Spectral and Biological Behaviour of Complexes Derived Some Bivalent Metals and Schiff Base

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ABSTRACT
Complexes of 2-Aminobenzimidazole-5-Bromosalicylaldehyde (L) with chlorides of nickel (II) and manganese (II) were synthesized. The molar ratio metal: ligand in the reaction of the complex formation was 1:2. It should be noticed that the reaction of the metal salts yielded bis (ligand) complexes of the general formula [M(L)₂]₂H₂O (M = Ni, Mn). The complexes were characterized by elemental analysis, molar conductivity measurements, magnetic susceptibility measurements, Infra-Red, electronic spectra, mass and thermal studies. Both the complexes behave as non-electrolytes and have octahedral configuration around the metal ion. In both the complexes, ligand act as tridentate (NNO donor) coordinating by participation of the imidazole nitrogen of the benzimidazole ring, nitrogen of the azomethine group and oxygen of the deprotonated hydroxyl group. The Schiff base and its metal complexes have been screened for their antifungal activity against Candida albicans and Aspergillus niger.

Keywords: 2-Aminobenzimidazole, complexes, nickel (II), manganese (II), spectroscopic studies, antifungal activity.

INTRODUCTION
Schiff bases are widely employed in synthetic organic and inorganic chemistry. They were reported to show diverse biological activity [1-4] and have many applications as ligands in coordination chemistry of transition metals [5,6]. The chemistry of metal complexes with Schiff base ligands and their application have aroused considerable attention mainly because of preparative accessibility, diversity and structural variability [7]. Schiff bases belong to a widely used group of organic intermediates important for production of special chemicals, e.g. pharmaceuticals or rubber additives and as amino protective groups in organic synthesis [8,9]. The Schiff base synthesized from 4-Aminobenzoic acid and 5-Bromosalicylaldehyde have phototropic and thermotropic properties. Schiff bases very similar to this compound have shown microbiological activity and antifungal properties [10]. The increasing interest in transition metal complexes containing a Schiff base ligand is derived from their well-established role in biological systems as well as their catalytic and pharmaceutical applications [11,12]. The metal complexes from bidentate ligands have often been studied recently because of their applications in enhancement of drug action [13,14]. Transition metals are essential for normal functioning of living organisms and are, therefore, of great interest as potential drugs [15]. The coordination chemistry of nitrogen donor ligands is an active area of research. Schiff bases derived from Salicylaldehyde are well known for their interesting ligational properties and exclusive applications in different fields [16,17]. In this paper, we are reporting the synthesis, characterization and antibacterial activity of metal complexes of 2-Aminobenzimidazole derived Schiff base on some pathogenic bacteria.

EXPERIMENTAL
Chemicals
All the chemicals used were of AR/GR grade. Pure sample of 2-Aminobenzimidazole (Ab), molecular formula C₇H₆N₂, molecular weight 133.15 g/mol, melting point 229-230°C was obtained from Himedia Pharmaceuticals Ltd. Metal salts like NiCl₂.6H₂O and MnCl₂.4H₂O were of Merck chemicals. Solvents used were ethanol, acetone and DMF.

2.2 Preparation of Schiff Base Ligand
The Schiff base was synthesized from 5-Bromosalicylaldehyde (BS) and 2-Aminobenzimidazole (Ab) by adding 500 ml of 5-Bromosalicylaldehyde ethanolic solution (1.005 g; 0.01 M) to same volume of ethanol
solution of 2-Aminobenzimidazole (0.8144 g; 0.01M), the mixture was refluxed for 2 hours and kept overnight at room temperature. The resulting solution was evaporated to 20% of its original solution and the product was collected by filtration, washed several times with ethanol and crystallized from hot ethanol and then dried. The melting point of yellow crystals was found to be 245°C.

Preparation of metal Schiff base complexes
For the synthesis of complexes, ligand-metal ratio was determined by conductometric titration using monovariation method on systrionics conductivity meter using dip type electrode. 20 ml of the ligand (0.01 M) was diluted to 200 ml using pure ethanol and titrated against metal salts (0.02 M) solution prepared in the same solvent. Conductance was recorded after each addition of metal salt solution. Graph is plotted between corrected conductance and volume of metal salt added. From the equivalence point in the graph, it has been concluded that the complex formation of the ligand with metal salts takes place in the ratio 2:1 (L:M).

Conductometric titration supported 2:1 (L:M) ratio in the complex, which was further supported by Job’s method of continuous variation[18] as modified by Turner and Anderson[19]. The solid complexes were prepared by mixing ethanolic solutions of the ligand L (0.31 g, 0.01 M) with ethanolic solution of chlorides of Ni(II), (0.059 g, 0.005 M) and Mn(II), (0.049 g, 0.005 M), separately. The resulting solutions were checked for pH and pH was adjusted by adding few drops of N/10 NaOH solution. The solutions were refluxed for 4 hours and the refluxed solutions were kept for some days, solid crystalline complexes appeared in the solution which were filtered off, washed thoroughly with same solvent and finally with acetone, vacuo dried and weighed. Melting points of the complexes were recorded.

