatography ( $\text{SiO}_2$ , hexane–ethyl acetate 1:0 to 19:1) to give stilbene oxide as colorless crystals. Yield: 0.040 g (37%). The product was identified as (*E*)-stilbene oxide by comparing its NMR spectrum ( $\delta \sim 3.85$  in  $\text{CDCl}_3$ ) with that of reported (*E*)-stilbene oxide<sup>7</sup> (see also Electronic supplementary information).

**Styrene catalyzed by 1.** Styrene (0.114 g, 1.1 mmol) and iodobenzene (0.49 g, 2.23 mmol) were added to a solution of **1** (0.032 g, 60  $\mu\text{mol}$ ) in acetonitrile (5 mL) and stirred at room temperature under nitrogen atmosphere. After completion of the reaction, the solvent was removed under vacuum and the residue was treated with  $\text{Et}_2\text{O}$  ( $6 \times 5$  mL). The  $\text{Et}_2\text{O}$  washings were combined together and concentrated to a small volume. Bromobenzene (0.075 g) was added as an internal standard and the volume was made up to 10 mL. The resulting solution was analyzed by gas chromatography and the product was identified as styrene oxide by comparing the retention time with that of the authentic sample (see Electronic supplementary information). Yield: 0.070 g (53%). Both epoxidation products, (*E*)-stilbene oxide and styrene oxide, were found to be racemic mixtures, as evidenced by polarimetric studies.

### X-Ray crystallography

X-Ray diffraction data were collected at room temperature (25 °C) for  $[\text{Mn}^{\text{IV}}\text{L}_2]$  on a Siemens P4 diffractometer equipped with a molybdenum tube and a graphite monochromator. A dark brown crystal of approximate dimensions  $0.62 \times 0.50 \times 0.42 \text{ mm}^3$  was mounted on a glass fiber using epoxy

resin. Unit cell dimensions were determined from several accurately centered reflections using XSCANS program.<sup>8</sup> Scans were of the  $\omega$  type. Three standard reflections measured after every 97 reflections exhibited no significant loss of intensity. The data were corrected for Lorentz polarization effects and absorption. Additional details of the data collection and refinement are collected in Table 1.†

The compound crystallized in the chiral monoclinic space group  $C2$  with four molecules in the unit cell. The structure was solved by direct methods and refined by least-squares techniques adopting the full-matrix weighted least-squares scheme,  $w^{-1} = \sigma^2 F_o^2 + (0.0341P)^2 + 0.53P$ , where  $P = (F_o^2 + 2F_c^2)/3$ , on  $F^2$  using SHELXS-97 and SHELXL-97 programs, respectively.<sup>9</sup> All atoms were located in the difference maps during successive cycles of least-squares refinement. The sites of the non-hydrogen atoms were refined anisotropically, whereas those of the hydrogen atoms were refined isotropically. The absolute configuration for the compound molecule was successfully determined by refining the Flack parameter [0.028(15)].<sup>10</sup> The final Fourier difference synthesis showed minimum and maximum peaks of  $-0.153$  and  $+0.112 \text{ e } \text{Å}^{-3}$ .

## Results and discussion

### Synthesis of $\text{H}_2\text{L}$ and manganese complex **1**

The enantiopure ligand  $\text{H}_2\text{L}$  is prepared in quantitative yield in a Schiff base condensation reaction (shown in Scheme 1) of 1 equiv of (*S*)-(+)-2-phenylglycine with 1 equiv of salicylaldehyde in methanol.

Reaction of  $\text{Mn}(\text{II})$  acetate and the optically pure ligand  $\text{H}_2\text{L}$  afforded the neutral and optically active complex  $[\text{Mn}^{\text{IV}}\text{L}_2]$ , **1**, in good yield. Compound **1** was characterized by different physical techniques including CV, EPR and CD studies. Remarkably, oxidation of the manganese(II) center directly to the manganese(IV) species  $[\text{Mn}^{\text{IV}}\text{L}_2]$  proceeds easily in the presence of air, indicating that the tridentate ligand  $\text{L}^{2-}$  containing two  $\text{O}^-$  donors effectively stabilizes an enigmatic Mn(IV) oxidation state. Stabilization of Mn(IV) species by similar ligands/phenolate oxygens has been previously reported.<sup>6(t)</sup>

