# Synthesis, Crystal Structure, and Magnetic Property of Four Manganese(II) Complexes with Bulky Schiff Bases Derived from Amantadine and Rimantadine<sup>1</sup>

X. D. Jin<sup>a, \*</sup>, X. X. Feng<sup>a</sup>, L. C. Bu<sup>a</sup>, W. C. Wang<sup>a</sup>, J. Tong<sup>a</sup>, P. Zhang<sup>a</sup>, Y. D. Qi<sup>a</sup>, and C. Yang<sup>a</sup>

<sup>a</sup>College of Chemistry, Liaoning University, Shenyang, 110036 P.R. China \*e-mail: jinxudong@lnu.edu.cn

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**Abstract**—The reactions of manganese(II) chloride tetrahydrate and four bulky Schiff base ligands derived from amantadine (or rimantadine) and salicylaldehyde (or 4-methoxysalicylaldehyde) generated four novel complexes,  $C_{34}H_{42}Cl_2MnN_2O_2$  (I),  $C_{36}H_{46}Cl_2MnN_2O_4$  (II),  $C_{38}H_{50}Cl_2MnN_2O_2$  (III), and  $C_{40}H_{54}Cl_2MnN_2O_4$  (IV), respectively. These complexes were characterized by melting point, infrared spectra, elemental analysis, magnetic susceptibility, molar conductance and single-crystal X-ray diffraction (CIF files CCDC nos. 1540253 (I), 1540254 (II), 1540255 (III), 1540256 (IV)). Single-crystal X-ray diffraction analysis reveals that I, III and IV crystallize in the orthorhombic system with space groups  $P_{2_1}/n$ . Each asymmetric unit for I–IV consists of one manganese(II) atom, two Schiff base ligands and two chlorine atoms. The central manganese(II) atoms lie on a twofold rotation axis in III and IV, whereas manganese(II) atoms lie on general positions in I and II. In these complexes molecules, manganese(II) atoms is four-coordinated *via* two chlorine atoms and two oxygen atoms from the corresponding Schiff base ligands, forming a distorted tetrahedral geometry.

*Keywords:* manganese(II) complexes, bulky Schiff base, synthesis, crystal structure, magnetic property **DOI:** 10.1134/S1070328419030047

# INTRODUCTION

In many countries, amantadine (Symmetrel<sup>TM</sup>) and rimantadine (Flumadine<sup>TM</sup>) have been used as efficacious remedies to prevent or treat seasonal influenza [1-5]. In addition, they can alleviate the Parkinson syndrome [6, 7]. Salicylaldehyde and its derivatives were used to produce efficient herbicides, insecticides and fungicides [8]. The Schiffbases derived from a reaction of aromatic aldehvdes and aliphatic amines represent an important series of widely studied organic ligands owing to their biological and anti-cancer activity [9-12], they also brought about many metal-based pharmaceuticals [13–15]. For instance, transition metal complexes with Schiff bases were found exhibiting biological activity as antibiotics, antiviral and antitumour agents because of their specific structures [16, 17]. Manganese (Mn) is an essential trace element and necessary for physiological processes that support development, growth and neuronal function for human health. Manganese can also function as a cofactor for enzymes, regardless of its significance, it has been reported that the overexposure causes neurotoxicity manifested as extrapyramidal symptoms similar to those observed in Parkinson disease [18–20]. In addition, manganese(II) Schiff base complexes displayed significant magnetic properties in the field of magneto-chemistry [21]. Based on the reasons above, we designed and managed to synthesize a series of manganese(II) complexes for attempting to evaluate their biological and medical activates as well as magnetic physics. As an extension of our previous work on metal complexes with bulky Schiff bases derived from amantadine or rimantadine [22–28], in this paper, four fourcoordinated manganese(II) complexes bis(2-((E)-adamantan-1-yliminomethyl)phenolato-kO)dichloromanganese(II) (I), bis(2-(E)-adamantan-1-yliminomethyl)-5-methoxyphenolato-kO)dichloromanganese(II) bis(2-((E)-1-(adamantan-1-yl)ethyliminome-**(II)**. thyl)phenolato-kO)dichloromanganese(II) (III), and bis(2-((E)-1-(adamantan-1-yl)ethyliminomethyl)-5-methoxyphenolato-kO)dichloromanganese(II) (IV), respectively, were synthesized.