Physical measurements
Elemental analysis was carried out on VarioMICRO V2.20 ElementarAnalysenSysteme GmbH, from IIIM, Jammu. Metal contents were determined gravimetrically[20].The infrared spectra were recorded on FT-InfraRed Spectrophotometer Model RZX (Perkin Elmer) using KBr pellets from SAIF, Panjab University, Chandigarh. Molar conductance measurements were made in 10 \textsuperscript{-3} M DMF solution on a Systronics direct reading Conductivity Meter (Model 303). The melting points of the ligand and the complexes were recorded in open capillaries on a capillary melting point apparatus. Electronic spectra were recorded on a UV-VIS-NIR-Spectrophotometer Model Lambda 750 Perkin Elmer from SAIF, PU, and Chandigarh. The magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer (VSM) from IIT, Roorkee. The mass spectra were recorded at SAIF/CIL, PU, and Chandigarh by LC-MS spectrometer Model Q-ToF MicroWaters. The thermo-gravimetric analysis was carried out in nitrogen atmosphere (0.001 l/min.) with a heating rate of 10°C min \textsuperscript{-1} at ambient pressure using Perkin Elmer TG Analyzer within a temperature range from room temperature to 950°C at Department of Chemistry, University of Jammu, Jammu.

In vitro antimicrobial studies
The antifungal activities of the ligand and their complexes were tested in vitro for growth inhibitory against Candida albicans and Aspergillus niger by agar well diffusion method at different concentrations compared with Griseofulvin as the positive control[21,22].

RESULTS AND DISCUSSION
Through a condensation reaction, an amino group available in the pure compound was allowed to react with 5-Bromosalicyaldehyde to form a Schiff base ligand (HL) which was subsequently, reacted with metal ions to from Schiff base metal complexes. The ligand and the metal (II) complexes were isolated pure from EtOH in good yields and they are of various colours. The ligand is yellow, nickel complex is also yellow and manganese complex is Olive in colour.

The nickel complex melts at 205°C whereas manganese complex gets decomposed at 230°C. The analytical data of the complexes correspond with 1:2 (metal: ligand) stoichiometry. Thus, the general formula [M(L)_2].2H_2O where (M(II) = Ni, Mn), have been assigned to the metal complexes, respectively. They are very air stable solids at room temperature without decomposition for a long time. The complexes are non-hygroscopic, insoluble in water and other common organic solvents but soluble in DMF and DMSO. The molar conductance values of the complexes (measured in 10 \textsuperscript{-3} M DMSO) are 17.1
and 1.64 Scm\(^{-2}\) mol\(^{-1}\), indicating / revealing the non-electrolytic nature of the complexes. The magnetic moment data indicated both the complexes to be paramagnetic in nature. Thermograms of the metal complex indicate the presence of lattice water molecules and are gets lost up to 100\(^{\circ}\) C. The analytical data and molar conductance values are given in Table 1.

**Magnetic measurements**

The magnetic moment data are presented in Table 1. The Ni(II) complex showed magnetic moment values of 2.95 \(\mu B\) slightly higher than the spin only (2.83 B.M.) value, indicating an octahedral environment around Ni(II) ion\([24]\). The Mn(II) complex showed a value of 5.42 \(\mu B\), which is slightly lower than the spin only value of 5.92 \(\mu B\) for high spin octahedral Mn(II) complexes\([25]\).

**Electronic spectra**

The electronic spectra of the complexes were recorded in the solution state. The energies of the observed spin allowed bands in all the complexes agreed with the octahedral geometry. The electronic spectrum of paramagnetic Mn(II) complex shows four weak bands at bands at 600 nm, 441 nm, 408 nm, and 382 nm which can be assigned to \(\text{d}^{5}\text{g}(F)\text{A} \rightarrow \text{d}^{5}\text{g}(F)\text{E}\), \(\text{d}^{5}\text{g}(F)\text{A} \rightarrow \text{d}^{5}\text{g}(F)\text{B}\), \(\text{d}^{5}\text{g}(F)\text{A} \rightarrow \text{d}^{5}\text{g}(F)\text{C}\), and \(\text{d}^{5}\text{g}(F)\text{A} \rightarrow \text{d}^{5}\text{g}(F)\text{D}\) transitions, respectively, for a Mn(II) ion in an octahedral field\([26]\).

