

## Template synthesis of Cu(II), Co(II), Fe(III), Mn(II), Zn(II) and Cd(II) complexes of 2-aminophenol in presence of 4-benzyloxybenzaldehyde and 2-butanal

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Received 22 August 2007; revised 8 January 2008

Reaction of 2-aminophenol with Cu(II), Co(II), Fe(III), Mn(II), Zn(II) and Cd(II) ions in presence of 4-benzyloxybenzaldehyde and 2-butanal yields the complexes  $[\text{Cu}(\text{L})_2]$  **1**,  $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$  **2**,  $[\text{Fe}(\text{L})_2(\text{H}_2\text{O})\text{Cl}]$  **3**,  $[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2]$  **4**,  $[\text{Zn}(\text{L})_2]$  **5**,  $[\text{Cd}(\text{L})_2]$  **6**,  $[\text{Cu}(\text{L}')_2]$  **7**,  $[\text{Co}(\text{L}')_2(\text{H}_2\text{O})_2]$  **8**,  $[\text{Fe}(\text{L}')_2(\text{H}_2\text{O})\text{Cl}]$  **9**,  $[\text{Mn}(\text{L}')_2(\text{H}_2\text{O})_2]$  **10**,  $[\text{Zn}(\text{L}')_2]$  **11** and  $[\text{Cd}(\text{L}')_2]$  **12** (where  $\text{L} = \text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{O}$  and  $\text{L}' = \text{CH}_3\text{CHCHCH}=\text{NC}_6\text{H}_4\text{O}$ ). The complexes have been formed by template method, not via ligand formation. Complexes **1** and **7** are square planar, **2-4** and **8-10** are octahedral and **5-6** and **11-12** are tetrahedral in nature. Nickel(II) does not form complexes under the experimental condition. All the complexes are biologically active against six pathogenic bacteria (*S. dysenteria*, *E. coli*, *P. aeruginosa*, *B. subtilis*, *S. lutea* and *S. aureus*). Complexes **1**, **2**, **6**, **9**, **10**, **11** and **12** show good activity as compared to the ligand precursor, 2-aminophenol, with complex **10** showing the best activity (MIC of complex **10** = 16  $\mu\text{g}/\text{mL}$  for *S. dysenteria* and *B. subtilis*).

**IPC Code:** Int. Cl.8 C07F1/08; C07F3/06; C07F3/08; C07F15/02; C07F15/06; C07F13/00

Generally reactions of amines ( $\text{RNH}_2$ ) or hydrazines with aldehydes ( $\text{R}'\text{CHO}$ ) or ketones give Schiff bases,  $\text{RN}=\text{CHR}'$ , where R and R' are alkyl or aryl groups. Transition metal complexes of salicylaldimine are well known and form six-membered chelate ring complexes through ON donor atoms<sup>1-3</sup>. Similar imine complexes are obtained by the reaction of 2-aminophenol with different aldehydes or ketones to give five-membered chelate ring to the metal through ON donor atoms<sup>4-7</sup>. The imine complexes of various transition metals have been reported by using 2-aminophenol with  $\pi$ -conjugated aldehydes such as 3-phenylpropanal and non-conjugated aldehydes such as n-butanal<sup>8</sup>. There are no clear reports on whether the compounds are formed through ligand formation or template method. It is well known that the imine group of the Schiff bases and their metal complexes are responsible for their biological activity<sup>9,10</sup>. The salicylaldimine or their Ni(II) and Cu(II) complexes having long chain pendant arms show liquid crystalline or mesogenic behaviour<sup>1,2</sup>. We report herein the synthesis of Schiff base complexes with different transition metals with 2-aminophenol and a bulky aldehyde such as 4-benzyloxybenzaldehyde to investigate whether the complexes will be formed via ligand formation or by template method. The antibacterial activity of the complexes against some pathogenic bacteria is also reported.

### Materials and Methods

All the reagents were Analar grade and the solvents were purified by standard methods<sup>11</sup>. IR spectra ( $4000\text{-}400\text{ cm}^{-1}$ ) were taken as KBr disc using a Shimadzu FT IR-8101 spectrophotometer. Mass spectra were obtained by using a micromass ZAB SE mass spectrometer. Microanalyses for carbon, hydrogen and nitrogen were obtained by using a Perkin-Elmer 2400 CHN elemental analyzer. Magnetic moments were measured on a magnetic susceptibility balance (Sherwood Scientific). Conductances were determined on a conductivity meter (CG 857 Schott-Grate GmbH) in DMSO with a dip-type cell having platinum electrodes. The UV-visible spectra were run on a Shimadzu UV-160 spectrophotometer (200-900 nm) in nujol mull. Melting points were recorded on an electro-thermal melting point apparatus. Metal content was determined by fuming the complexes with sulfuric acid and perchloric acid and finally titrating with EDTA<sup>12</sup>. The presence of chloride was detected by the Lassaigne's test.

