

A chiral Mn(IV) complex and its supramolecular assembly: Synthesis, characterization and properties

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Abstract. The open air reaction of the chiral Schiff base ligand H₂L, prepared by the condensation of L-phenylalaninol and 5-bromosalicylaldehyde, with Mn^{II}(CH₃COO)₂·4H₂O yielded dark brown complex [Mn^{IV}L₂].0.5 DMF (**1**). Compound **1** was characterized by elemental analysis, IR, UV–visible, CD and EPR spectroscopy, cyclic voltammetry and room temperature magnetic moment determination. Single-crystal X-ray analysis revealed that compound **1** crystallises in the monoclinic *P*2₁ space group with six mononuclear [Mn^{IV}L₂] units in the asymmetric unit along with three solvent DMF molecules. In the crystal structure, each Mn(IV) complex, acting as the building unit, undergoes supramolecular linking through C–H...O bonds leading to an intricate hydrogen bonding network.

Keywords. Synthesis; characterization; crystal structure; chiral Mn(IV) complex; C–H...O hydrogen bonding interaction.

1. Introduction

The chemistry of higher valent manganese, especially Mn(IV), has been the subject of considerable research for the last couple of decades.¹ This is because of the importance of higher valent manganese in various biological systems like the OEC (oxygen evolving complex) of photosystem II.² In addition to their biological roles, Mn(IV) systems are also important with respect to asymmetric catalysis.³ The role of chiral Mn(IV) species in the catalytic asymmetric epoxidation of olefins has been the subject of some current publications.⁴

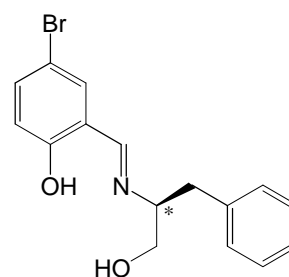
Tridentate ligands derived from substituted salicylaldehydes and chiral amino alcohols are among the 'privileged' ligand templates, generally employed for various asymmetric transformations.⁵ Complexes of these ligand systems with metal ions such as Ti⁴⁺, V⁵⁺, Cu²⁺ etc. have been successfully applied for various asymmetric transformations as chiral catalysts.⁶ However, the manganese chemistry of such ligand systems has not been explored much. Recently, we have reported our preliminary studies on manganese chemistry of chiral amino alcohols based Schiff base ligands.⁷ In continuation of our previous work, we report herein the synthesis, structural cha-

acterization and properties of a chiral Mn(IV) mononuclear complex [Mn^{IV}L₂].0.5 DMF (**1**); the relevant chiral Schiff base ligand system H₂L is described in scheme 1.

2. Experimental

2.1 Materials and methods

L-Phenylalaninol [(*S*)-(-)-2-Amino-3-phenyl-1-propanol] and 5-bromosalicylaldehyde were purchased from Lancaster and used as received. TBAP (tetrabutylammonium perchlorate), used as the supporting electrolyte in electrochemical measurement, was purchased from Acros India. Solvents were purified by standard methods. All other chemicals were of



Scheme 1. Schematic representation of H₂L. The chiral centre is represented by an asterisk.

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analytical grade and were used without further purification.

Microanalytical (C, H, N) data were obtained with a Flash EA 1112 Series CHNS Analyzer. A Shimadzu 3101-PC UV/Vis/NIR spectrophotometer was used to record the electronic spectra. Infrared spectra were recorded on KBr pellets with a Jasco-5300 FT-IR spectrophotometer. ^1H spectra of the ligand H_2L in CDCl_3 solution were recorded on a Bruker 400 MHz spectrometer using $\text{Si}(\text{CH}_3)_4$ as internal standard. Room temperature solid state magnetic susceptibility was measured by using a Sherwood Scientific magnetic susceptibility balance. A CH-Instruments model 620A electrochemical analyzer was used for cyclic voltammetric experiment on an acetonitrile solution of the complex **1** containing 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 Ag/AgCl reference electrode. CD spectra were measured with a Jasco J-810 spectropolarimeter. EPR spectra were recorded on a Jeol JES-FA200 spectrometer.

