INTRODUCTION

Transition metal complexes containing N-heterocycles have attracted considerable attention over several years, in view of their catalytic activity, biological importance, interesting spectral, magnetic and structural aspects [1-13]. Rosenberg et al. [14] have demonstrated a remarkable chemotherapeutic potential of cis-Pt(NH3)Cl2 (cisplatin) in a large variety of human cancers [15,16]. The replacement of ammonia by other amines, such as, cyclopentylamine and cyclohexylamine in cisplatin have shown higher therapeutic indices [17,18]. Nevertheless these drugs suffer from drawbacks of low water solubility, high nephrotoxicity and low activity against gastrointestinal tumors [19]. Coordination geometry and complex formation processes of palladium(II) are very similar to those of platinum(II). As a consequence palladium(II) ions are frequently employed to mimic the binding properties of various platinum(II) species. Based on this, Gill et al. [19] have reported several palladium complexes with coordinated bidentate amine ligands that have exhibited anticancer activities comparable to or greater than cisplatin. Large amount of work has been performed on the equilibrium constant studies of palladium(II) complexes with aliphatic amines [20-22]. N-heterocycles act as σ-donors and can also function as effective π-acceptors. This will enhance mechanism of complex formation with DNA subunits that are the principal targets in chemotherapy of tumors [23,24]. Such enormous importance of palladium complexes, prompted us to initiate study on other palladium complexes with N-heterocycles, such as 2-salicylidene-4-aminophenyl benzimidazole (SAPbzlH).

The Schiff base, 2-salicylidene-4-aminophenyl benzimidazole (I, SAPbzlH) in ethanolic medium reacts with palladium(II) in acidic medium (HCl/HBr) and coordinated SAPbzlH undergoes hydrolysis at -N=CH- bond to yield salicylaldehyde and square planar complexes having composition [Pd(C13H11N3)2X2]·2HX (II) (X = Cl, Br). The obtained complexes have been characterized by elemental analysis, atomic absorption spectra, infrared, electronic and extensive utility of NMR. Possible mechanism for the hydrolysis of coordinated 2-salicylidene-4-aminophenyl benzimidazole (SAPbzlH) has been proposed.

Keywords: Schiff base, Divalent palladium, Correlation spectroscopy, Hydrolysis.

EXPERIMENTAL

Elemental analyses were carried out using Elementer Vario EI 111 and Carlo Erba-1108 instruments. The IR spectra of the complexes (KBr) were recorded on a Nicolet-impact-400D spectrometer in the range 4000-400 cm⁻¹. The metal content was determined by Atomic Absorption spectrometer ECIL model-
Electronic spectra of SAPbzlH, 4-APbzlH and Pd(II) complexes were recorded in the range 200-600 nm on a Elico SL 159 UV-Visible spectrophotometer in DMSO.

The 1H and 13C [1H] NMR spectra of Schiff base and palladium complexes were recorded in DMSO-d6 on Bruker DRX-500 MHz and Avance-III 400.13 MHz NMR spectrometers equipped with 5 mm inverse detection probe and Z-gradient coil, at ambient temperature with TMS as internal reference. The operating frequencies for 1H and 13C are 500.13, 400.13 for 1H and 125.76 and 100.61 MHz, respectively. The experimental parameters for one-dimensional 1H/13C NMR spectra used were spectral width of 17.35 ppm in F2 dimension and 54.85 ppm in F1 dimension. The delay responsible for the direct dimension corresponds to single quantum detection and the acquisition data size was 320 × 4 K, respectively. Eight transients were accumulated for each of 256 t1 increments with 2 s relaxation delay. For HSQC experiment, the spectral width of 17.36 ppm in F2 dimension and 200 ppm in the F1 dimension were used. The optimized τ delay for efficient transfer of magnetization was set to one bond JCH of 145 Hz. The size of the time domain data was 320 × 5554 points and the number of accumulations was 8 for each t1 data point with a relaxation delay of 1.5 s between transients. The gradient ratio was maintained at 80:20. In the case of HMBC experiment, the spectral widths used were 2.88 ppm in F1 dimension and 54.85 ppm in F1 dimension. The delay responsible for polarization transfer was optimized for 13C→1H coupling of 8 Hz. The size of 2D data was 256 × 2048 points. The number of scans for each increment was 32 and a relaxation delay of 2 s was used between the transients. Gradient ratio was 50:30:40.

For DEPT-135 experiments the time domain data size was maintained at 32 K and the number of scans was 500, with a relaxation delay of 2 s between each transient.

For 4Q-SQ correlation experiments, indirect dimension pertains to non-selective excitation and detection of 4th quantum and the direct dimension corresponds to single quantum detection. The spectral widths of 3.20 and 12.00 ppm were employed in F2 and F1 dimensions, respectively. Eight scans were accumulated for each τ1 increment with a recycle delay of 2 s. The optimized τ delay was 10.6 μs. The 4th quantum signal was detected using the appropriate gradient ratio of 1:1.