### Preparation of complexes 1-12

*Preparation of  $[\text{Cu}(\text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{O})_2]$  bis[N-4-benzyloxybenzalidene-2-iminophenolato]Cu(II), (1)*

To an ethanolic solution of 2-aminophenol (0.436 g, 4.0 mmol in 20 mL), 4-benzyloxy-

benzaldehyde (0.848 g, 4.0 mmol in 20 mL ethanol) solution was added. To the above mixture copper(II) acetate monohydrate (0.399 g, 2.0 mmol in 10 mL ethanol) solution was added and the resultant mixture was stirred for 4 hours at ambient temperature. The brown precipitate which formed was filtered off and washed thoroughly with hot ethanol (3×25mL) followed by pet-ether (40-60°C) and dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub> (purity of the compound was checked by TLC). The compound was soluble in chloroform and DMSO.

The same procedure was applied for the preparation of complexes **2-6** using 2-aminophenol, 4-benzyloxybenzaldehyde and Co(OAc)<sub>2</sub>, FeCl<sub>3</sub>, MnCl<sub>2</sub>, Zn(OAc)<sub>2</sub>, Cd(OAc)<sub>2</sub> respectively. Similarly, complexes **7-12** were prepared by the reaction of 2-aminophenol and 2-butenal with Cu(OAc)<sub>2</sub>, Co(OAc)<sub>2</sub>, FeCl<sub>3</sub>, MnCl<sub>2</sub>, Zn(OAc)<sub>2</sub> and Cd(OAc)<sub>2</sub> respectively.

#### Preparation of complexes 1-4 and 7-10, via aminophenolate complex formation

*Preparation of [Cu(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>] (1) via [Cu(H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>] (13)*

To an ethanolic solution of 2-aminophenol (0.436 g, 4.0 mmol in 20 mL), copper(II) acetate monohydrate solution (0.399 g, 2.0 mmol in 10 mL ethanol) was added and stirred for 1 hour at ambient temperature. A grey precipitate was formed, (possibly [Cu(H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>], **13**). To this grey precipitate, 4-benzyloxybenzaldehyde (0.848 g, 4.0 mmol in 20 mL ethanol) solution was added and stirred for 4 hours. The brown precipitate which formed was filtered off and washed thoroughly with hot ethanol (3×25 mL) and finally with petroleum ether (40-60°C). The product was identified as complex **1**.

Similarly, Co(II) gave deep brown complex **2**, Fe(III) gave deep brown complex **3**, Mn(II) gave yellow orange complex **4** via intermediate aminophenolate brick red complex **14**, reddish brown complex **15** and grey complex **16** respectively. Complexes **7-10** were formed similarly via complexes **13-16** using 2-butenal.

Attempts were made to prepare ligands [LH = N-4-benzyloxy-benzalidene-2-iminophenol and L'H = N-2-butenylidene-2-iminophenol] using 2-aminophenol with 4-benzyloxybenzaldehyde and 2-butenal. Attempts were made to prepare nickel(II) Schiff base complexes of the ligands (LH, L'H) using 2-aminophenol with nickel(II) acetate in the presence of 4-benzyloxybenzaldehyde and 2-butenal. Attempt was

also made to prepare aminophenolate complexes of Ni(II) using 2-aminophenol with Ni(II) acetate. Attempts were also made to prepare aminophenolate complexes of Zn(II) and Cd(II) using 2-aminophenol with Zn(II) and Cd(II) acetate at room temperature or even at slight warming.