2.2 Synthesis of ligand H_2L

L-Phenylalaninol [(S)-(-)-2-amino-3-phenyl-1-propanol] (0.151 g, 1 mmol) and 5-bromosalicylaldehyde (0.201 g, 1 mmol) were stirred together in methanol (15 ml) for 1 h at room temperature. The resulting yellow solution was filtered and the filtrate was kept for 2 days in an open beaker for slow evaporation. Yellow precipitate of H_2L thus obtained was washed with hexane and dried at room temperature. Yield was 0.284 g (85%).

Analysis: Calc. for $\text{C}_{16}\text{H}_{16}\text{NO}_2\text{Br}$: C, 57.5; H, 4.83; N, 4.19%. Found: C, 57.1; H, 4.77; N, 4.11%.

FT-IR (KBr): 3364, 1633, 1599, 1570, 1510, 1477, 1365, 1275, 1186, 1072, 1035, 968, 925, 825, 750, 704, 625, 557, 472 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 2.95 (m, 2H, CH_2 -Ph), 3.55 (m, 1H, CH), 3.82 (m, 2H, CH_2 -OH), 6.86 (d, 1H, Ar, ortho to OH), 7.13–7.404 (m, 7H, Ar), 8.01 (s, 1H, HC=N).

UV/Vis (CH_3CN): I_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 326 (4747), 255 (12120).

2.3 Synthesis of complex **1**

$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.245 g, 1 mmol) was added to a methanolic solution (15 ml) of ligand H_2L

(0.334 g, 1 mmol). The mixture was allowed to stir at room temperature in air for 12 h. The dark brown solution obtained was evaporated to dryness using a rotavapor and vacuum pump. The solid, thus obtained, was dissolved in dichloromethane, washed twice with water and once with brine solution (using a separating funnel), and then dried over anhydrous Na_2SO_4 . The resulting dark brown solution, on slow evaporation, gave the brown microcrystalline solid, **1**. Yield was 0.525 g (73%).

Analysis: Calc. for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_4\text{Br}_2\text{Mn}$: C, 53.43; H, 3.92; N, 3.89%. Found: C, 53.60; H, 4.01; N, 3.95%.

FT-IR (KBr): 1610, 1520, 1452, 1369, 1300, 1170, 1045, 798, 746, 700, 644, 574, 520, 455 cm^{-1} .

UV/Vis (CH_3CN): I_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 550 nm (sh, 1430), 470 nm (sh, 2719), 404 (5753) nm, 345 (sh, 7008), 287 (sh, 17200).

2.4 X-ray crystallography

Data were measured at 298(2) K on a Bruker SMART APEX CCD area detector system [$I(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$], graphite monochromator, 2400 frames were recorded with an ω scan width of 0.3° each for 10 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction was done by SAINTPLUS⁸ structure solution using SHELXS-97⁹ and refined using SHELXH-97.¹⁰ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions and included in the refinement riding on their respective parent atoms. Additional details of the data collection parameters and refinement are collected in table 1. The absolute configuration of the compound was successfully determined by refining the Flack parameter (0.005(5)).¹¹ The final Fourier difference synthesis showed minimum and maximum peaks of -0.672 and $+0.988 e\text{\AA}^{-3}$. CCDC-294223 contains the supplementary crystallographic data for complex **1**. This can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

3. Results and discussion

The chiral ligand H_2L was synthesized in good yields as a yellow solid by the Schiff base condensation of 5-bromosalicylaldehyde with the chiral amino alcohol L-phenylalaninol. Open air reaction of a methanolic

solution of the ligand with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in 1 : 1 ratio yielded the corresponding Mn(IV) complex as a dark brown solid. Atmospheric oxygen is the possible oxidizing agent here, and oxidizes the Mn(II) salt to the corresponding Mn(IV) complex. The presence of phenolato and alcoholato groups in the ligand facilitates the oxidation of Mn(II) to Mn(IV).

The IR spectrum of the Schiff base ligand, H_2L , exhibits a broad band at 3364 cm^{-1} due to the intramolecularly hydrogen bonded $\text{n}(\text{OH})$. This band is absent in the complex revealing the deprotonation of the OH group during complexation. Also the Schiff base exhibits $\text{n}(\text{C}=\text{N})$ band at 1633 cm^{-1} , which shifts to lower energy by $\sim 20\text{ cm}^{-1}$ in the complex indicating nitrogen coordination of the ligand.