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I:  $R_1 = H$ ,  $R_2 = adamantan-1-yl$ ; II:  $R_1 = OCH_3$ ,  $R_2 = adamantan-1-yl$ ; III:  $R_1 = H$ ,  $R_2 = 1$ -(adamantan-1-yl)ethyl; IV:  $R_1 = OCH_3$ ,  $R_2 = 1$ -(adamantan-1-yl)ethyl.

Their structures were characterized by the means of IR, elemental analysis, molar conductance and single-crystal X-ray diffraction. Their magnetic behavior was investigated.

### EXPERIMENTAL

Materials and methods. All chemicals and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd., and were of analytical grade and used as received. Elemental analysis was carried out on Perkin Elmer Flash EA 1112. Infrared spectrum (IR) was scanned in the range 4000 to 400 cm<sup>-1</sup> with KBr pellets on a Nicolet NEXUS FT-IR 5700 spectrophotometer. Melting points were measured on a WRS-1B micro melting point apparatus, which was not corrected. The molar conductance of the complexes in DMF ( $1.0 \times 10^{-3} \text{ mol } \text{L}^{-1}$ ) was measured on a DDS-11A conductometer. Temperature-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-XL-7 magnetometer under an applied field of 1 K Oe in the temperature range of 2–300 K. The experimental data were corrected for the diamagnetism of the sample holder, measured in the same range of field and temperature, and for the intrinsic diamagnetic contribution for the sample estimated through Pascal's constants for all constituent atoms [29].

Synthesis of the ligands. Schiff base ligands, 2-((E)-adamantan-1-yliminomethyl)phenol (L<sup>1</sup>), 2-((E)-adamantan-1-yliminomethyl)-5-methoxyphenol (L<sup>2</sup>), 2-((E)-1-(adamantan-1-yl)-ethyliminomethyl)phenol (L<sup>3</sup>) and 2-((E)-1-(adamantan-1-yl))ethyliminomethyl)-5-methoxyphenol (L<sup>4</sup>) were prepared analogously to the literatures [27, 28, 30].

The Schiff base ligands were prepared by refluxing a mixture of amantadine hydrochloride (375 mg, 2.0 mmol) or rimantadine hydrochloride (432 mg, 2.0 mmol), KOH (112 mg, 2.0 mmol) and salicylaldehyde (244 mg, 2.0 mmol) or 4-methoxy substituted salicylaldehyde (304 mg, 2.0 mmol) in 20 mL anhydrous ethanol for 1 h and then cooled to room temperature, respectively. the colored Schiff base precipitates were obtained after one week under slow solvent evaporation.

L<sup>1</sup>: 439 mg, yield 86%, yellowish powder, m.p. 92.0~ 92.7°C [30].

L<sup>2</sup>: 371 mg, yield 65%, yellow powder, m.p. 106.3~ 106.7°C [27].

L<sup>3</sup>: 419 mg, yield 74%, yellowish powder, m.p. 88.3~ 88.6°C [28].

L<sup>4</sup>: 470 mg, yield 75%, yellowish powder, m.p. 102.8~103.3°C [28].

Synthesis of the complexes. Four novel complexes were prepared in a similar procedure starting from their corresponding freshly synthetic Schiff base ligands and manganese(II) chloride tetrahydrate in anhydrous ethanol, respectively.

Manganese(II) chloride tetrahydrate (198 mg, 1.0 mmol) in 10 mL anhydrous ethanol was added to a solution of a Schiff base ligand (2.0 mmol) in 10 mL anhydrous ethanol. The mixture was stirred at 30°C for 2 h, concentrated until a large amount of precipitate was observed, and then cooled to room temperature. The pearlescent solids were suction filtered, washed with anhydrous ethanol, and dried under vacuum to afford each complex.

