

## Synthesis, Characterization, Crystal Structure and Antibacterial Activities of Transition Metal(II) Complexes of Schiff Base

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Five complexes of the general composition  $[ML_2(NO_3)_2]$  (**1-5**) [M = Mn(II), Co(II), Ni(II), Cu(II), Cd(II)] were synthesized from the reaction of a Schiff base ligand 2-[(4-methylphenylimino)methyl]-6-methoxy-phenol ( $C_{15}H_{15}NO_2$ , L) and  $M(NO_3)_2 \cdot nH_2O$ , where the Schiff base was obtained by condensation of *o*-vanillin (2-hydroxy-3-methoxybenzaldehyde) with *p*-toluidine. They were characterized by elemental analysis, molar conductance, FT-IR, UV-vis spectra and thermal analysis. The structure of complex **1** was determined by single-crystal X-ray diffraction technique. Its crystal structure is of triclinic, space group P-1 with  $a = 0.93135(4)$ ,  $b = 1.04613(4)$ ,  $c = 1.77348(7)$  nm,  $\alpha = 73.868(2)$ ,  $\beta = 85.681(2)$ ,  $\gamma = 64.902(2)^\circ$ ,  $V = 1.50137(10)$  nm<sup>3</sup>,  $Z = 2$ ,  $M_r = 661.52$ ,  $F(000) = 686$ ,  $D_c = 1.463$  g cm<sup>-3</sup>,  $\mu$  ( $M_oK_\alpha$ ) = 0.504 mm<sup>-1</sup>. Schiff base and its metal complexes have been tested *in vitro* to evaluate their antibacterial activity against bacteria, viz., *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis*. It has been found that all the metal complexes have higher activity than the corresponding free Schiff base ligand against these bacteria and the Cd(II) complex has the highest activity.

**Key Words:** Transition metal(II) complex, Crystal structure, Schiff base, *o*-Vanillin, *p*-Toluidine, Antibacterial activities.

### INTRODUCTION

Transition metals are necessary for our life, especially Mn, Co, Ni, Cu and Zn<sup>1,2</sup>. *o*-Vanillin is a natural aldehyde found in *Andropogon nardus*. It is used to treat bellyaches and also in spicery<sup>3,4</sup>. The condensation of primary amines with carbonyl compounds yields Schiff bases<sup>5,6</sup>. Schiff base ligands which usually contain O, N donor atoms play an important role in coordination chemistry since the late 19th century. Metal complexes with Schiff base ligands resulting from condensation of, for example, salicylaldehyde and its derivatives with a primary amine have been studied for many years. Among these studies a relatively small number has involved Schiff's base in which the primary amine is aniline and its *o*-, *m*-, *p*-substituted derivatives<sup>7,8</sup>. They behave as bidentate ligands and form complexes of the type  $M(L)_2$  with divalent first row metal ions<sup>9-12</sup>. A large number of reports are available on the chemistry and the biocidal activities of transition metal complexes containing O, N donor atoms<sup>13-17</sup>. A literature survey reveals that Schiff base derived from *o*-vanillin and *p*-toluidine has been prepared, their metal complexes and biological activity have scarcely been investigated<sup>18-20</sup>. In view of this, we describe here, the synthesis, characterization, single crystal structure and antibacterial properties of transition metal(II) complexes with a Schiff base in the neutral form 2-[(4-methyl-

phenylimino)methyl]-6-methoxyphenol derived from *o*-vanillin and *p*-toluidine.

### EXPERIMENTAL

$M(NO_3)_2 \cdot nH_2O$ , *o*-vanillin, *p*-toluidine and other chemical reagents were obtained from commercial sources and used without further purification. The metal contents were determined by EDTA complexometric titration. Elemental analyses for C, H and N were carried out on an Elementar Vario EL III elemental analyzer. IR spectra on KBr pellets were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer in the range of 4000-400 cm<sup>-1</sup>. Molar conductivity of the complexes were measured with a Shanghai DDS-11A conductivity meter in methanol ( $1.0 \times 10^{-3}$  mol L<sup>-1</sup>). UV-Vis spectra of Schiff base ligand and the complexes were measured with a Shimadzu UV-2501PC spectrophotometer in methanol ( $1.0 \times 10^{-4}$  mol L<sup>-1</sup>) at the range of 200-700 nm. Thermal analyses were carried out using Mettler-Toludo TGA/SDTA851e thermal analyzer with a heating rate of 10 °C min<sup>-1</sup> from 30-900 °C in air atmosphere.