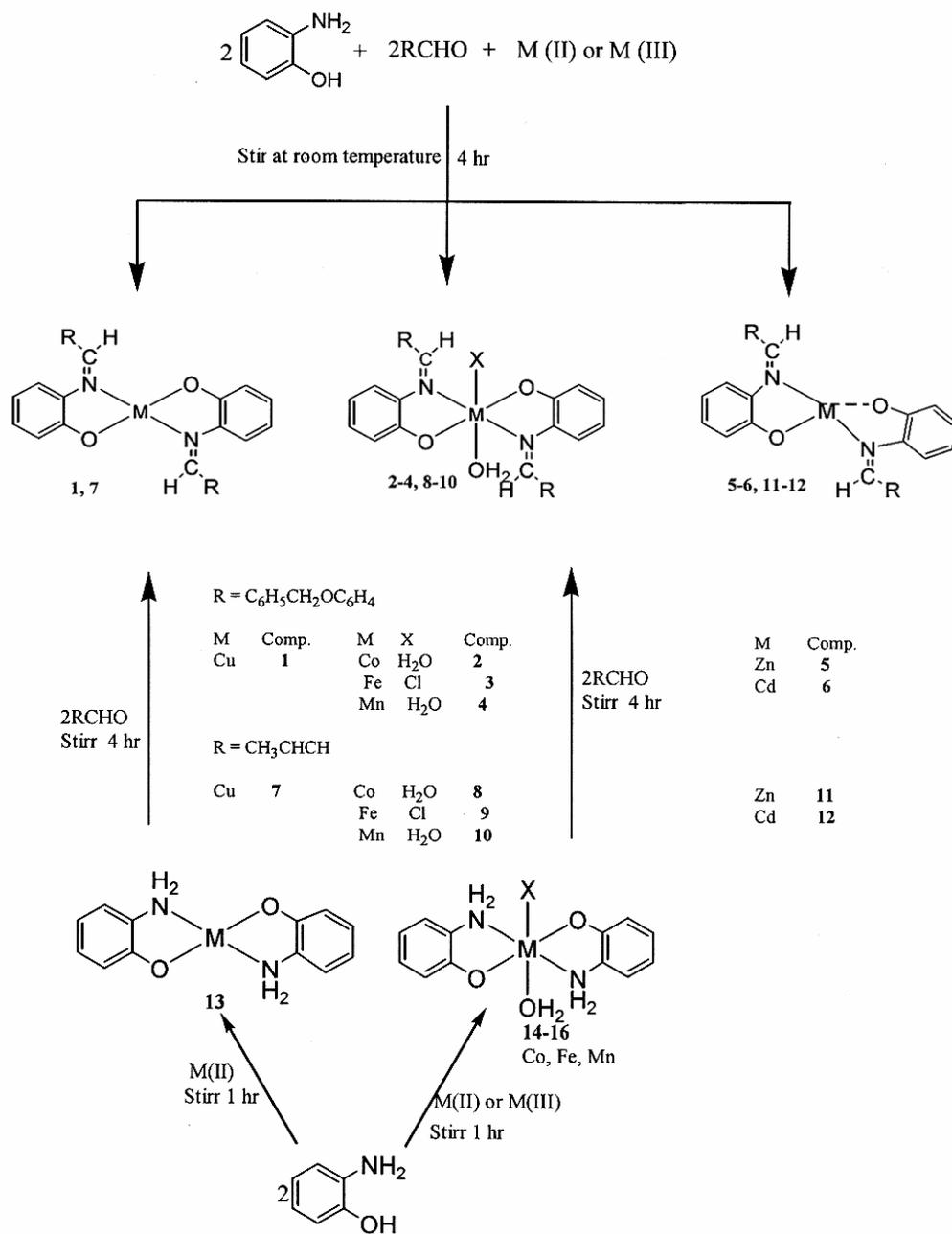
#### Antibacterial activity

Antibacterial activities of the compounds were measured against six pathogenic bacteria, gram negative (*viz.*, *Shigella dysenteria*, *Escherichia coli*, *Pseudomonas aeruginosa*) and gram positive (*viz.*, *Bacillus subtilis*, *Sarcina lutea*, *Staphylococcus aureus*). The antibacterial activity was measured by disc diffusion method<sup>13</sup>. The results were compared with the standard compound kanamycin (C<sub>18</sub>H<sub>36</sub>O<sub>11</sub>N<sub>4</sub>), 2-(aminomethyl)-6-[4, 6-diamino-3, 5-dihydroxy-6-hydroxymethyl]tetrahydropyran-2-yl]oxy-2-hydroxy-cycloxy]-tetrahydropyran-3,4,5-triol. The minimum inhibitory concentration was measured by serial dilution method (*i.e.*, turbidimetric assay)<sup>14</sup>.