I: 461 mg, yield 72%, yellow powder, m.p. 298.2°C. IR (KBr; v, cm<sup>-1</sup>): 3421 w, 2919 m, 2853 m, 1638 s, 1609 s, 1541 s, 1489 s, 1311 m, 1240 m, 1203 m, 1153 m, 1081 w, 901 w, 767 w, 582 w.

For  $C_{34}H_{42}N_2O_2Cl_2Mn$  (*M* = 636.54)

Anal. calcd., %	C, 64.16	Н, 6.65	N, 4.40
Found, %	C, 64.15	H, 6.67	N, 4.43

**II**: 326 mg, yield 47%, yellowish powder, m.p. 267.2°C. IR (KBr; v, cm<sup>-1</sup>): 3433 w, 2914 m, 2853 m, 1638 s, 1611 s, 1534 s, 1489 m, 1358 m, 1302 m, 1228 s, 1118 m, 1084 m, 1025 m, 848 w, 605 w, 535 w.

For  $C_{36}H_{46}N_2O_4Cl_2Mn$  (*M* = 696.59)

Anal. calcd., %	C, 62.07	H, 6.66	N, 4.02
Found, %	C, 62.05	Н, 6.69	N, 4.04

**III**: 428 mg, yield 62%, yellow powder, m.p. 252.4°C. IR (KBr; v, cm<sup>-1</sup>): 3409 w, 2904 s, 2848 m, 1644 s, 1606 s, 1541 s, 1487 s, 1323 w, 1281 w, 1238 m, 1147 m, 1028 w, 902 w, 767 m, 578 w, 527 w.

For  $C_{38}H_{50}N_2O_2Cl_2Mn$  (*M* = 692.64)

Anal. calcd., %	C, 65.90	H, 7.28	N, 4.04
Found, %	C, 65.87	H, 7.31	N, 4.05

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Fig. 1. Molecular structures of I (a), II (b), III (c), and IV (d). Hydrogens are omitted for clarity.

**IV**: 419 mg, yield 56%, yellowish powder, m.p. 271.8°C. IR (KBr; v, cm<sup>-1</sup>): 3423 w, 2905 m, 2849 m, 1643 s, 1611 s, 1524 s, 1490 m, 1371 m, 1318 m, 1232 s, 1221 m, 1025 w, 975 w, 848 w, 801 w, 529 w.

For $C_{40}H_{54}N_2O_4Cl_2Mn$ ( <i>M</i> = 752.69)						
Anal. calcd., %	C, 63.83	Н, 7.23	N, 3.72			
Found, %	C, 63.79	Н, 7.26	N, 3.71			

X-ray crystallography. Single crystals of four complexes suitable for X-ray analysis were grown from a solution of  $CH_3OH/CH_2Cl_2$  (1 : 1, v/v) using solvent evaporation. The crystallographic data collections were conducted on a Bruker Smart Apex II CCD with graphite monochromated Mo $K_{\alpha}$  radiation ( $\lambda$  = 0.71073 Å) at 293(2) or 298(2) K using the  $\omega$ -scan technique [31]. The data were integrated by using the SAINT program, which also corrected the intensities for Lorentz and polarization effect [32]. An empirical absorption correction was applied using the SADABS program [33]. The structures were solved by direct methods using the program SHELXS-2014 [34]. All non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares technique using the SHELXL and OLEX2 crystallographic software package [35]. The hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELXL-2014 crystallographic software package. The details of the crystal parameters, data collection and refinement are summarized in Table 1. Selected bond lengths and angles with their estimated standard deviations are given in Table 2. The molecular structures of four complexes are shown in Fig. 1, they were visualized by Diamond [36].