The chemicals used for the synthesis of Schiff base and metal complexes were of Merck make. The solvents were distilled prior to use. The products: bis(4-aminophenyl benzimidazole)-dichloropalladium(II) dihydrochloride [Pd(C13H11N3)2Cl2]-2HCl (1); bis(4-aminophenyl benzimidazole)dibromopalladium(II) dihydrobromide, [Pd(C13H11N3)2Br2]-2HBr (2).

**Synthesis:** To an ethanolic solution (10 mL) of palladium(II) chloride (0.11 g; 0.60 mmol) in conc. HCl/conc. HBr (0.5 mL) was added 2-salicylidene-4-aminophenyl benzimidazole (0.38 g; 1.20 mmol) dissolved in ethanol (10 mL). The mixture was refluxed on a steam-bath for about 6 h, during which an orange coloured solid precipitated. The solid was separated from the solution by filtration and washed with ethanol and dried in vacuum (yield: 0.39/0.42 g; 95.0/83.0 %). The filtrate was subjected to Schiff reagent test, which showed the presence of salicylaldehyde after work up (solid, m.p. 250 ºC). The solids were analyzed for the formula Pd(C13H11N3)4X2·2HX; X = Cl (1), Br (2); m.p. > 250 ºC. The test indicated the formation of salicylaldehyde during the reaction; m.p. > 250 ºC. Analytical analysis calcd. (found) % for C28H21N3Br4Pd: (1): C, 46.65 (46.65); H, 3.58 (4.11); N, 12.55 (11.66); Pd, 15.99 (15.60). IR (KBr, νmax, cm-1): 3419, 3334, 1629, 1503.

Analytical analysis calcd. (found) % for C28H21N3Br4Pd: (2): C, 36.85 (37.11); H, 2.83 (3.65); N, 9.92 (9.87); Pd, 12.63 (12.10). IR (KBr, νmax, cm-1): 3479, 3280, 1612, 1604, 1502.

RESULTS AND DISCUSSION

Palladium(II) salts in ethanol react with SAPbzlH in molar ratio (1:2) in presence of conc. HCl/conc. HBr at refluxing temperature to produce complexes having composition [Pd(C13H11N3)X2]-2HX (II). The complexes are non-hygroscopic orange coloured crystalline solids. They are soluble in DMF and DMSO and insoluble in other organic solvents. The IR spectrum of Schiff base, SAPbzlH showed a band in the range 3450-3300 cm-1 and due to ν(OH) and ν(NH). The spectrum also displayed multiple peaks in the range 3050-2660 cm-1 and these are assigned to ν(CH) of phenyl and methine groups. Two bands at 1600 and 1618 cm-1 are respectively ascribed to ν(N=CH) and ν(C=C) of CH2 rings. A peak at 1572 cm-1 is assigned to ν(N=C) of imidazole ring. A band at 1276 cm-1 is attributed to ν(C-O) of phenolic group. The IR spectrum of 4-aminophenyl benzimidazole (4-APbzlH) showed bands at 3439 and 3356 cm-1 which are assigned to ν(NH2) and ν(NH), respectively. A single and broad band at 1608 cm-1 is assigned to both ν(N=C) and ν(C=C). The appearance of a peak at 1502 cm-1 is ascribed to bending mode of NH2.

The IR spectra of palladium complexes displayed minor shifts in the positions of the bands as compared to those of 4-APbzlH. Bands observed at 3419 and 3379 cm-1 are assigned to ν(NH2). The ν(NH) band observed at 3334 and 3280 cm-1 has shifted by nearly 160 cm-1. The band around 1620 cm-1 is assigned to ν(N=C) of benzimidazole moiety and the same is split on coordination to metal ion. These observations have indicated that 4-APbzlH acts as a monodentate ligand bonding through tertiary nitrogen of benzimidazole. The band at 1502 cm-1 observed in the spectrum of 4-APbzlH is assigned to NH2-bending mode and this has not undergone any observable shift in the spectra of the complexes implying that the amino group is not involved in the coordination to the metal ion [25-28]. A band around 1572 cm-1 due to νN=C present in the spectrum of Schiff base-2-salicylidene-4-aminophenyl benzimidazole is absent in the spectra of the complexes implying the cleavage of -N=C=H- bond.

**Electronic spectral studies:** The electronic spectrum of SAPbzlH in DMSO exhibits three bands and they are observed at 297 (33,670 cm-1) to 379 (26,385 cm-1) and at 414 (24,154 cm-1) nm. These are assigned to π→π* and n→π* transitions. The electronic spectrum of 4-APbzlH in DMSO exhibits three bands and observed at 36832, 26350, 26075 cm-1. These are assigned to π→π* and n→π* transitions.
The spectra of palladium complexes (II, Table-1) displayed multiple absorption bands at 23,148 and 23,255 cm$^{-1}$ and these are ascribed to $^{1}A_{1g} \rightarrow ^{1}B_{1g}$ transitions, respectively. Two doublets observed at 7.93 ppm ($J_{HH} = 8.61$ Hz) and the other at 6.77 ppm ($J_{HH} = 8.4$ Hz) are assigned to sets of two sets of protons 3′, 5′ and 2′, 6′, respectively. Another two multiplets observed at δ 7.70 and 7.47 ppm are assigned to sets of two sets of protons 4, 5 and 6, 7 respectively. Assignments were observed based on TOCSY experiment (Fig. 2).