#### Results and Discussion

The reaction of 2-aminophenol with Cu(II), Co(II), Fe(III), Mn(II), Zn(II) and Cd(II) ions in presence of 4-benzyloxybenzaldehyde and 2-butenal gave the complexes **1-12** (Scheme 1). The ligands (LH and L'H) were not formed by direct reaction of 2-aminophenol and 4-benzyloxybenzaldehyde or 2-butenal. However, the complexes of the ligands were formed by metal template method. 2-Aminophenol reacts with Cu(II), Co(II), Fe(III) and Mn(II) to give the aminophenolate complexes **13-16** as precipitate (in solution), which on further treatment with 4-benzyloxybenzaldehyde and 2-butenal gave the desired complexes **1-4** and **7-10** respectively. Zn(II) and Cd(II) ions did not form aminophenolate complexes when 2-aminophenol was used with metal(II) ions, instead they remained unreactive (as shown by TLC). However, Zn(II) and Cd(II) ions gave complexes **5-6** and **11-12** when 2-aminophenol, metal ions [Zn(II), Cd(II)] and aldehydes (4-benzyl-oxybenzaldehyde and 2-butenal) were reacted together. This may be due to the combination of all the three (*i.e.*, metal ion, 2-aminophenol and aldehyde), and not that of any two alone. Ni(II) ion did not react with 2-aminophenol and 4-benzyloxybenzaldehyde or 2-butenal.

While the reaction of 2-aminophenol with Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) in the presence of  $\pi$ -conjugated aldehyde such as 3-phenylpropenal (C<sub>6</sub>H<sub>5</sub>CHCHCHO) gave stable bright colour



Scheme 1

complexes<sup>8</sup>, non-conjugated aldehyde such as *n*-butanal (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO) did not form any complex<sup>8</sup>. 2-Butenal (CH<sub>3</sub>CHCHCHO), a  $\pi$ -conjugated aliphatic aldehyde gave complexes with all the studied metals except Ni(II). 2-Butenal behaves as intermediate between 3-phenylpropenal and *n*-butanal. Therefore,  $\pi$ -conjugation may be responsible for the formation of complex compound. The elemental analyses (Table 1)

of the complexes **1-12** are consistent with the proposed formula. The conductance measurement values reveal that the complexes are non-electrolytic in nature<sup>15</sup>.

The infrared spectra (Table 2) of the complexes **1-6** showed a strong band at 1590-1601 cm<sup>-1</sup> and for the complexes **7-12** at 1616-1637 cm<sup>-1</sup> for the  $\nu(\text{C}=\text{N})$  stretching frequencies<sup>16</sup>. The absence of any bands at

Table 1— Analytical, conductance and magnetic moments data of the complexes

Comp. <sup>a</sup> Colour	Yield (%)	M. pt (°C)	Found (Calc.) (%)				$\mu_{\text{eff}}$ (B. M.)	Molar cond. (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
			C	H	N	M		
[Cu(L) <sub>2</sub> ] ( <b>1</b> ) Brown	60	200	71.40 (71.89)	4.80 (4.82)	4.15 (4.19)	9.00 (9.50)	1.85	8.0
[Co(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] ( <b>2</b> ) Vand yke brown	62	245	69.00 (68.66)	5.15 (5.18)	4.05 (4.00)	8.00 (8.42)	4.97	5.0
[Fe(L) <sub>2</sub> (H <sub>2</sub> O)Cl] ( <b>3</b> ) Deep brown	65	290	67.00 (67.28)	4.72 (4.80)	3.90 (3.92)	8.00 (7.82)	5.97	4.0
[Mn(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] ( <b>4</b> ) Orange yellow	61	180	68.50 (69.06)	5.25 (5.21)	4.00 (4.02)	7.60 (7.90)	5.94	7.0
[Zn(L) <sub>2</sub> ] ( <b>5</b> ) Orange yellow	70	155	71.10 (71.70)	4.80 (4.81)	4.14 (4.18)	9.40 (9.75)	Dia	0.0
[Cd(L) <sub>2</sub> ] ( <b>6</b> ) Yellow	67	280	66.50 (66.00)	4.45 (4.50)	3.88 (3.90)	15.00 (15.67)	Dia	0.0
[Cu(L') <sub>2</sub> ] ( <b>7</b> ) Brown	65	220	62.00 (62.56)	5.20 (5.25)	7.32 (7.30)	16.00 (16.55)	1.92	2.0
[Co(L') <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] ( <b>8</b> ) Reddish brown	66	225	57.38 (57.83)	5.78 (5.82)	6.70 (6.74)	14.00 (14.19)	4.95	5.0
[Fe(L') <sub>2</sub> (H <sub>2</sub> O)Cl] ( <b>9</b> ) Deep brown	60	190	55.50 (55.90)	5.13 (5.16)	6.50 (6.52)	13.50 (13.00)	6.00	8.0
[Mn(L') <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] ( <b>10</b> ) Brown	55	200	58.00 (58.40)	5.83 (5.88)	6.83 (6.81)	13.00 (13.35)	5.78	3.0
[Zn(L') <sub>2</sub> ] ( <b>11</b> ) Light yellow	60	180	62.00 (62.27)	5.20 (5.22)	7.22 (7.26)	16.50 (16.94)	Dia	0.0
[Cd(L') <sub>2</sub> ] ( <b>12</b> ) Orange yellow	55	190	55.21 (55.50)	4.64 (4.66)	6.42 (6.47)	25.00 (25.97)	Dia	0.5