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1540253 (I), 1540254 (II), 1540255 (III), 1540256 (IV); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

#### **RESULTS AND DISCUSSION**

The C, H, N contents both theoretically calculated values and found values for all complexes are in agreement with the formula of  $MnCl_2L_2^n$  (n = 1, 2, 3, 4), it suggests that complexes **I**–**IV** consist of one manganese(II), two chloride atoms and two ligands. All the complexes are soluble in methanol, dichloromethane and chloroform, the complexes are less soluble than their corresponding ligands in other solvents, such as ethanol, tetrahydrofuran, benzene and ethyl acetate.

Donomotor	Value						
Parameter	Ι	II	III	IV			
Fw	636.54	696.59	692.64	752.69			
Crystal size, mm	$0.21\times0.19\times0.18$	$0.20 \times 0.18 \times 0.17$	$0.20\times0.18\times0.16$	$0.20\times0.16\times0.10$			
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic			
Color	Yellow	Yellowish	Yellow	Yellowish			
Space group	$P2_{1}2_{1}2_{1}$	$P2_1/n$	Pbcn	Pcan			
<i>a</i> , Å	10.2574(7)	12.3933(6)	14.4168(11)	12.2858(6)			
<i>b</i> , Å	16.5613(10)	17.4322(7)	10.7556(7)	13.4127(7)			
<i>c</i> , Å	18.2282(14)	16.7841(10)	23.1167(17)	24.7093(12)			
β, deg	90.00	102.948(5)	90.00	90.00			
V, Å <sup>3</sup>	3096.5(4)	3533.9(3)	3584.5(4)	4071.7(4)			
Ζ	4	4	4	4			
$\theta$ Range, deg	2.72-25.32	2.60-25.10	2.83-23.86	0.91-0.95			
Index ranges	$-12 \le h \le 7,$	$-7 \le h \le 14,$	$-12 \le h \le 18,$	$-14 \le h \le 14,$			
	$-12 \le k \le 19,$	$-20 \le k \le 19,$	$-13 \le k \le 12,$	$-15 \le k \le 12,$			
	$-21 \le l \le 19$	$-19 \le l \le 17$	$-28 \le l \le 28$	$-29 \le l \le 29$			
$\rho$ , g cm <sup>-3</sup>	1.365	1.309	1.283	1.228			
$\mu$ , mm <sup>-1</sup>	0.633	0.565	0.552	0.495			
Reflections collected/ unique ( $R_{int}$ )	8128/4856 (0.0313)	13418/6211 (0.0243)	9372/3676 (0.041)	24031/3589 (0.032)			
Refinement parameters	370	406	205	224			
GOOF	1.005	1.024	1.007	1.077			
<i>F</i> (000)	1340	1468	1468	1596			
<i>Т</i> , К	293(2)	293(2)	293(2)	298(2)			
$R_1/wR_2 (I \ge 2\sigma(I))^*$	0.0454/0.0896	0.0603/0.1593	0.0547/0.1307	0.0545/0.1483			
$R_1/wR_2$ (all data)	0.0659/0.1011	0.0939/0.1848	0.1096/0.1633	0.0641/0.1573			
Largest difference peak and hole, e $Å^{-3}$	0.39/-0.26	0.80/-0.42	0.36/-0.22	0.30/-0.21			

 Table 1. Crystallographic data and structure refinement for complexes I–IV

\*  $R_1 = \Sigma ||F_0| - |F_c|| / |F_0|, wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}.$ 

The molar conductance values ( $\Lambda_{\rm M}$ ) in DMF for **I**–**IV** are 33.3, 35.3, 32.9 and 30.1 S cm<sup>2</sup> mol<sup>-1</sup>, indicating a non-electrolyte behavior [37].

The broad and intensity absorptions at 3409-3443 cm<sup>-1</sup> for ligands and complexes can be attributed to O–H stretching vibration, illustrating that phenolic hydroxyls of ligands are not deprotonated as the complexes are formed. The strongest absorptions at 1630, 1625, 1630, and 1623 cm<sup>-1</sup> for ligands as well as 1638, 1638, 1644, and 1643 cm<sup>-1</sup> for complexes are identified as C=N stretching vibration. In metal complexes these bands undergo upward shift by 8, 13, 14, and 20 cm<sup>-1</sup> are due to the effect of intramolecular hydrogen. The spectra of ligands show strong bands at 1221–1281 cm<sup>-1</sup>, which are assigned to C–O stretching vibration, these bands were observed in complexes at near frequency  $1228-1240 \text{ cm}^{-1}$ . In addition, in low frequency regions, the presence of absorptions at 486–535 cm<sup>-1</sup> for complexes reveals Mn–O vibrations, indicating that oxygen of the Schiff base ligands is coordinated to manganese(II).