Selected IR data for the complex **1** are given in the Experimental section. The IR band that conveys important

**Table 1** Crystallographic data for **1**

Empirical formula	$\text{C}_{30}\text{H}_{26}\text{MnN}_2\text{O}_4$
FW	533.47
Crystal system	Monoclinic
Space group	$C2$
$\lambda/\text{Å}$	0.71073
$a/\text{Å}$	23.052(7)
$b/\text{Å}$	8.9826(8)
$c/\text{Å}$	12.684(3)
$\beta/^\circ$	107.504(12)
$U/\text{Å}^3$	2504.8(10)
$Z$	4
$\mu/\text{mm}^{-1}$	0.567
$T/^\circ\text{C}$	25
Independent reflections	2637
$R_{\text{int}}$	0.0138
Obs reflections [ $F > 4\sigma(F)$ ]	2552
$R_1^a$ [ $F > 4\sigma(F)$ ]	0.0236
$wR_2^b$	0.0622

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad ^b wR_2 = \frac{[\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{1/2}}$$

† CCDC reference numbers 217503. See <http://www.rsc.org/suppdata/nj/b3/b315658c/> for crystallographic data in .cif or other electronic format.

information is the peak due to the  $\nu(\text{OH})$  vibration, which occurs as a broad feature in the IR spectrum. For the free ligand there is a strong peak at  $3214\text{ cm}^{-1}$  present before complexation. This band is missing in the IR spectrum of complex **1**, indicating deprotonation of the ligand on complexation/coordination with the Mn(IV) center.

### Crystal structure of **1**

As one would expect, compound **1** crystallizes in a chiral space group, which is  $C_2$  in the present case. The asymmetric unit contains two independent MnL (half of the complex) units, in which each manganese occupies a special position lying on a crystallographic  $C_2$  axis. Therefore, in the crystal structure, two independent mononuclear Mn(IV) complexes are paired and both have the same enantiomeric configuration. The overall geometry about the central manganese ion is octahedral with an  $\text{N}_2\text{O}_4$  core, whereby two chiral ligands coordinate through ONO donor atoms. The tridentate ligands are meridionally coordinated to the manganese center in **1**. The four oxygen atoms are located at the four corners of an approximately square plane (equator) and two N donors occupy trans (axial) positions and complete the octahedron (Fig. 1). The average Mn–N and Mn–O bond lengths for **1** are 1.975(2) and 1.879(2) Å, respectively. These average Mn–N and Mn–O bond distances are comparable to those for various reported Mn(IV) complexes containing similar ligation.<sup>6h,6i</sup> In the  $\text{MnN}_2\text{O}_4$  coordination sphere, the O–Mn–O and O–Mn–N angles are close to  $90^\circ$  (within  $\pm 5^\circ$ ). Selected bond lengths and angles are presented in Table 2. The optical activity of the Mn complex **1** is induced by the enantiopure ligand,  $\text{H}_2\text{L}$ .

### Electronic spectrum and circular dichroism

The electronic spectrum of ligand  $\text{H}_2\text{L}$  in MeCN (inset, Fig. 2) is characterized by three intraligand charge transfer transitions, judging from their molar extinction coefficient values. The UV-visible spectrum of the manganese complex **1** in MeCN is dominated by an intense absorption band at 240 nm and two shoulders at  $\sim 350$  and  $\sim 420$  nm. The circular

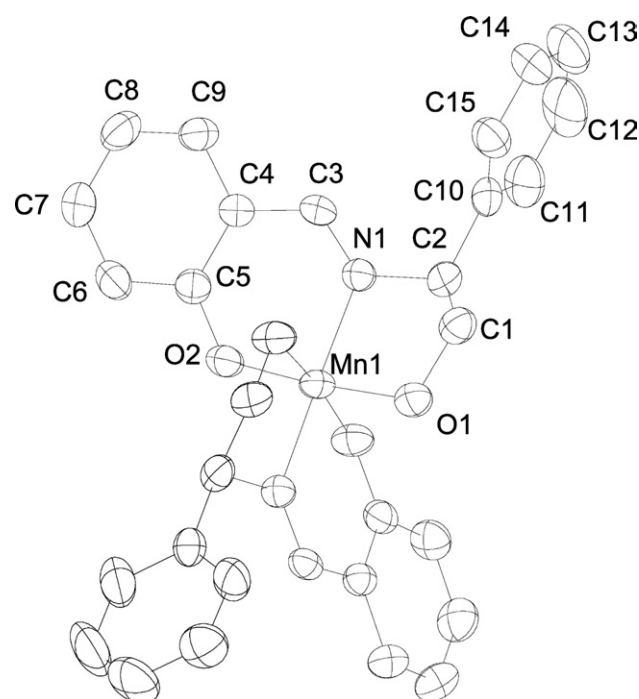


Fig. 1 Thermal ellipsoid plot (50% probability) and atom labelling for **1**.

