Schiff bases have an important position in the development of coordination chemistry due to their synthetic accessibility and physico-chemical properties. Transition metal complexes of azomethines have photochemical, catalytic, medicinal and electrochemical applications [1-3]. Tetradentate ONNO type Schiff bases have been reported for designing macrocyclic biomolecules that help in understanding biological processes [4,5]. Palladium(II) complexes have been investigated for its catalytic activity [6], photoluminescence properties as well as anti-tumor, anti-HIV and antimicrobial activities [7].

The reactions of tetradentate Schiff bases acquired from salicylaldehyde and diamines are a subject of interest of many authors [8,9] due to the ease of preparation and variable geometries. In the present paper, an attempt has been made to synthesize Ni(II) and Pd(II) complexes of tetradentate Schiff bases and further investigate the structure these complexes by spectral characterization and powder X-ray diffraction studies.

**INTRODUCTION**

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The reactions of tetradentate Schiff bases acquired from salicylaldehyde and diamines are a subject of interest of many authors [8,9] due to the ease of preparation and variable geometries. In the present paper, an attempt has been made to synthesize Ni(II) and Pd(II) complexes of tetradentate Schiff bases and further investigate the structure these complexes by spectral characterization and powder X-ray diffraction studies.

**EXPERIMENTAL**

All the chemicals used were of analytical reagent grade purchased from SDFCL Mumbai, India and used as such without further purification.
solution (0.001 mol). The solution was refluxed with continuous stirring for about 4-5 h at 60 °C. The precipitated complexes were cooled and filtered, washed with cold methanol and dried in vacuum.

**Biological studies:** The *in vitro* growth inhibition assay of the compounds were tested for their antimicrobial activity against the bacterial species *Staphylococcus aureus*, *Escherichia coli* and fungi *Aspergillus niger* and *Candida albicans* by the agar well diffusion method [11].

### RESULTS AND DISCUSSION

The crystalline solid complexes of Ni(II) and Pd(II) are bright in colour, stable in air and decompose at higher temperature (> 300 ºC). The complexes are insoluble in water and other common organic solvents but soluble in DMF and DMSO. The elemental analysis data confirmed 1:1 (metal:ligand) stoichiometry for all the complexes. The low values of molar conductance in DMSO (10⁻³ M) solution at room temperature indicate that these complexes are non-electrolytic in nature [12].

**IR spectra:** The preliminary identification regarding the formation of Schiff bases and their complexes were obtained from IR spectral data (Table-2). The IR spectra of free ligands showed characteristic broad band of medium intensity in the region 3500-3200 cm⁻¹ assigned to intramolecular hydrogen bonding v(O-H) stretching vibration [13]. The disappearance of these bands in the corresponding metal complexes indicates involvement of phenolic oxygen in coordination to the metal after deprotonation. This is further confirmed by the shift in the position of v(C-O)) band to lower wave numbers by 20-30 cm⁻¹ [14]. The participation of azomethine nitrogen is proved by the shift of strong and sharp bands at 1613 and 1602 cm⁻¹ for H₂L¹ and H₂L², respectively to a lower frequencies after complexation [15]. All the complexes showed an additional non-ligand bands in the regions 550-510 and 466-409 cm⁻¹ assigned to ν(M-O) and ν(M-N) stretching vibrations, respectively.

**¹H NMR spectra:** The ¹H NMR spectra of Schiff base ligands and their metal complexes were recorded in DMSO solvent. The ¹H NMR spectra of the parent ligands H₂L¹ and H₂L² exhibited singlet signals at 12.89 and 12.94 ppm, respectively which was attributed to phenolic -OH proton [16]. These OH signals disappeared when ¹H NMR spectra were performed in presence of D₂O. Also, the two ligands H₂L¹ and H₂L² showed singlets at 8.93 and 8.89 ppm, respectively, corresponding to -CH=N moiety.

On complexation the proton signals of azomethine carbon appeared to be deshielded as they were shifted downfield compared to the respective ligands indicating coordination through azomethine nitrogen atom [17]. The multiplets in the region 6.65-7.90 ppm were assigned to aromatic ring protons (Table-2).

**Electronic absorption spectra and magnetic susceptibility:** The electronic spectrum of Schiff base ligands and their metal complexes were explored in DMSO solution (1 × 10⁻³ M). The absorption spectra of the Schiff base ligands exhibited two high intensity bands at around 270 and 330 nm (Table-2) which is attributed to benzene π→π' transition and n→π' transition of non-bonding electrons present on azomethine nitrogen in the Schiff bases, respectively. These two transitions were shifted in the spectra of all the complexes with appropriate shifts. The appearance of band around 480 nm in Ni(II) complexes is due to ¹A₁g→¹B₁g transition favouring a square planar geometry [18]. The Pd(II) complexes display band in the regions of 255-259, 353-378 and 455-477 nm. The broad bands in the region 455-477 nm were considered due to d-d transition (¹A₁g→¹B₁g) of square planar configuration [19]. Magnetic susceptibility measurements supported the diamagnetic behaviour of all the complexes.