In each asymmetric unit of **I**–**IV**, there is only one independent complex molecule. The central manganese(II) atom is four-coordinated via two chlorine atoms and two oxygen of phenolic hydroxyls of two monodentate ligands. The coordination geometry about the manganese atom in all complexes were distorted tetrahedral as indicated by an index  $\tau_4$ , value of  $\tau_4 = 0.85$ , 0.88, 0.93 and 0.94 for I, II, III, and IV, respectively (the structure index is defined as  $\tau_4 = [360 - (\alpha + \beta)]/141^{\circ}$  [38], where  $\alpha$  and  $\beta$  are the largest coordination angles),  $\tau_4 = 0.00$  for an ideal square

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Table 2.	Selected bond	length (	Å)	and angles	s (deg)	in	complexes	I–IV*
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Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
		I	
Mn(1)-Cl(1)	2.3124(12)	Mn(1)–O(2)	2.050(3)
Mn(1)-Cl(2)	2.3346(13)	N(1)-C(7)	1.289(5)
Mn(1)–O(1)	2.028(3)	N(2)–C(24)	1.291(5)
		II	
Mn(1)-Cl(1)	2.3528(13)	Mn(1)–O(3)	2.033(3)
Mn(1)-Cl(2)	2.3217ω(13)	N(1)-C(7)	1.298(5)
Mn(1)–O(1)	2.040(3)	N(2)-C(26)	1.290(5)
		III	
Mn(1)-Cl(1)	2.3278(10)	N(1)-C(7)	1.284(4)
Mn(1)–O(1)	2.028(2)	N(1)-C(8)	1.462(4)
		ĪV	
Mn(1)-Cl(2)	2.3332(8)	N(1)-C(7)	1.282(4)
Mn(1)–O(1)	2.0213(19)	N(1)-C(8)	1.459(4)
Angle	ω, deg	Angle	ω, deg
		Ι	
Cl(1)Mn(1)Cl(2)	116.32(6)	Cl(2)Mn(1)O(1)	110.40(11)
O(1)Mn(1)O(2)	96.70(12)	Cl(2)Mn(1)O(2)	96.03(8)
Cl(1)Mn(1)O(1)	110.89(10)	C(7)N(1)C(8)	126.7(4)
Cl(1)Mn(1)O(2)	124.20(9)	C(24)N(2)C(25)	126.2(3)
	•	П	
Cl(1)Mn(1)Cl(2)	122.50(6)	Cl(2)Mn(1)O(1)	103.84(9)
O(1)Mn(1)O(3)	103.62(11)	Cl(2)Mn(1)O(3)	112.14(9)
Cl(1)Mn(1)O(1)	112.85(8)	C(7)N(1)C(9)	127.6(3)
Cl(1)Mn(1)O(3)	100.60(8)	C(26)N(2)C(27)	127.3(3)
		III	
Cl(1)Mn(1)Cl(1A)	115.51(6)	Cl(1)Mn(1)O(1A)	109.79(8)
O(1)Mn(1)O(1A)	93.71(13)	C(7)N(1)C(8)	126.1(3)
Cl(1)Mn(1)O(1)	113.03(7)	C(7)N(1)H(1)	117.0
		IV	
Cl(2)Mn(1)Cl(2 <i>A</i> )	115.26(5)	Cl(2)Mn(1)O(1A)	109.76(7)
O(1)Mn(1)O(1A)	95.12(13)	C(7)N(1)C(8)	126.1(3)
Cl(2)Mn(1)O(1)	112.62(6)	C(7)N(1)H(1)	117.0