Table 2 Selected bond lengths and angles for **1**

Mn(1)–O(1)	1.867(2)	N(1)–C(2)	1.484(3)
Mn(1)–O(2)	1.900(2)	O(2)–C(5)	1.316(3)
Mn(1)–N(1)	1.9696(18)	C(1)–C(2)	1.524(4)
O(1)–C(1)	1.403(3)	C(2)–C(10)	1.513(3)
N(1)–C(3)	1.285(3)	C(3)–C(4)	1.423(3)
O(1)–Mn(1)–O(2)	173.78(10)	N(1)–C(2)–C(10)	115.9(2)
O(1)–Mn(1)–N(1)	84.97(10)	N(1)–C(2)–C(1)	102.7(2)
O(2)–Mn(1)–N(1)	89.60(9)	C(10)–C(2)–C(1)	117.2(2)
C(1)–O(1)–Mn(1)	112.54(17)	N(1)–C(3)–C(4)	124.8(2)
C(3)–N(1)–C(2)	126.8(2)	C(9)–C(4)–C(3)	118.9(2)
C(3)–N(1)–Mn(1)	124.97(17)	C(3)–C(4)–C(5)	122.1(2)
C(2)–N(1)–Mn(1)	108.09(14)	O(2)–C(5)–C(6)	119.3(2)
C(5)–O(2)–Mn(1)	125.15(17)	O(2)–C(5)–C(4)	122.9(2)
O(1)–C(1)–C(2)	108.2(2)	C(15)–C(10)–C(2)	122.1(3)

dichroism (CD) spectrum of the synthesized chiral ligand  $\text{H}_2\text{L}$  [ $S(-)$ ] shows a negative band around 315 nm as shown in Fig. 2. The CD spectrum of **1**, as expected, exhibits a negative band but shifted in position (at around 340 nm) as compared to the band of the free ligand  $\text{H}_2\text{L}$ . This red shift in the band positions is also consistent with the respective electronic spectra. Deprotonation of ligands during complex formation might produce this slight shift in the band positions. It may be noted that the present circular dichroism is of a “Type II” nature, as described by Moscovitz.<sup>11</sup>

### EPR spectroscopy

The complex **1** is paramagnetic as expected for a Mn(IV)  $d^3$  system. The room temperature magnetic moment of  $\mu_{\text{eff}} = 4.20$  (at 298 K) for complex **1** indicates an  $S = 3/2$  spin state. The EPR measurements were performed with the X-band frequency (9221.599 MHz) at liquid nitrogen temperature. The major feature of the spectrum is a strong and broad signal at  $g \sim 4$  and a weak but resolved response at  $g \sim 2$  (Fig. 3). This