<sup>a</sup> L = C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>O and L' = CH<sub>3</sub>CHCHCH=NC<sub>6</sub>H<sub>4</sub>O

Table 2— IR, UV-visible and mass spectral data of the complexes

Comp.	IR (cm <sup>-1</sup> )				$\lambda_{\text{max}}$ (nm)	Mass peak ( <i>m/z</i> )
	$\nu$ (OH/H <sub>2</sub> O)	$\nu$ (C=N)	$\nu$ (M-N)	$\nu$ (M-O)		
<b>1</b>	-	1593	599	440	500	667 (M <sup>+</sup> ), 576, 457, 302 (100%), 199, 91, 77, 51
<b>2</b>	3410	1597	596	450	686, 585	
<b>3</b>	3400	1590	600	508	250, 310, 400	713(CI <sup>35</sup> ) (M <sup>+</sup> ), 636, 606, 503, 302 (100%), 199, 91, 77, 65, 51
<b>4</b>	3384	1597	592	484	600, 483	
<b>5</b>		1601	560	445	275, 330	
<b>6</b>		1599	590	497	270, 320	
<b>7</b>		1616	595	440	550	383 (M <sup>+</sup> ), 368, 342, 160 (100%), 120, 93, 77, 51, 28
<b>8</b>	3390	1620	590	460	675, 580	
<b>9</b>	3400	1629	582	428	260, 340, 420	429(M <sup>+</sup> ), 414, 388, 361, 160 (100%), 120, 93, 77, 51, 28
<b>10</b>	3400	1618	572	466	610, 500	
<b>11</b>		1637	582	461	270, 320	
<b>12</b>		135	570	449	260, 315	

3100-3350 cm<sup>-1</sup> region for  $\nu$ (N-H) stretching in the complexes suggests that condensation has taken place between the -NH<sub>2</sub> and -CHO moieties of the 2-aminophenol and aldehyde respectively. The complexes showed a band at 560-600 cm<sup>-1</sup> region for the  $\nu$ (M-N) stretching, providing unequivocal evidence for the formation of complexes through the

N atom of the ligand<sup>16</sup>. The complexes showed a band at 428-508 cm<sup>-1</sup> region represent the  $\nu$ (M-O) stretching, which indicates that the phenolic -OH moiety is deprotonated and forms chelate complexes through O atom<sup>16</sup>. The complexes **2-4** and **8-10** showed a broad band at 3384-3410 cm<sup>-1</sup> due to the coordinated water molecule<sup>17</sup>.

The magnetic moment (Table 1) of the complexes **1** and **7** are 1.85 and 1.92 B.M. respectively corresponding to one unpaired electron of  $d^0$ -system of square planar Cu(II). The Co(II) complexes **2** and **8** showed magnetic moments of 4.97 and 4.95 B.M. respectively, suggestive of a high spin octahedral environment of three unpaired electrons. These values are higher than the spin only momentum (3.89 B.M.) due to the orbital contribution, which is generally observed for Co(II) complexes<sup>18</sup>. The magnetic moments of Fe(III) complexes **3** and **9**, 5.97 and 6.00 B.M. respectively, correspond to high spin octahedral environment of five unpaired electrons. These values are very close to the spin only value of 5.90 B.M. since the ground state (derived from  $^5S$  state of free ion) has no orbital angular momentum<sup>18</sup>. The Mn(II) complexes **4** and **10** showed magnetic moments 5.94 and 5.78 B.M. respectively, corresponding to high spin octahedral symmetry of five unpaired electrons. The complexes **5**, **11** and **6**, **12** are diamagnetic in nature, consistent with the tetrahedral geometry of Zn(II) and Cd(II) complexes.