**IR Spectral studies**

The comparison of the IR spectra of Schiff bases (HL\(_2\)) and their metal complexes indicated that the ligands are principally coordinated to the metal ions in three ways, thus acting as tridentate ligands. The band appearing at \(\sim 1603 \text{ cm}^{-1}\) due to azomethine linkages\([28]\) in the ligands is shifted to higher frequencies by \(\sim 33\) to \(40 \text{ cm}^{-1}\) in the complexes, indicating the participation of the azomethine nitrogen in interaction with the metal ion\([29]\). The band at \(\sim 1563 \text{ cm}^{-1}\), assigned to the nitrogen of the imidazole ring (C=N), is shifted to lower frequency by \(\sim 7\) to \(12 \text{ cm}^{-1}\), which is indicative of the involvement of the imidazole ring N in the coordination with metal ions\([30]\). A broad band appearing at \(\sim 3200 \text{ cm}^{-1}\) assigned to OH in the Schiff base, was no longer found in the spectra of the investigated metal complexes\([31,32]\) and instead, appearance of a new band at \(\sim 1265\) to \(1305 \text{ cm}^{-1}\) due to (C=O) stretching vibrations, indicated deprotonation\([33]\) and coordination of the hydroxyl oxygen to the metal ion. Further conclusive evidence of coordination of these Schiff bases with the metal ions was shown by the appearance of low frequency new bands at 440 \text{ cm}^{-1}\) and 463 \text{ cm}^{-1}\) and at 620 \text{ cm}^{-1}\) and 635 \text{ cm}^{-1}\). These were assigned to the metal-nitrogen (M-N) and metal-oxygen (M-O) vibrations, respectively, and were observed in the spectra of the investigated metal complexes and not in the spectra of the uncomplexed Schiff bases, thus confirming participation of the O and N atoms in the coordination\([34,35]\). The appearance of bands at 3366 and 3325 \text{ cm}^{-1}\) are due to lattice water molecules\([36]\) which were futher confirmed by the appearance of new bands at 831 and 836 \text{ cm}^{-1}\) frequencies due to OH (rocking). The bands at 544, 535 and 539 \text{ cm}^{-1}\) are due to C-Br stretching vibrations in the Schiff base and the respective metal complexes.

**Mass spectra**

The mass spectrum of [Mn(C\(_{28}H_{32}N_{4}Br_{2}O_{4}\))] shows molecular ion peaks at \(m/z\) value 720.10 due to [Mn(L\(_2\))]\(^{+}\), which is in accordance with the proposed formula of the complex. The other peaks at \(m/z\) values of 403.7, 308.7, 267.9, 132.0, 271.9, 170.8 and 100.9 may be due to the fragments ([C\(_{13}H_{10}N_{3}BrOZN])\(^{+}\), [C\(_{13}H_{10}N_{3}BrOZN])\(^{+}\), [C\(_{13}H_{10}N_{3}BrOZN])\(^{+}\), [C\(_{13}H_{10}N_{3}BrOZN])\(^{+}\), [C\(_{13}H_{10}N_{3}BrOZN])\(^{+}\), and [C\(_{13}H_{10}N_{3}BrOZN])\(^{+}\). The base peaks at \(m/z\) 132.0 may be due to the metal Mn linked to the donor atoms of the ligand. Such type of fragmentation pattern has been reported by many workers\([37,38]\).

**Thermal Studies**

The TGA for the complex was carried out within a temperature range from room temperature to 950\(^{\circ}\) C. The TG studies indicate that complex showed a slight depression at 20-100\(^{\circ}\) C. The weight loss at this temperature range is found to be equivalent to two water molecules for the complex indicating to be lattice water. Thereafter, the complex showed rapid decomposition of the organic constituents. The decomposition continues up to 920\(^{\circ}\) C and finally metal oxide gets formed in addition to other organic constituents\([40,41]\). The complete result of thermal analysis is shown in fig.3, and given in table 3.

**Antimicrobial Activity**

For antifungal activity the ligand and its metal complexes were screened against *Candida albicans* and *Aspergillus niger* and the findings are given in Table 4. These complexes showed higher activity with 13.45-17.00 mm inhibition than the ligand which showed only 11.48 mm inhibition at the same concentration as that of the test compound for *Candida albicans*. However, ligand and their complexes showed lower activity as compared to standard drug griseofulvin with 19.38 mm inhibition at the same concentration.
Antifungal activity studies of ligand and its complexes against *Aspergillus niger* showed that all the complexes with 14.33–21.22 mm inhibition showed higher activity than the ligand which showed only 10.38 mm inhibition only. Ni(II) complex showed higher activity than standard drug which showed 18.22 mm inhibition at the same concentration as that of the test drug. It is known that chelation tends to make the ligand act as more powerful and potent antimicrobial agent, thus inhibiting more of the microbes than the parent ligand[39].