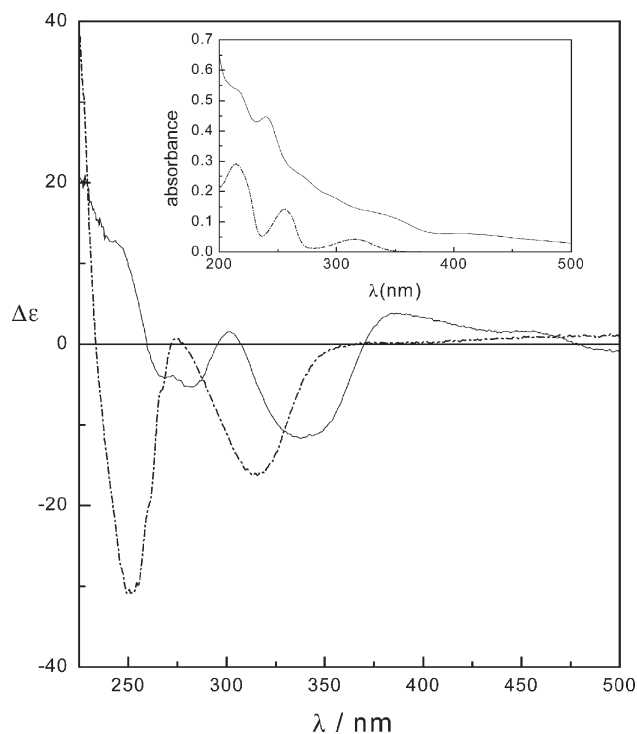


Fig. 2 The circular dichroism spectra of **1** (solid line) and the ligand  $\text{H}_2\text{L}$  (dashed line) in acetonitrile solution. Inset: electronic spectra of **1** (solid line) and the ligand  $\text{H}_2\text{L}$  (dashed line) in acetonitrile solution.



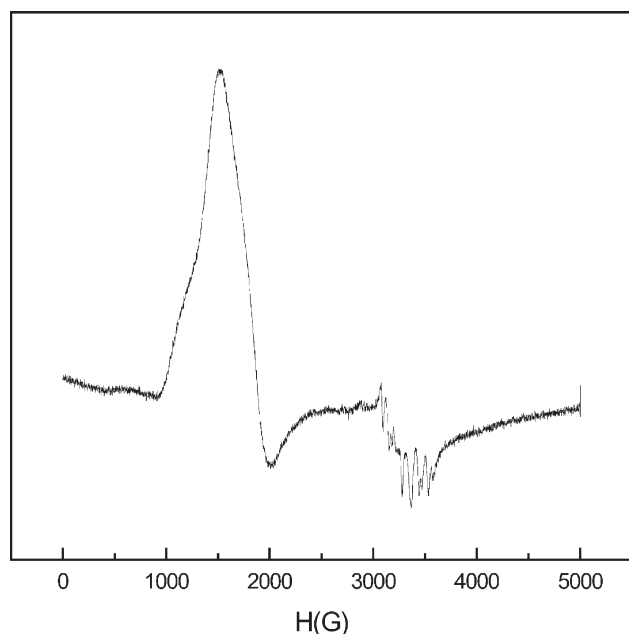


Fig. 3 X-Band EPR spectrum of **1** in methanol-toluene (1:1) solution at liquid nitrogen temperature.

corresponds to strong axial distortion with small zero-field splitting,  $2D \gg h\nu$  ( $h\nu$   $0.31 \text{ cm}^{-1}$  at the X-band frequency). The  $^{55}\text{Mn}$  hyperfine structure is resolved ( $A = 87.7 \text{ G}$ ) at around  $g = 2$ . This type of spectral feature has been seen in similar  $\text{MnO}_4\text{N}_2$  complexes with achiral ligands such as  $\text{Mn}^{\text{IV}}(\text{azc})_2$  ( $\text{H}_2\text{azc} = 2\text{-hydroxy-2'-carboxy-5-methylazobenzene}$ ).<sup>6h,6j</sup>

#### Cyclic voltammetry

The cyclic voltammogram of **1** in 0.1 M  $\text{TBAClO}_4/\text{CH}_3\text{CN}$  (platinum working electrode, 298 K) shows a nearly reversible reduction at  $-0.37 \text{ V vs. SCE}$  ( $\Delta E = 92 \text{ mV}$ ), which can be assigned to the  $[\text{Mn}^{\text{IV}}\text{L}_2] + e^- \rightleftharpoons [\text{Mn}^{\text{III}}\text{L}_2]^-$  couple (Fig. 4).

#### Epoxidation of olefins

In order to determine the catalytic activity of the monomeric manganese(IV) complex **1**, the oxidation reactions of (*E*)-stilbene and styrene were performed in acetonitrile solutions using