**Syntheses:**  $C_{15}H_{15}NO_2(L)$ : Schiff base ligand was prepared by the direct solution reaction, *p*-toluidine (10 mmol, 1.07 g) and *o*-vanillin (10 mmol, 1.52 g) was refluxed in ethanol (*ca.* 60 mL) on a water bath for 2 h. The solution was cooled to

room temperature and then the orange red crystals (Fig. 1) was gotten, washed with absolute alcohol, dried. Yield 1.96 g (81 %), m.p. ca. 100 °C. It was recrystallized in methanol before used.

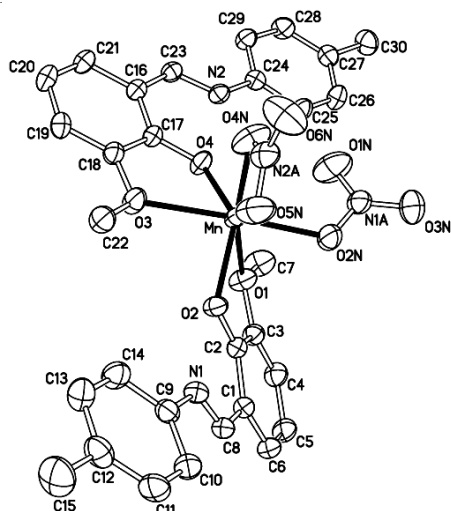


Fig. 1. Molecular structure of the complex **1** (probability of ellipsoid is 30 %)

**ML<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O**: M(NO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O (1 mmol) dissolved in 10 mL of anhydrous alcohol was stirred with 0.48 g (2 mmol) of Schiff base in 30 mL anhydrous alcohol and refluxed for 2 h at water bath, then solid deposited after cooled to room temperature, washed with ethanol, dried. Yield (%) 0.40-0.42 g. Red single crystals of complex (**1**) were obtained suitable for X-ray diffraction from mother liquid after 10 days by slow evaporation at room temperature.

**Crystal structure determination**: Single crystals with approximate dimensions 0.585 × 0.252 × 0.119 mm<sup>3</sup> for (**1**) was selected and coated with vaseline. Intensity data for the complex (**1**) was measured with a Rigaku R-axis rapid diffractometer with graphite-monochromated Mo-K<sub>α</sub> radiation (λ = 0.071073 nm) at 296 K. Empirical absorption corrections were applied by use of the ABSCOR program. The structures were solved by direct methods and all calculations were performed with the aid of the SHELXL PC program<sup>21</sup>. The structures were refined by full-matrix, least-squares minimization of Σ(F<sub>o</sub> - F<sub>c</sub>)<sup>2</sup> with anisotropic thermal parameters for all atoms except H atoms. The crystal data of the complexes **1** was summarized in Table-1, selected bond lengths and angles in Table-2.

## RESULTS AND DISCUSSION

The compositions of complexes are summarized in Table-3. The C, H, N, M contents both theoretically calculated values and actual values are in accordance with the formula M(NO<sub>3</sub>)<sub>2</sub>L<sub>2</sub> and it shows that the Schiff base ligand is neutral. This can be explained by the absences of any deprotonating agent during the synthesis. Recent studies<sup>22,23</sup> refer to complexes of transition metal(II) ions in which the Schiff base coordinates in this unusual structural characteristic *via* the phenolic hydroxy oxygen atom, the nitrogen atom remaining uncoordinated. Their molar conductance in DMF solvent lie in the range of 17-19 S cm<sup>2</sup> mol<sup>-1</sup>, as expected for non-electrolytes<sup>24</sup>. The complexes are stable in air and soluble in most common organic solvents.