**Table-1: Analytical and physico-chemical data of Schiff base and its complexes.**

<table>
<thead>
<tr>
<th>Ligand / Complexes</th>
<th>Mol. Wt.</th>
<th>Elemental Analysis Found (calcd.) (%)</th>
<th>Colour (yield%)</th>
<th>M.Pt. (°C)</th>
<th>M.Conduc tance S cm² mol⁻¹</th>
<th>μeff (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HL₂] (C₁₄H₁₀N₃BrO)</td>
<td>316.14</td>
<td>54.21 (53.18) 53.55 (3.19) 13.7 (13.29)</td>
<td>Yellow (58)</td>
<td>-</td>
<td>245</td>
<td>----</td>
</tr>
<tr>
<td>Ni₂(C₂₈H₂₀N₆Br₂O₂).2H₂O</td>
<td>725.0</td>
<td>47.03 (46.38) 3.00 (3.05) 10.70 (11.6)</td>
<td>Yellow (53)</td>
<td>205</td>
<td>17.1</td>
<td>2.95</td>
</tr>
<tr>
<td>[Mn(C₂₈H₂₀N₆Br₂O₂)].2H₂O</td>
<td>721.23</td>
<td>46.70 (46.63) 3.03 (3.07) 12.10 (11.7)</td>
<td>Olive (50)</td>
<td>230 (Decomp osition)</td>
<td>16.4</td>
<td>5.42</td>
</tr>
</tbody>
</table>

**Table-2: Important IR spectral bands (cm⁻¹) of the ligand and its complexes.**

<table>
<thead>
<tr>
<th>Ligand / Complexes</th>
<th>νC=O</th>
<th>νC=N</th>
<th>νOH</th>
<th>νH₂O</th>
<th>νM=O</th>
<th>νM=N</th>
<th>νC-Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₁₄H₁₀N₃BrO)</td>
<td>1281s</td>
<td>1603s</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>544b</td>
</tr>
<tr>
<td>(C₂₈H₂₀N₆Br₂O₂Ni)</td>
<td>1265s</td>
<td>1636m</td>
<td>----</td>
<td>3366s</td>
<td>620m</td>
<td>440s</td>
<td>535b</td>
</tr>
<tr>
<td>(C₂₈H₂₀N₆Br₂O₂Mn)</td>
<td>1302s</td>
<td>1643s</td>
<td>----</td>
<td>3325s</td>
<td>635s</td>
<td>463s</td>
<td>539s</td>
</tr>
</tbody>
</table>

**Fig. 3. TGA Spectrum of Ab-BS-Ni Complex**

**Table-3: Thermoanalytical (TG) results of the metal complex.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Steps</th>
<th>Temp. (°C)</th>
<th>TG Mass%</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1ˢᵗ</td>
<td>20-100</td>
<td>5.2</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>2ⁿᵈ</td>
<td>100-310</td>
<td>10.8</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>3ʳᵈ</td>
<td>310-600</td>
<td>16.9</td>
<td>17.3</td>
</tr>
<tr>
<td>[Ni(C₂₈H₂₀N₆Br₂O₂)].2H₂O</td>
<td>4ᵗʰ</td>
<td>600-750</td>
<td>35.3</td>
<td>34.6</td>
</tr>
<tr>
<td></td>
<td>5ᵗʰ</td>
<td>750-950</td>
<td>11.4</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.66</td>
<td>23.6</td>
<td>-NO + C₆H₄(Org. moiety), Residue</td>
</tr>
</tbody>
</table>
Table 4: Antifungal activity of ligand and its metal complexes.

<table>
<thead>
<tr>
<th>Ligands/complexes</th>
<th>Candida albicans</th>
<th>Aspergillus niger</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;BrO)</td>
<td>11.48</td>
<td>10.38</td>
</tr>
<tr>
<td>[Ni(C&lt;sub&gt;28&lt;/sub&gt;H&lt;sub&gt;18&lt;/sub&gt;N&lt;sub&gt;6&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;].2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>17.00</td>
<td>21.22</td>
</tr>
<tr>
<td>[Mn(C&lt;sub&gt;28&lt;/sub&gt;H&lt;sub&gt;18&lt;/sub&gt;N&lt;sub&gt;6&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)].2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>13.45</td>
<td>14.33</td>
</tr>
<tr>
<td>Grisofulvin</td>
<td>19.38</td>
<td>18.22</td>
</tr>
</tbody>
</table>

CONCLUSION

Based on stoichiometry and analytical data it can be concluded that the ligand is neutral, tridentate coordinating through the "N", "N" and "O" of the azomethine, imidazole and phenolic groups, respectively. Both the complexes possesses 1:2(M:L) stoichiometry based on analytical and spectral data and octahedral structures has been proposed for the complexes. The ligand and the complexes showed very good activity against all bacteria. Hence, the proposed structure for the metal complexes is given as below:

![Structure of Metal complexes](image)

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