Single crystals of **1** suitable for X-ray analysis were grown from dimethylformamide (DMF) solution by the slow evaporation method. The molecule crystallizes in the monoclinic chiral space group $P2_1$. The asymmetric unit contains six mononuclear manganese complexes along with three DMF solvent molecules. In each of these mononuclear units, present in the asymmetric unit, Mn is hexacoordinated with N_2O_4 coordination sphere. Two tridentate ONO donor ligands satisfy the coordination sites of the

metal in a meridional manner. Each ligand contains deprotonated phenolic and alcoholic groups along with an imine nitrogen. The overall coordination geometry around the Mn in each complex can be considered roughly as distorted octahedron (figure 1). Four oxygen atoms can be taken as constituting a square plane about which the two imine nitrogens are situated at axial trans positions. The $\text{Mn}-\text{O}_{\text{phe}}$, $\text{Mn}-\text{O}_{\text{alk}}$, and $\text{Mn}-\text{N}_{\text{imi}}$ distances vary in the range $1.878(5)$ – $1.913(5)$, $1.835(5)$ – $1.862(5)$ and $1.964(6)$ – $1.989(6)$ Å respectively. The average $\text{Mn}-\text{O}_{\text{phe}}$ ($1.896(5)$), $\text{Mn}-\text{O}_{\text{alk}}$ ($1.849(5)$) and $\text{Mn}-\text{N}_{\text{imi}}$ ($1.976(6)$) distances observed are comparable to those reported for Mn(IV) complexes with similar ligation.^{1b} Selected bond lengths and angles are given for a representative mononuclear unit in table 2.

All six mononuclear Mn(IV) complexes, present in the asymmetric unit, are involved in hydrogen-bonding interactions in forming an intricate three-dimensional hydrogen-bonding network. These six Mn(IV) complexes can be named as Mn(1), Mn(2), Mn(3), Mn(4), Mn(5) and Mn(6) units. In the asymmetric unit, Mn(1) and Mn(2) complexes are

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

Emp. formula	$\text{C}_{32}\text{H}_{28}\text{Br}_2\text{MnN}_2\text{O}_4 \cdot 0.5\text{DMF}$
FW	755.87
Crystal system	Monoclinic
Space group	$P2_1$
I (Å)	0.71073
a (Å)	19.677(6)
b (Å)	21.013(7)
c (Å)	24.573(8)
β (°)	105.123(6)
V (Å ³)	9808(6)
Z	6
m (mm ⁻¹)	2.890
ρ_{calcd} (g cm ⁻³)	1.536
T (°C)	25
Scan type	w
Independent reflns	115256 ($R_{\text{int}} = 0.0834$)
Obsd. reflns. [$F > 4\sigma(F)$]	46128
No. of parameters	2352
S_{gof} on F^2	0.929
R_1^a [$F > 4\sigma(F)$]	0.0563
wR_2^b	0.1018
Absolute structure parameter	0.005(5)
Largest diff. peak and hole (eÅ ⁻³)	0.988 and -0.672

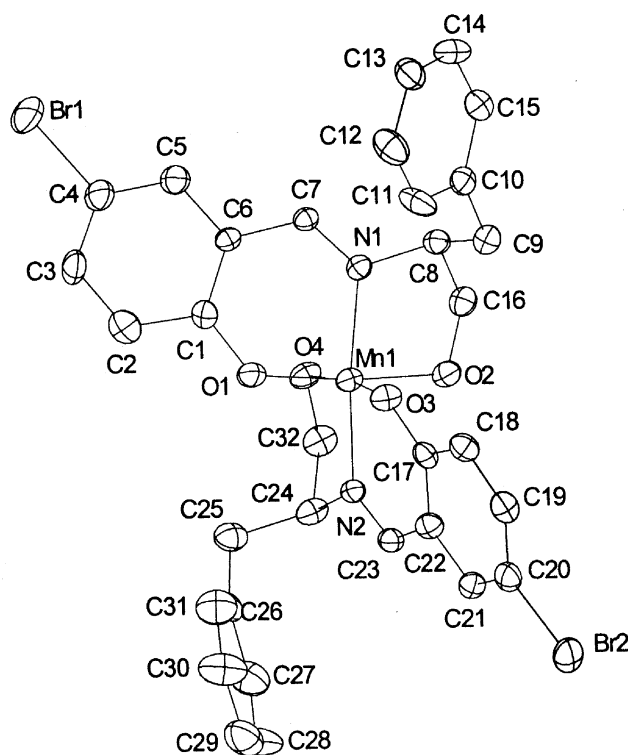


Figure 1. Thermal ellipsoidal plot of the title Mn(IV) complex **1** with atom labelling scheme. One representative complex, among six Mn(IV) complexes, present in the asymmetric unit has been taken.