TABLE-1  
CRYSTALLOGRAPHIC DATA AND STRUCTURE  
REFINEMENTS FOR COMPLEX **1**

Empirical formula	C <sub>30</sub> H <sub>30</sub> N <sub>4</sub> O <sub>10</sub> Mn
Formula weight	661.52
T/ K	296(2)
Wavelength/ nm	0.071073
Crystal system	Triclinic
Space group	P-1
a (nm)	0.93135(4)
b (nm)	1.04613(4)
c (nm)	1.77348(7)
α (°)	73.868(2)
β (°)	85.681(2)
γ (°)	64.902(2)
V (nm <sup>3</sup> )	1.50137(10)
Z	2
Density (g/cm <sup>3</sup> )	1.463
μ (mm <sup>-1</sup> )	0.504
F(000)	686
Crystal size/mm	0.585 × 0.252 × 0.119
Max. and min. trans.	0.942, 0.859
Data/restraints/parameters	5245/0/406
θ range/°	2.23-25.00
Limiting indices	11 ≤ h ≤ 9, -12 ≤ k ≤ 12, -21 ≤ l ≤ 21
Reflections collected/ unique	19323/5245
Observable reflections	4558
R <sub>int</sub>	0.0251
GOOF on F <sup>2</sup>	1.073
R and wR [I > 2σ(I)]	R <sub>1</sub> = 0.0445, wR <sub>2</sub> = 0.1389
R indices (all data)	R <sub>1</sub> = 0.0512, wR <sub>2</sub> = 0.1430
(Δρ) <sub>max</sub> , (Δρ) <sub>min</sub> (e/nm <sup>3</sup> )	319 and -278

IR spectra of the metal complexes are summarized in Table-4. The broad absorption band at 3452 cm<sup>-1</sup> attributed to the hydroxy group in the spectra of the free ligand appears at lower frequency in the corresponding complexes 3418-3414 cm<sup>-1</sup>, showing coordination of oxygen atom of the phenolic hydroxy with the central M(II) ion. The shift of the C-O stretching vibration of the phenolic part of *o*-vanillin from 1258, 1232 and 1239 cm<sup>-1</sup> also supports the coordination of oxygen atoms. So the coordination bond were formed between metal ion and oxygen atoms of phenolic hydroxy and methoxy group<sup>7</sup>. However, a strong band in the free Schiff base ligand occurring at 1617 cm<sup>-1</sup> attributed to C=N stretching is found shifted to higher frequency 1642-1636 cm<sup>-1</sup>, but the nitrogen atom of azomethine was regarded as no complexation with M(II)<sup>25-27</sup>. A new band in 492-486 cm<sup>-1</sup> region attributed to M-O stretching vibration, whereas it was none in ligand. A band at 3027 cm<sup>-1</sup> assignable to the stretching of O-H bond of free Schiff base ligand is found to be broadened within the frequency range of 3037-3031 cm<sup>-1</sup>. Three absorption peaks at 1455, 1294 and 1026 cm<sup>-1</sup> in the spectra of complex **1** are coordinated nitrate nitrate anions which behaves as monodentate ligand<sup>27-29</sup>. This observation implies that the H atom from the OH group in free and complexation Schiff base ligand has a tendency to migrate to azomethine N atom *via* the O-H...N intramolecular hydrogen bonding as reported earlier<sup>30</sup>.

**UV-Vis spectra**: Three absorption peaks of the free Schiff base ligand appeared at 317.5, 277.5 and 227.0 nm in the range of 200-400 nm. The band of 317.5 nm may be