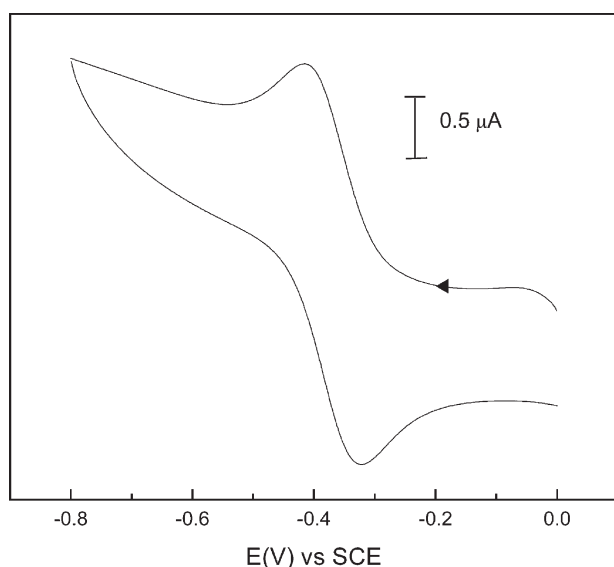


Fig. 4 Cyclic voltammogram (scan rate,  $100 \text{ mV s}^{-1}$ ) of  $\sim 10^{-3} \text{ M}$  solution (0.1 M TBAP) of **1** in acetonitrile at a platinum electrode at 298 K.

iodosobenzene (PhIO) as the oxidant. In these oxidation reactions, compound **1** was found to activate PhIO at room temperature to give the corresponding epoxidation products, (*E*)-stilbene and styrene oxides in moderate yields. For (*E*)-stilbene, the product was isolated and characterized by NMR spectroscopy and the turnover was found to be  $\sim 7.0$ . For styrene, the epoxidation reaction was monitored by GC using bromobenzene as an internal standard to quantify the final yield. The turnover for the formation of styrene oxide was determined to be  $\sim 10.0$ . It is important to note that, in both epoxidation reactions, the oxidized products were identified as racemic mixtures, although the catalyst **1** contains chiral centers. The possible reason for this non-enantioselectivity might be the degradation of the catalyst (by detaching of the enantiopure ligands) during the binding process of the substrate to the manganese center.

#### Conclusions

A new chiral octahedral manganese(IV) complex with a  $\text{N}_2\text{O}_4$  coordination environment has been described. The oxidation state of manganese was confirmed by IR and EPR studies as well as X-ray crystallography and a magnetic moment determination. The chirality of the complex was also evidenced by circular dichroism studies. Complex **1** provides the first example of a structurally characterized enantiopure mononuclear manganese(IV) compound. The title complex **1** catalyzes the oxidation of (*E*)-stilbene and styrene to their corresponding epoxides using iodosobenzene as the oxidant.

#### Acknowledgements

We acknowledge the Department of Science and Technology, Government of India, for financial support. We thank Dr. S. Pal for helpful discussions. Special thanks are due to Dr. N. Arulsamy for providing X-ray data. C. P. P. thanks UGC, Government of India, for a fellowship. We are grateful to UGC, New Delhi, for infrastructure facility at the University of Hyderabad under a UPE grant.

#### References

- (a) *Manganese Redox Enzymes*, ed. V. L. Pecoraro, VCH Publishers, New York, 1992; (b) V. K. Yachandra, V. J. DeRose, M. J. Latimer, I. Mukherji, K. Sauer and M. P. Klein, *Science*, 1993, **260**, 675; (c) R. Manchanda, G. W. Brudvig and R. H. Crabtree, *Coord. Chem. Rev.*, 1995, **144**, 1; (d) R. J. Debus, *Biochim. Biophys. Acta*, 1992, **1102**, 269; (e) O. R. Hansson, R. Aasa and T. Vanngard, *Biophys. J.*, 1987, **51**, 825.
- (a) V. C. Quee-Smith, L. DelPizzo, S. H. Jureller, J. L. Kerschner and R. Hage, *Inorg. Chem.*, 1996, **35**, 6461; (b) J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, 1987, **109**, 3812; (c) J. A. Smegal and C. L. Hill, *J. Am. Chem. Soc.*, 1983, **105**, 2920; (d) J. A. Smegal, B. C. Schardt and C. L. Hill, *J. Am. Chem. Soc.*, 1983, **105**, 3510; (e) J. A. Smegal and C. L. Hill, *J. Am. Chem. Soc.*, 1983, **105**, 3515.
- (a) *Comprehensive Asymmetric Catalysis*, eds. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer-Verlag, New York, 1999; (b) T. Katsuki, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH Publishers, New York, 2000.
- W. Adam, C. Mock-Knoblauch, C. R. Saha-Moller and M. Herderich, *J. Am. Chem. Soc.*, 2000, **122**, 9685.
- (a) A. V. Lakshmi, N. R. Sangeetha and S. Pal, *Indian J. Chem., Sect. A*, 1997, **36A**, 844; (b) S. Pal, *J. Chem. Res. (S)*, 1995, 236; (c) V. Manivannan, S. Dutta, P. Basu and A. Chakravorty, *Inorg. Chem.*, 1993, **32**, 769; (d) S. Pal, P. Ghosh and A. Chakravorty, *Inorg. Chem.*, 1985, **24**, 3704; (e) T. Matsushita and T. Shono, *Polyhedron*, 1983, **2**, 613; (f) D. T. Richens and D. T. Sawyer, *J. Am. Chem. Soc.*, 1979, **101**, 3681; (g) M. Koikawa, H. Okawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1988, 641; (h) M. Fujiwara, T. Matsushita and T. Shono, *Polyhedron*, 1985, **4**, 1895; (i) H. Okawa, M. Nakamura and S. Kida, *Bull. Chem.*