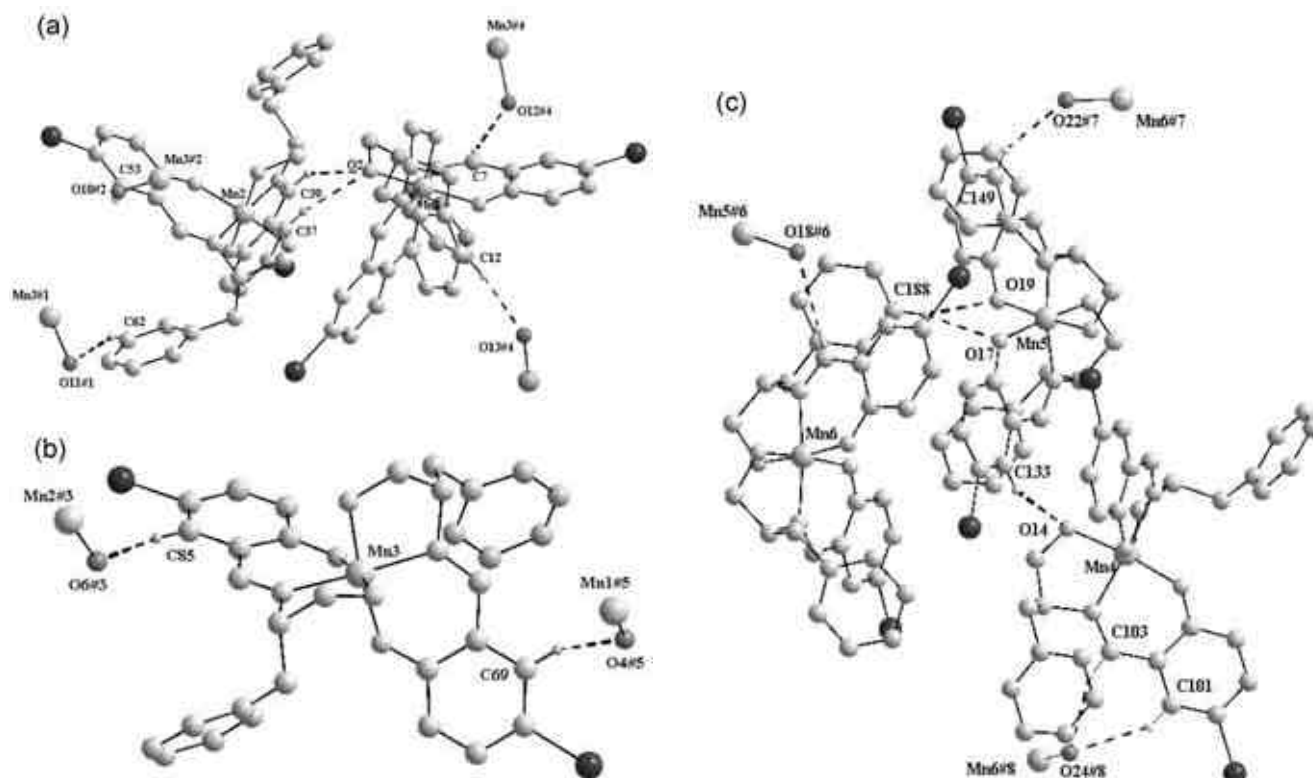


Figure 2. (a) Mn(1)–Mn(2) hydrogen-bonded dimer formed in the asymmetric unit and its surrounding hydrogen-bonding interactions with other Mn complexes. (b) Hydrogen-bonding interactions of the Mn(3) complex with other two Mn complexes. (c) Mn(4)–Mn(5)–Mn(6) hydrogen-bonded trimer formed in the asymmetric unit and its surrounding hydrogen-bonding interactions with other Mn complexes.

Table 2. Selected bond lengths (Å) angles (°) for a representative Mn(IV) unit.