TABLE-2  
SELECTED BOND DISTANCES (nm) AND  
BOND ANGLES (°) OF COMPLEX 1

Mn-O(4)	0.21079(18)	N(2)-C(23)	0.1299(3)
Mn-O(2)	0.21329(17)	N(2)-C(24)	0.1416(3)
Mn-O(2N)	0.2180(2)	N(2)-H(2A)	0.086
Mn-O(4N)	0.2195(3)	N(2A)-O(6N)	0.1204(4)
Mn-O(3)	0.23655(19)	N(2A)-O(5N)	0.1227(3)
Mn-O(1)	0.2392(2)	N(2A)-O(4N)	0.1249(4)
N(1)-C(8)	0.1301(4)	O(1)-C(3)	0.1371(3)
N(1)-C(9)	0.1420(4)	O(1)-C(7)	0.1424(4)
N(1)-H(1A)	0.086	O(2)-C(2)	0.1299(3)
N(1A)-O(3N)	0.1212(4)	O(3)-C(18)	0.1377(3)
N(1A)-O(1N)	0.1224(4)	O(3)-C(22)	0.1418(3)
N(1A)-O(2N)	0.1255(3)	O(4)-C(17)	0.1304(3)
O(4)-Mn-O(2)	133.25(8)	C(23)-N(2)-C(24)	128.7(2)
O(4)-Mn-O(2N)	122.72(8)	C(23)-N(2)-H(2A)	115.7
O(2)-Mn-O(2N)	89.97(8)	C(24)-N(2)-H(2A)	115.7
O(4)-Mn-O(4N)	89.40(9)	O(6N)-N(2A)-O(5N)	125.1(3)
O(2)-Mn-O(4N)	126.98(9)	O(6N)-N(2A)-O(4N)	119.3(3)
O(2N)-Mn-O(4N)	88.82(11)	O(5N)-N(2A)-O(4N)	115.6(3)
O(4)-Mn-O(3)	71.07(7)	C(3)-O(1)-C(7)	117.8(2)
O(2)-Mn-O(3)	83.34(7)	C(3)-O(1)-Mn	110.39(16)
O(2N)-Mn-O(3)	164.59(9)	C(7)-O(1)-Mn	126.08(19)
O(4N)-Mn-O(3)	84.21(10)	C(2)-O(2)-Mn	118.21(16)
O(4)-Mn-O(1)	82.22(7)	N(1A)-O(2N)-Mn	113.45(18)
O(2)-Mn-O(1)	70.01(7)	C(18)-O(3)-Mn	112.23(15)
O(2N)-Mn-O(1)	81.10(9)	C(22)-O(3)-Mn	124.39(18)
O(4N)-Mn-O(1)	160.51(10)	C(17)-O(4)-Mn	119.61(16)
O(3)-Mn-O(1)	109.31(8)	N(2A)-O(4N)-Mn	110.1(2)
C(8)-N(1)-C(9)	126.8(2)	N(1)-C(8)-C(1)	123.7(2)
C(8)-N(1)-H(1A)	116.6	C(14)-C(9)-N(1)	118.8(2)
C(9)-N(1)-H(1A)	116.6	C(10)-C(9)-N(1)	121.6(3)
O(3N)-N(1A)-O(1N)	125.3(3)	N(2)-C(23)-C(16)	122.8(2)
O(3N)-N(1A)-O(2N)	117.8(3)	C(29)-C(24)-N(2)	122.9(2)
O(1N)-N(1A)-O(2N)	116.9(3)	C(25)-C(24)-N(2)	117.4(2)

assigned to  $n-\pi^*$  transition of conjugation between lone-pair electron of  $\pi$  orbital of N atom in C=N group and big  $\pi$  bond of benzene ring. A peak at 277.5 nm is assigned to  $\pi-\pi^*$  transition of conjugation system of Schiff base. The spectra of 5 complexes are very similar and almost the same as Schiff base ligand (Table-5).

TABLE-5  
DATA OF UV SPECTRA FOR COMPOUNDS  
(SOLVENT:METHANOL)

Comp.	$\lambda_{1\max}$ (nm)	$\lambda_1$ (cm <sup>2</sup> mol <sup>-1</sup> )	$\lambda_{2\max}$ (nm)	$\lambda_2$ (cm <sup>2</sup> mol <sup>-1</sup> )	$\lambda_{3\max}$ (nm)	$\lambda_3$ (cm <sup>2</sup> mol <sup>-1</sup> )
L	317.5	4889	277.5	3629	227.0	7268
1	318.0	9126	278.0	6903	226.5	13632
2	318.0	14420	277.0	10900	226.5	22182
3	314.5	8001	278.5	7437	225.0	16367
4	315.0	5704	283.0	5802	225.0	13271
5	318.0	5716	283.5	6016	228.5	11243