The UV-visible spectra (Table 2) of the complexes **1** and **7** showed absorption bands at 500-550 nm which is assigned to the  $^2E_g \rightarrow ^3T_{2g}$  transition characteristics of square planar copper(II) complexes<sup>17,19</sup>. The complexes **2** and **8** show absorption bands at 686-675 and 585-580 nm suggested for the  $^4T_{1g} \rightarrow ^4A_{2g}(F)$ ,  $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$  transitions for the octahedral Co(II) complexes. For octahedral Co(II),  $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$  occurs in the near infrared region, which is seldom observed because it is in the 1000-2000 nm region of the spectrum<sup>18</sup>. The complexes **3** and **9** showed three absorption bands at 250-260, 310-340, and 400-420 nm for the  $\sigma\text{-}\sigma^*$ ,  $\pi\text{-}\pi^*$  and  $L \rightarrow M$  charge transfer bands respectively<sup>20</sup>. Trivalent iron has a greater tendency for charge transfer bands in the near UV region which is associated with strong energy of the visible region that obscure the very weak spin forbidden  $d\text{-}d$  bands<sup>18</sup>. The complexes **4** and **10** showed bands at 600-610 and 483-500 nm characteristic of octahedral Mn(II). The Zn(II) and Cd(II) complexes showed  $\sigma\text{-}\sigma^*$ ,  $\pi\text{-}\pi^*$  transition bands only.

The mass spectra (Table 2) of the complexes **1**, **3**, **7** and **9** showed molecular ion ( $M^+$ ) peak and other peaks that are consistent with the proposed formula. Complex **1** showed molecular ion peaks  $m/z$  at 667( $M^+$ ), and other peaks at 576( $M\text{-}C_6H_5CH_2$ )<sup>+</sup>, 457 ( $M\text{-}C_6H_5CH_2\text{-}HOC_6H_4CN$ )<sup>+</sup>, 302 (100%)

( $C_6H_5CH_2OC_6H_4CN=NC_6H_4O$ )<sup>+</sup>, 199 ( $C_6H_5CH_2O\ C_6H_4O$ )<sup>+</sup>, 91( $C_6H_5CH_2$ )<sup>+</sup>, and 77( $C_6H_5$ )<sup>+</sup>. Similarly, the complex **3** showed molecular ion peak  $m/z$  at 713 ( $M^+$ ) and 302(100%) ( $C_6H_5CH_2OC_6H_4CN=NC_6H_4O$ )<sup>+</sup>. The complex **7** gave molecular ion peak  $m/z$  at 383 ( $M^+$ ) and 160(100%) ( $CH_3CHCHCHNC_6H_4O$ )<sup>+</sup>. The complex **9** showed  $m/z$  at 429 ( $M^+$ ) and 160(100%) ( $CH_3CHCHCHNC_6H_4O$ )<sup>+</sup>.

#### Antibacterial activity

Microbial activities of the metal complexes or metal chelates are usually greater than the ligands, and depend upon the metal ions i.e., size, charge distribution, shape and redox potential of the metal chelates<sup>21-22</sup>. The microbial activity of the complexes **1-12** and the ligand precursor 2-aminophenol has been tested against six pathogenic bacteria; gram negative (viz., *S. dysenteria*, *E. coli*, *P. aeuginosa*) and gram positive (viz., *B. subtilis*, *S. lutea*, *S. aureus*). Nutrient agar was used as culture media and the activity was measured by disc diffusion method<sup>13</sup>. All the complexes showed biological activity against these bacteria. Complexes **1**, **2**, **6** and **9-12** showed good activity as compared with ligand precursor, with complex **10** showing the best activity. The antibacterial activity increased with increase in concentration of the tested compounds. The results are comparable with that of the standard compound, kanamycin ( $C_{18}H_{36}O_{11}N_4$ ). The minimum inhibitory concentration (MIC) of the complexes **1**, **2**, **6** and **9-12** were measured by serial dilution method<sup>14</sup>. The best MIC was shown by complex **10** (16  $\mu\text{g/mL}$ ) for *S. dysenteria* and *B. subtilis*.

#### Acknowledgement

Authors are grateful to Rajshahi University authority for financial support and Department of Pharmacy, Rajshahi University, for help in testing antibacterial activity.

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