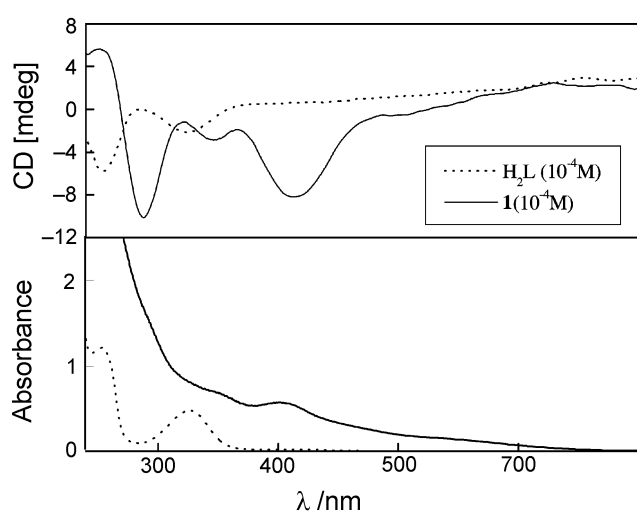
Mn(1)–O(1)	1.892(5)	Mn(1)–N(2)	1.989(5)
Mn(1)–O(2)	1.859(5)	N(1)–C(7)	1.287(7)
Mn(1)–N(1)	1.981(5)	N(2)–C(23)	1.287(8)
Mn(1)–O(3)	1.913(5)	O(1)–C(1)	1.334(8)
Mn(1)–O(4)	1.839(5)	O(3)–C(17)	1.303(8)
O(2)–Mn(1)–O(1)	173.7(2)	O(1)–Mn(1)–N(1)	91.0(2)
O(4)–Mn(1)–O(3)	171.7(2)	O(3)–Mn(1)–N(1)	95.0(2)
O(4)–Mn(1)–O(2)	92.2(2)	O(2)–Mn(1)–N(2)	87.6(2)
O(4)–Mn(1)–O(1)	89.9(2)	O(4)–Mn(1)–N(2)	84.0(2)
O(2)–Mn(1)–O(3)	92.9(2)	O(1)–Mn(1)–N(2)	98.5(2)
O(1)–Mn(1)–O(3)	85.7(2)	O(3)–Mn(1)–N(2)	89.7(2)
O(2)–Mn(1)–N(1)	83.1(2)	N(1)–Mn(1)–N(2)	169.7(2)
O(4)–Mn(1)–N(1)	92.1(2)		

hydrogen-bonded to form an Mn(1)–Mn(2) hydrogen-bonded dimer (figure 2a). This is formed by acceptance of the C–H protons of the Mn(2) complex by the O(2) oxygen of the Mn(1) complex. The Mn(3) complex, which is not hydrogen-bonded to any asymmetric unit components, is attached to the

Mn(1) and Mn(2) units via two respective C–H...O bonds (figure 2b). Mn(4), Mn(5) and Mn(6) units are linked via hydrogen-bonds in the asymmetric unit, forming a hydrogen-bonded trimer (Mn(4)–Mn(5)–Mn(6)) as shown in figure 2c. The formation of this trimer can be described by the bifurcated

Table 3. Hydrogen-bonding parameters (Å, °) for **1**.

D H...A	D-H	H...A	D...A	D-H...A	Symmetry operator of A
C(7) H(7)...O(12)	0.93	2.57	3.413(8)	151.6	1 - x, 0.5 + y, 1 - z
C(12) H(12)...O(13)	0.93	2.37	3.294(10)	172.7	1 - x, 0.5 + y, 1 - z
C(37) H(37)...O(2)	0.93	2.62	3.371(9)	138.6	x, y, z
C(39) H(39)...O(2)	0.93	2.40	3.223(8)	147.4	x, y, z
C(53) H(53)...O(10)	0.93	2.46	3.237(9)	141.6	-x, 0.5 + y, 1 - z
C(62) H(62)...O(11)	0.93	2.47	3.316(10)	151.0	x, 1 + y, z
C(69) H(69)...O(4)	0.93	2.41	3.193(8)	141.7	1 - x, -0.5 + y, 1 - z
C(85) H(85)...O(6)	0.93	2.53	3.392(9)	155.2	-x, -0.5 + y, 1 - z
C(101) H(101)...O(24)	0.93	2.51	3.367(9)	153.3	1 - x, -0.5 + y, 2 - z
C(103) H(103)...O(24)	0.93	2.59	3.433(8)	151.1	1 - x, -0.5 + y, 2 - z
C(133) H(133)...O(14)	0.93	2.63	3.471 (9)	151.0	x, y, z
C(149) H(149)...O(22)	0.93	2.41	3.259(9)	151.8	-x, -0.5 + y, 2 - z
C(183) H(183)...O(18)	0.93	2.55	3.296(8)	137.4	-x, 0.5 + y, 2 - z
C(188) H(188)...O(17)	0.93	2.42	3.288(11)	156.1	x, y, z