**Crystal structure:** The structure of the complex **1**, [MnL<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>], is shown in Fig. 1 and the main bond lengths and angles are listed in Table-2. The crystal structure reveals that the molecule of complex **1** is consist of one Mn(II) ion, two L ligands and two nitrate ions. The Mn(II) ion is coordinated by 6 O atoms in a distorted octahedral and 4 of which come from two L ligands and the other 2 O atoms come from two nitrate ions. Uncommonly, the nitrates link to the Mn(II) ion using monodentate mode with the Mn-O bond lengths 0.21798(32) and 0.21948(46) nm, respectively, which are longer than the classic Mn-O lengths in bidentate and bridge mode<sup>31,32</sup>. The two L ligands connect to the Mn(II) ion with bidentate mode *via* deprotonated phenolic O atom and methoxyl O atom, in which the bond lengths between Mn and O atoms are Mn-O(1) = 0.23923(28) nm, Mn-O(2) = 0.21329(16) nm, Mn-O(3) = 0.23651(25) nm, Mn-O(4) = 0.21079(21) nm. In addition, because the imine N is protonated, the L ligands are electrically neutral wholly. Present Schiff base contains two aromatic rings and mostly they are

TABLE-3  
ELEMENTAL ANALYSIS, MOLAR CONDUCTANCE DATA OF THE COMPOUNDS

Compound	m.p. (°C)	Colour	Elemental analysis (%)				$\Lambda_M$ (S cm <sup>2</sup> mol <sup>-1</sup> )
			C	H	N	M	
L	ca. 100	Orange red	74.59 (74.66)	6.30 (6.17)	5.77 (5.81)	–	2
1 [Mn(NO <sub>3</sub> ) <sub>2</sub> L <sub>2</sub> ]	>260	Red	54.58 (54.46)	4.63 (4.57)	8.37 (8.47)	8.21 (8.30)	18
2 [Co(NO <sub>3</sub> ) <sub>2</sub> L <sub>2</sub> ]	>260	Red	54.06 (54.14)	4.51 (4.54)	8.33 (8.42)	8.79 (8.85)	17
3 [Ni(NO <sub>3</sub> ) <sub>2</sub> L <sub>2</sub> ]	>260	Yellow	54.03 (54.16)	4.55 (4.54)	8.32 (8.42)	8.78 (8.82)	17
4 [Cu(NO <sub>3</sub> ) <sub>2</sub> L <sub>2</sub> ]	>260	Brown	53.73 (53.76)	4.50 (4.51)	8.29 (8.36)	9.41 (9.48)	19
5 [Cd(NO <sub>3</sub> ) <sub>2</sub> L <sub>2</sub> ]	>260	Yellow	49.98 (50.11)	4.13 (4.21)	7.68 (7.79)	15.55 (15.63)	19

\*Data in the brackets are the calculated values.

TABLE-4  
IR SPECTRA DATA OF COMPOUNDS (cm<sup>-1</sup>)

Compound	$\nu$ (OH)	$\nu$ (C=N)	$\nu$ (C-O)	$\nu$ (NO <sub>3</sub> <sup>-</sup> )	$\nu$ (NO <sub>3</sub> <sup>-</sup> )	$\nu$ (NO <sub>3</sub> <sup>-</sup> )	$\nu$ (M-O)
L	3452 w	1617 s	1258 s	–	–	–	–
[MnL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3416 w	1636 s	1235 m	1440 s	1299 s	1030 m	487 w
[CoL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3416 w	1641 s	1234 m	1420 s	1303 s	1022 m	488 w
[NiL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3418 w	1642 s	1232 m	1421 s	1304 s	1020 m	486 w
[CuL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3414 w	1640 s	1234 m	1430 s	1294 s	1022 m	492 w
[CdL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3415 w	1636 s	1239 m	1429 s	1292 s	1025 m	489 w