**Powder X-ray diffraction analysis:** To understand the crystal structure, X-ray diffraction data of complexes were obtained in the range 5º to 70º (2θ) value and an independent indexing for the X-ray powder diffraction data was done. The inter-planar spacing (dₐₜ) were calculated by using Bragg’s equation for the major reflexes. The preliminary data in the form of 1/d² value and an independent indexing for the X-ray powder diffraction data was done. The inter-planar spacing (dₐₜ) were calculated by using Bragg’s equation for the major reflexes. The preliminary data in the form of 1/d² were fed to the computer and all the differences were calculated as required for Hess and Lipson's method. The reflexes were indexed and refined for obtaining the Miller indices h, k, l using Back-cal program computational method. The precise lattice parameters and deviations were then obtained by using program X-ray and program error matrix, respectively. There-

### TABLE I

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.w. (Colour)</th>
<th>m.p. (°C)</th>
<th>Microanalysis (%): Found (Calculated)</th>
<th>Λₐₜ (S cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L¹</td>
<td>[C₉H₉N₅O₃Cl]</td>
<td>385.00 (Bright orange)</td>
<td>220</td>
<td>62.71 (62.32)</td>
</tr>
<tr>
<td>NiL¹</td>
<td>[C₉H₉N₅O₃ClNi]</td>
<td>441.71 (Browish red)</td>
<td>&gt; 300</td>
<td>54.28 (54.33)</td>
</tr>
<tr>
<td>PdL¹</td>
<td>[C₉H₉N₅O₃ClPd]</td>
<td>489.42 (Yellow)</td>
<td>&gt; 300</td>
<td>49.52 (49.04)</td>
</tr>
<tr>
<td>H₂L²</td>
<td>[C₉H₉N₅O₃Br₂]</td>
<td>473.80 (Yellow)</td>
<td>199</td>
<td>50.51 (50.65)</td>
</tr>
<tr>
<td>NiL²</td>
<td>[C₉H₉N₅O₃Br₂Ni]</td>
<td>530.51 (Brick red)</td>
<td>&gt; 300</td>
<td>45.05 (45.23)</td>
</tr>
<tr>
<td>PdL²</td>
<td>[C₉H₉N₅O₃Br₂Pd]</td>
<td>578.22 (Ochre yellow)</td>
<td>&gt; 300</td>
<td>41.58 (41.50)</td>
</tr>
</tbody>
</table>
After the densities of all the indexed compounds were determined using a 5 cm$^3$ specific gravity bottle and toluene as displacing liquid. After indexing, the space group is determined via systematic and critical evaluation of each reflux in the powder pattern [20]. All the complexes were successfully indexed into monoclinic system with $Z = 4$ and space group $P2_1/m$. The lattice parameters are summarized in Table-3. The closeness in the value of observed density and calculated density suggest that each reflux of X-ray diffraction pattern is indexed with perfectness.

**Antimicrobial activity:** The ligands and their metal complexes were assayed in *vitro* for their ability to inhibit the growth of representative Gram positive (*Staphylococcus aureus*) and Gram negative (*Escherichia coli*) bacteria and the fungus *Candida albicans* and *Aspergillus niger*. The susceptibilities of certain strains of bacteria and fungus were evaluated by measuring the size of the bacteriostatic diameter. The results (Table-4) indicated that (a) Schiff bases are more active against the fungus than their complexes, (b) all the complexes showed higher activity against the bacteria, and (c) Pd(II) complexes showed higher antibacterial and antifungal activities in comparison with Ni(II) complexes.

**Conclusion**

On the basis of analytical and spectral studies, it is observed that the synthesized Schiff bases behave as dibasic, ONNO tetradentate ligands and coordinated to the central metal ions via deprotonated phenolic oxygen and azomethine nitrogen atoms with 1:1 (metal:ligand) stoichiometry (Fig. 1). A square planar structure is proposed for all Ni(II) and Pd(II) complexes. The powder X-ray diffraction data suggested monoclinic crystal system for these complexes with space group $P2_1/m$. The antimicrobial results indicated that all the complexes are biologically active, however, Pd(II) complexes showed higher antimicrobial activity compared to Ni(II) complexes.

**REFERENCES**


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