\* Symmetry codes:  $^{i}-x + 1$ , y, -z + 3/2;  $^{ii}x$ , -y + 1, -z + 1/2.

planar and  $\tau_4 = 1.00$  for an ideal tetrahedral. The distorted tetrahedral geometry with the smallest angle of O(2)Mn(1)Cl(2) 96.03(8)° for I, O(3)Mn(1)Cl(1) 100.60(8)° for II, O(1*A*)Mn(1)O(1) 93.71(13)° for III (symmetry code: <sup>i</sup> -x + 1, *y*, -z + 3/2), and O(1*A*)Mn(1)O(1) 95.12(13)° for IV (symmetry code: <sup>ii</sup> *x*, -y + 1, -z + 1/2); the biggest angle of O(2)Mn(1)Cl(1) 124.20(9)° for I, Cl(2)Mn(1)Cl(1) 122.50(6)° for II, Cl(1*A*)Mn(1)Cl(1) 115.51(6)° for III, and Cl(2)Mn(1)Cl(2*A*) 115.26(5)° for IV, where the dihedral angle between the two coordination planes defined by O(1)Mn(1)O(2) and Cl(1)Mn(1)Cl(2) is 79.75° for I, by O(3)Mn(1)O(1)and Cl(2)Mn(1)Cl(1) is 82.83° for II, by Cl(1A)Mn(1)Cl(1) and O(1A)Mn(1)O(1) is 87.56° for III, and by Cl(2)Mn(1)Cl(2A) and O(1A)Mn(1)O(1) is 87.86° for IV. The two phenyl rings are in the intersecting planes with a dihedral angle of 76.28°, 83.67°, 80.95°, and 76.93° for I, II, III, and IV, respectively. And I–IV are expected for a typical Schiff base ligand (containing a short C=N bond distance of 1.289(5)/1.291(5) Å for I, 1.298(5)/1.290(5) Å for II,



Fig. 2. The short contacts  $(C-H\cdots Cl \text{ and/or } C-H\cdots \pi)$  in I (a), II (b), III (c), and IV (d) packing.

1.284(4) Å for III, and 1.282(4) Å for IV) coordinated to a metal centre. this coordination pattern of the manganese(II) complexes is similar to that of zinc(II) complexes we previously reported [22, 27]. Crystal structures of I–IV also involve significant intramolecular hydrogen bonds between the imino N and phenol O atoms forming an additional six-membered ring because of no deprotonated ligands. The distances of O–H, H…N and O…N are 0.85/0.85, 1.79/2.02 and 2.580(6)/2.628(5) Å for I, 0.90/0.90, 1.91/1.95 and 2.602(4)/2.588(4) Å for II, N–H, H…O and N…O are 0.86, 1.91 and 2.593(3) Å for III, 0.86, 1.92 and 2.597(3) Å for IV. The hydrogen bond angles O–H…N are 153°/128° for I and 132°/126° for II, N–H…O are 135° for III and 134° for IV. In both III and IV, C(8) and C(8*A*) positions are chiral centers (*RR*), other stereoisomers (*SS*) can be identified easily in the lattice. In general, they show the diastereoisomer (*RR/SS*) (Figs. 1c and 1d). Although these complexes molecules possess no  $\pi$ – $\pi$  stacking interactions, weak C–H… $\pi$  in I and II or C–H…Cl interactions in III and IV certainly are responsible for the packing (Fig. 2, Table 3).

The variable-temperature magnetic susceptibilities of **I**–**IV** were measured in an applied magnetic field of 1000 Oe in the temperature range of 2–300 K. The  $\chi_{\rm M}T$  and  $\chi_{\rm M}^{-1}$  versus *T* plots are shown in Fig. 3, respectively, in which the  $\chi_{\rm M}$  is the molar magnetic susceptibility. It can be observed that the magnetism behavior of four complexes is quite identical. At room tempera-