**Figure 3.** Circular dichroism (above) and electronic (below) spectra of **1** and ligand H₂L in acetonitrile solutions.

C-H...O hydrogen-bonding interactions between Mn(5) and Mn(6) complexes, followed by the interaction of the Mn(5) complex with the Mn(4) complex. Interestingly, this trimer, formed in the asymmetric unit, is additionally hydrogen-bonded to three surrounding Mn complexes (namely Mn(5), Mn(6) and Mn(6)) in the crystal structure. The hydrogen-bonded dimer is further hydrogen-bonded to four Mn complexes (three Mn(3) and one Mn(4)). These interactions result in the formation of a multifaceted hydrogen-bonding network. The packing of these manganese complexes results in the formation of helical channels when viewed down to the crystallographic *a* axis. We believe that the chirality of the

complex [Mn^{IV}L₂] plays an important role in forming such helical channels. The relevant C-H...O hydrogen bonding parameters are described in table 3.

Electronic spectra of the ligand H₂L show prominent peaks at 326 and 255 nm which can be assigned to transitions of the intramolecularly hydrogen-bonded salicylideneimino chromophore. Cotton effects of negative sign are observed for these bands in the corresponding circular dichroism spectra which can be correlated with the absolute configuration of the amino alcohol moiety used.¹²

Electronic and circular dichroism spectra of the complex **1** show red shift in the band position compared to the bands of the free ligand H₂L (figure 3). In the visible region, an octahedral Mn(IV) *d*³ system is expected to exhibit two electronic absorption bands due to *d-d* transitions viz. ⁴A_{2g} → ⁴T_{2g} and ⁴A_{2g} → ⁴T_{1g}. A shoulder at 470 nm and a broad band at 550 nm observed for the complex **1** in acetonitrile solution are probably due to the *d-d* transitions. The rather high intensity of these bands may be due to the strong UV tail in the visible region. The intense bands observed in the high energy portions of the absorption spectrum of **1** can be assigned to charge-transfer transitions judging from their molar extinction coefficients values. The electronic spectrum of **1** is in good agreement with those reported for the hydroxyl-rich mononuclear Mn(IV) Schiff base complexes in the literature.^{1m}

Redox properties of compound **1** were investigated by cyclic voltammetry at a platinum disc working electrode in acetonitrile solution using a silver-silver chloride reference electrode. The cyclic voltammogram of complex **1** is shown in figure 4. A

quasi-reversible one-electron reduction of the Mn(IV) complex occurs at $E_{1/2} = -0.44$ V with $\Delta E_p = 110$ mV [$E_{1/2} = \frac{1}{2}(E_{pa} + E_{pc})$, $\Delta E_p = E_{pa} - E_{pc}$, E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively]. The negative reduction potential shown by this complex demonstrates the stability of this complex in acetonitrile solution and also the ability of doubly deprotonated Schiff base ligand to stabilize the higher oxidation state of manganese.