TABLE-6  
INHIBITORY OF COMPOUNDS AGAINST BACTERIA GROWTH

Compound	Diameter of inhibition zone (mm)					
	<i>Escherichia coli</i>		<i>Staphylococcus aureus</i>		<i>Bacillus subtilis</i>	
	10 (mg mL <sup>-1</sup> )	5 (mg mL <sup>-1</sup> )	10 (mg mL <sup>-1</sup> )	5 (mg mL <sup>-1</sup> )	10 (mg mL <sup>-1</sup> )	5 (mg mL <sup>-1</sup> )
L	12.6 ± 0.07	10.9 ± 0.09	11.3 ± 0.11	10.7 ± 0.08	11.8 ± 0.07	10.0 ± 0.00
1	13.2 ± 0.19	11.7 ± 0.07	12.3 ± 0.06	10.3 ± 0.06	13.7 ± 0.15	10.1 ± 0.02
2	16.3 ± 0.06**	11.1 ± 0.11	14.2 ± 0.08*	11.2 ± 0.10	21.0 ± 0.29**	12.3 ± 0.06**
3	13.3 ± 0.07	11.4 ± 0.08	13.5 ± 0.38	10.0 ± 0.00	14.9 ± 0.14*	13.2 ± 0.16*
4	14.1 ± 0.01*	11.9 ± 0.10	22.6 ± 0.03**	12.7 ± 0.05*	17.7 ± 0.34*	13.0 ± 0.02**
5	31.1 ± 0.20**	11.8 ± 0.08	33.7 ± 0.21**	23.1 ± 0.14**	23.9 ± 0.24**	13.6 ± 0.07**

Note: Data in the table are the average values of three experiments and the diameter of filter paper is 10 mm. \*\*Very significance of difference; \*Significance of difference

parallel approximately<sup>33</sup>, however, in this complex one dihedral angle is 27.177(84)° and the other is common [3.265(94)°]. The molecules packed together with  $\pi$ - $\pi$  interactions between the aromatic rings of the ligands.

**Thermal analysis:** The TG-DTG curves of complexes are very similar and the complex (1) was discussed for example. The TG-DTG curves of complex (1) are shown in Fig. 2. The DTG curves show mainly two stages for the decomposition process. The first stage decomposition temperature is in the range of 190-230 °C with a mass loss 13.78 % which corresponds to the loss of NO<sub>2</sub> [calcd. (%) 13.91]. The second stage of decomposition in the 230-350 °C temperature range, in which the two Schiff base ligands are lost with mass loss 56.90 % [calcd. (%) 57.07], the final products are metal oxides Mn<sub>2</sub>O<sub>3</sub> 11.85 % [calcd. (%) 11.93]. These results are in good accordance with the composition of the complex 1.

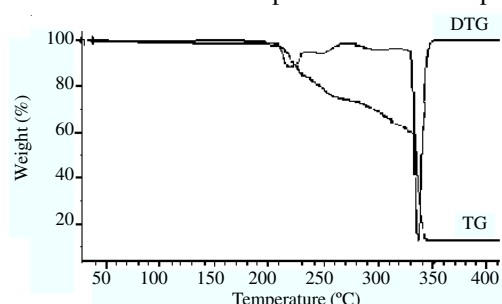


Fig. 2. TG-DTG curve of complex 1

**Antibacterial activity:** The *in vitro* antibacterial screening of the Schiff base and its metal complexes dissolved in DMF has been carried out against three bacteria, viz., *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis*, with a method of filter paper<sup>34</sup>, using agar medium and the concentrations of test solutions are 10 and 5 mg mL<sup>-1</sup>. Table-6 shows the zone of inhibition for the test solutions on three bacteria. It has been observed from the data that both the Schiff base and its metal complexes exhibit antibacterial activities against these three bacteria. It is noteworthy that the complexes have higher activity than the corresponding free Schiff base against the same bacteria (cadmium complex is the best), hence, complexation increases the antibacterial activity. On the other hand, susceptibility of Schiff base ligand is almost the same for three bacteria while its complexes are some difference.

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