Compound	D. HA	Summatru aada		Angle		
Compound D-H···A	Symmetry code	D–H	Н…А	D…A	D–H…A, deg	
Ι	C(9)–H(9 <i>A</i> )····Cl(2)	-1/2 + x, 3/2 - y, -z	0.97	2.80	3.770(8)	178
	$C(12)-H(12A) \rightarrow Cg$	-1/2 + x, $3/2 - y$ , $-z$	0.98	2.85	3.697(4)	145
II	$C(15)-H(15A) \rightarrow Cg$	-x, -y, 1-z	0.98	2.82	3.844(8)	146
III	C(7)–H(7)····Cl(1)	-1/2 + x, $-1/2 + y$ , $3/2 - z$	0.93	2.73	3.549(5)	148
IV	$C(7)-H(7)\cdots Cl(2A)$	1/2 + x, $1/2 + y$ , $1/2 - z$	0.93	2.68	3.569(3)	159

**Table 3.** Weak C–H···Cl and/or C–H··· $\pi$  interactions in the complexes packing

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**Fig. 3.** Thermal variation of magnetic susceptibility,  $\chi_M T$  versus T (square) and  $\chi_M^{-1}$  versus T (filled circle) of **I** (a), **II** (b), **III** (c), and **IV** (d) under an applied field of 1000 Oe in the temperature range of 2–300 K.

ture, the values of the  $\chi_{\rm M}T$  product are 3.98, 4.07, 4.04, and 4.07 cm<sup>3</sup> K mol<sup>-1</sup> for I, II, III, and IV, respectively, which is near the calculated spin-only value of 4.375 cm<sup>3</sup> K mol<sup>-1</sup> for high-spin Mn<sup>2+</sup> ions (g = 2 and S = 5/2). On decreasing the temperature, the  $\chi_M T$  value increases gradually and reach to the maximum 4.20, 4.26, 4.22, and 4.27 cm<sup>3</sup> K mol<sup>-1</sup> at 17.93, 21.95, 24.91, and 18.95 K, respectively, then decrease rapidly, down to 4.09, 4.19, 4.08, and 4.18 cm<sup>3</sup> K mol<sup>-1</sup> around 5 K. Between 5 and 300 K, the  $\chi_{\rm M}^{-1}$  versus *T* curves of **I**–**IV** were fitted, and fitting results were all linear, so the behavior of the magnetic susceptibility obeys the Curie–Weiss rule ( $\chi_M^{-1} = (T - \chi_M^{-1})$  $(\theta)/C$ , with  $C = 3.98 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $\theta = 2.80 \text{ K for I}$ ,  $C = 4.07 \text{ cm}^3 \text{ K mol}^{-1}, \theta = 2.65 \text{ K for II}, C = 4.04 \text{ cm}^3$ K mol<sup>-1</sup>,  $\theta = 2.35$  K for III, and C = 4.07 cm<sup>3</sup> K mol<sup>-1</sup>,  $\theta = 2.50$  K for IV. The nature of the  $\chi_{\rm M} T$  versus T plot (300-20 K) and the positive  $\theta$  value clearly indicates that the dominant ferromagnetic interaction in I-IV. Thus, the decrease sharply in  $\chi_M T$  upon cooling in the low temperature range of 20-5 K might be ascribed to the effect of several factors: weak antiferromagnetic interactions between the Mn<sup>2+</sup> ions in the crystal lattice, presence of the zero-field splitting (ZFS) of the  $Mn^{2+}$  ions, and the presence of a paramagnetic impurity is indicated by the increase of the magnetic susceptibility at low temperatures [39–41].

Thus, four manganese(II) complexes have been prepared and their structures were characterized by the means of melting point, elemental analysis, IR and molar conductance. Single-crystal X-ray diffraction analysis reveals that each Schiff base serves as monodentate ligand coordinating through an oxygen atom in I–IV, or to be more exact, the central manganese(II) atom is four-coordinated via two chlorine atoms and two oxygen atoms from the corresponding Schiff base ligands. The geometry around the metal atom in I–IV is distorted tetrahedral structure. Magnetic studies reveal that I–IV exhibit ferromagnetic properties, respectively.

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