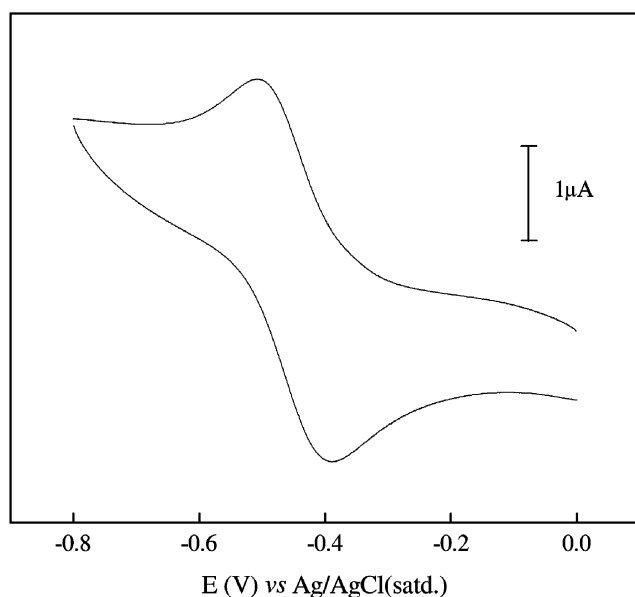


Figure 4. Cyclic voltammogram of $\sim 10^{-3}$ M acetonitrile solution of **1** at 298 K (0.1 M TBAP, scan rate 100 mVs^{-1} , platinum disc working electrode).

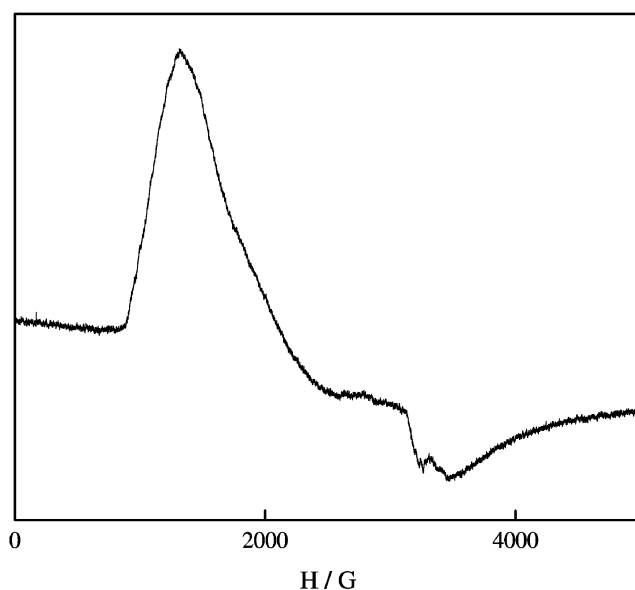


Figure 5. ESR spectrum of **1** in methanol solution at liquid nitrogen temperature.

The X-band ESR spectrum of **1** obtained from frozen methanol solution is shown in figure 5. The major feature of the spectrum is a weak unresolved resonance at $g \sim 2$ and a strong signal at $g \sim 4$. In the crystal field of O_h symmetry, manganese(IV) (a d^3 system) has a $^4A_{2g}$ ground state which affords an isotropic resonance at $g \sim 2$. In an axially distorted complex with the zero-field splitting parameter D larger as compared to the microwave quantum, two main resonances are expected: a strong one near $g = 4$ and a weaker one near $g = 2$. The low temperature ESR spectrum of **1** thus corresponds to a large axial zero-field splitting parameter, i.e. $2D \gg h\nu$.¹³

Room temperature magnetic moment of the complex **1** is found to be 4.00 BM which indicate an $S = 3/2$ spin state in the complex. This experimental m_{eff} value clearly indicates that the complex **1** is an Mn(IV) system in complete agreement with X-ray and other characterization results.

4. Conclusions

A new chiral mononuclear Mn(IV) complex has been synthesized and structurally characterized. This complex belongs to the limited number of structurally characterized manganese complexes of chiral amino alcohol based ligand systems. The chirality of complex **1** has been confirmed by circular dichroism studies, while the oxidation state (+4) of manganese is supported by electrochemical and ESR studies. We have shown that each Mn(IV) complex can act as a building unit to construct an intricate three-dimensional hydrogen-bonding network via C–H...O hydrogen bonds in the crystal structure.

Acknowledgements

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References

1. John R P, Sreekanth A, Kurup M R P and Fun H-K 2005 *Polyhedron* **24** 601; Weyhermuller T, Paine T K, Bothe E, Bill E and Chaudhuri P 2002 *Inorg. Chim. Acta* **337** 344; Rajendiran T M, Kampf J W and Pecoraro V L 2002 *Inorg. Chim. Acta* **339** 497; Perez-