- Soc. Jpn.*, 1982, **55**, 466.(j) R. Y. Saleh and D. K. Straub, *Inorg. Chem.*, 1974, **13**, 3017.
- 6 (a) T. Weyhermuller, T. K. Paine, E. Bothe, E. Bill and P. Chaudhuri, *Inorg. Chim. Acta*, 2002, **337**, 344; (b) T. M. Rajendiran, J. W. Kampf and V. L. Pecoraro, *Inorg. Chim. Acta*, 2002, **339**, 497; (c) P. Perez-Lourido, J. Romero, L. Rodriguez, J. A. Garcia-Vazquez, J. Castro, A. Sousa, J. R. Dilworth and O. R. Nascimento, *Inorg. Chem. Commun.*, 2002, **5**, 337; (d) H. Asada, M. Ozeki, M. Fujiwara and T. Matsushita, *Chem. Lett.*, 1999, 525; (e) M. Mikuriya, D. Jie, Y. Kakuta and T. Tokii, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 1132; (f) R. O. C. Hart, S. G. Bott, J. L. Atwood and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1992, 894; (g) S. M. Saadeh, M. S. Lah and V. L. Pecoraro, *Inorg. Chem.*, 1991, **30**, 8; (h) S. Dutta, P. Basu and A. Chakravorty, *Inorg. Chem.*, 1991, **30**, 4031; (i) S. K. Chandra, S. B. Choudhury, D. Ray and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1990, 474; (j) S. K. Chandra, P. Basu, D. Ray, S. Pal and A. Chakravorty, *Inorg. Chem.*, 1990, **29**, 2423; (k) P. Deplano, E. F. Trogu, F. Bigoli and M. A. Pellingheli, *J. Chem. Soc., Dalton Trans.*, 1987, 2407; (l) D. P. Kessissoglou, X. Li, W. M. Butler and V. L. Pecoraro, *Inorg. Chem.*, 1987, **26**, 2487;
- (m) P. S. Pavaicik, J. C. Huffman and G. Christou, *J. Chem. Soc., Chem. Commun.*, 1986, 43; (n) M. Tirant and T. D. Smith, *Inorg. Chim. Acta*, 1986, **121**, 5; (o) J. R. Hartman, B. M. Foxman and S. R. Cooper, *Inorg. Chem.*, 1984, **23**, 1381; (p) D. H. Chin, D. T. Sawyer, W. P. Schaefer and C. J. Simmons, *Inorg. Chem.*, 1983, **22**, 752; (q) M. J. Camenzind, F. J. Hollander and C. L. Hill, *Inorg. Chem.*, 1983, **22**, 3776; (r) C. G. Howard, G. S. Girolami, G. Wilkinson, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1983, 1163; (s) M. J. Camenzind, F. J. Hollander and C. L. Hill, *Inorg. Chem.*, 1982, **21**, 4301; (t) K. L. Brown, R. M. Golding, P. C. Healy, K. J. Jessop and W. C. Tennant, *Aust. J. Chem.*, 1974, **27**, 2075.
- 7 D. Das and C. P. Cheng, *J. Chem. Soc., Dalton Trans.*, 2000, 1081.
- 8 XSCANS Version 2.31, Siemens Energy and Automation, Inc., Madison, WI, USA, 1997.
- 9 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
- 10 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.
- 11 A. Moscovitz, *Tetrahedron*, 1961, **13**, 48.