- Lourido P, Romero J, Rodriguez L, Garcia-Vazquez J A, Castro J, Sousa A, Dilworth J R and Nascimento O R 2002 *Inorg. Chem. Commun.* **5** 337; Asada H, Ozeki M, Fujiwara M and Matsushita T 1999 *Chem. Lett.* 525; Mikuriya M, Jie D, Kakuta Y and Tokii T 1993 *Bull. Chem. Soc. Jpn.* **66** 1132; Hart R O C, Bott S G, Atwood J L and Cooper S R 1992 *J. Chem. Soc., Chem. Commun.* 894; Saadeh S M, Lah M S and Pecoraro V L 1991 *Inorg. Chem.* **30** 8; Dutta S, Basu P and Chakravorty A 1991 *Inorg. Chem.* **30** 4031; Chandra S K, Choudhury S B, Ray D and Chakravorty A 1990 *J. Chem. Soc., Chem. Commun.* 474; Chandra S K, Basu P, Ray D, Pal S and Chakravorty A 1990 *Inorg. Chem.* **29** 2423; Deplano P, Trogu E F, Bigoli F and Pellingheli M A 1987 *J. Chem. Soc., Dalton Trans.* 2407; Kessissoglou D P, Li X, Butler W M and Pecoraro V L 1987 *Inorg. Chem.* **26** 2487; Kessissoglou D P, Butler W M and Pecoraro V L 1986 *J. Chem. Soc., Chem. Commun.* 1253; Pavacik P S, Huffman J C and Christou G 1986 *J. Chem. Soc., Chem. Commun.* 43; Tirant M and Smith T D 1986 *Inorg. Chim. Acta* **121** 5
- Pecoraro V L (ed.) 1992 *Manganese redox enzymes* (New York: VCH); Yachandra V K, DeRose V J, Latimer M J, Mukerji I, Sauer K and Klein M P 1993 *Science* **260** 675; Manchanda R, Brudvig G W and Crabtree R H 1995 *Coord. Chem. Rev.* **144** 1; Debus R J 1992 *Biochim. Biophys. Acta* **1102** 269; Cole J, Yachandra Y K, Guiles R D, McDermott A E, Britt R D, Dexheimer S L, Sauer K and Klein M P 1987 *Biochim. Biophys. Acta* **890** 395; Zimmermann J L and Rutherford A W 1986 *Biochemistry* **25** 395
 - Jacobsen E N, Pfaltz A and Yamamoto H (eds) 1999 *Comprehensive asymmetric catalysis* (New York: Springer-Verlag); Katsuki T 2000 *Catalytic asymmetric synthesis* (ed.) I Ojima (New York: VCH)
 - Bryliakov K P, Kholdeeva O A, Vanina M P and Talsi E P 2002 *J. Mol. Catal.* **A178** 47; Adam W, Mock-Knoblauch C, Saha-Möllner C R and Herderich M 2000 *J. Am. Chem. Soc.* **122** 9685
 - Owens T D, Souers A J and Ellman J A 2003 *J. Org. Chem.* **68** 3; Jacobsen E N 2000 *Acc. Chem. Res.* **33** 421
 - Vicario J L, Badía D, Carrillo L, Reyes E and Etxebarria J 2005 *Curr. Org. Chem.* **9** 219; Lu G, Li Y-M, Li X-S and Chan A S C 2005 *Coord. Chem. Rev.* **249** 1736; Pu L and Yu H-B 2001 *Chem. Rev.* **101** 757; Ager D J, Prakash I and Schaad D R 1996 *Chem. Rev.* **96** 835
 - Pradeep C P, Htwe T, Zacharias P S and Das S K 2004 *New J. Chem.* **28** 735; Pradeep C P, Zacharias P S and Das S K 2005 *Polyhedron* **24** 1410
 - Software for the CCD Detector System, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1998
 - Sheldrick G M 1997 SHELXS-97, Program for structure solution, University of Göttingen, Germany
 - Sheldrick G M 1997 SHELXH-97, Program for crystal structure analysis, University of Göttingen, Germany
 - Flack H D 1983 *Acta Crystallogr.* **A39** 876
 - Smith H E, Padilla B G, Neergaard J R and Chen F-M 1979 *J. Org. Chem.* **44** 1690
 - McGarvey B R 1966 In *Transition metal chemistry* (ed.) R L Carlin (New York: Marcel Dekker) vol. 3, p 89; Pederson E and Toftlund H 1974 *Inorg. Chem.* **13** 1603; Bradley D C, Copperthwaite R G, Cotton S A, Sales K D and Gibson J F 1973 *J. Chem. Soc., Dalton Trans.* 191