The $^{1}$H NMR spectrum (Fig. 3) of [Pd(C$_6$H$_3$N$_2$)$_2$Br$_2$]·2HBr in DMSO displayed two singlets one at δ 14.41 ppm and the other at δ 6.41 ppm and are assigned to protons of NH and NH$_2$, respectively. Two doublets observed at 7.89 ppm ($J_{HH} = 8.61$ Hz) and the other at 6.77 ppm ($J_{HH} = 8.4$ Hz) are assigned to sets of two sets of protons 3′, 5′ and 2′, 6′, respectively.

### Table-1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-APbzI/Br</td>
<td></td>
</tr>
<tr>
<td>[Pd(C$_6$H$_3$N$_2$)$_2$Cl$_2$]-2HCl</td>
<td>383.5 (26, 075)</td>
</tr>
<tr>
<td>[Pd(C$_6$H$_3$N$_2$)$_2$Br$_2$]·2HBr</td>
<td>430 (23, 255)</td>
</tr>
</tbody>
</table>

### NMR spectral studies:

A detailed study of $^{1}$H and $^{13}$C NMR spectra of SAPbzI and 4-APbzI involving various 2D correlation experiments such as, COSY, TOCSY, HSQC, HMBC and 4Q-SQ have been reported earlier [34-36]. In the present investigation, NMR analysis of 4-APbzI coordinated to palladium ion has been carried out using TOCSY, HSQC, HMBC, DEPT-135 and 4Q-SQ correlated spectra.

The $^{1}$H NMR spectrum (Fig. 1; Table-2) of [Pd(C$_6$H$_3$N$_2$)$_2$Cl$_2$]-2HCl in DMSO displayed two singlets one at δ 14.51 ppm and the other at 6.42 ppm and these are assigned to protons of NH and NH$_2$, respectively. Two doublets observed at 7.93 ppm ($J_{HH} = 8.61$ Hz) are assigned to protons of 3′ and 5′ and 2′, 6′ respectively. Another two multiplets observed at δ 7.70 and 7.47 ppm are assigned to protons of 4, 5 and 6, respectively. Assignments have been observed based on TOCSY experiment (Fig. 2).

The $^{1}$H NMR spectrum (Fig. 3) of [Pd(C$_6$H$_3$N$_2$)$_2$Br$_2$]·2HBr in DMSO displayed two singlets one at δ 14.41 ppm.

### Table-2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Benimidazole ring</th>
<th>Aminophenyl ring</th>
<th>Salicylidene ring</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH</td>
<td>H$_2$</td>
<td>H$_4$</td>
</tr>
<tr>
<td>SAPbzIH</td>
<td>12.95s</td>
<td>7.53d (7.40)</td>
<td>7.68t (8.40)</td>
</tr>
<tr>
<td>4-APbzI</td>
<td>12.40s</td>
<td>7.48d (7.90)</td>
<td>7.46d (7.90)</td>
</tr>
<tr>
<td>[Pd(C$_6$H$_3$N$_2$)$_2$Cl$_2$]-2HCl</td>
<td>14.51s</td>
<td>7.70m (–)</td>
<td>7.70m (–)</td>
</tr>
<tr>
<td>[Pd(C$_6$H$_3$N$_2$)$_2$Br$_2$]·2HBr</td>
<td>14.41s</td>
<td>7.71m (–)</td>
<td>7.71m (–)</td>
</tr>
</tbody>
</table>

* Spectra have been recorded in DMSO-$d_6$; δ in ppm and coupling constant in Hz are given in parentheses.
Another two multiplets observed at $\delta$ 7.71 and other at $\delta$ 7.48 ppm are assigned to another two sets of protons 4, 7 and 5, 6 respectively.

The off-resonance $^{13}$C NMR spectrum of [Pd(C$_{13}$H$_{11}$N$_3$)$_2$Cl$_2$]-2HCl (Fig. 4; Table-3) in DMSO displayed eight resonances (four of them being doublets) for the carbons and four of them at 129.73d, 125.16d, 113.58d and 113.05d ppm are assigned respectively to the sets of protonated carbons (3',5'), (5,6), (2',6') and (4,7). The other four resonances each as a singlet observed at 154.05, 149.84, 131.34 and 107.77 ppm are assigned respectively to quaternary carbons 2, 4', (8, 9) and 1', respectively. These assignments have been made by the combined utility of HSQC (Fig. 5), HMBC (Fig. 6) and DEPT-135 (Fig. 7) experiments.

The off-resonance $^{13}$C NMR spectrum of [Pd(C$_{13}$H$_{11}$N$_3$)$_2$Br$_2$]·2HBr (Fig. 8) in DMSO displayed eight resonances (four of them being doublets) for the carbons and four of them observed at 129.67d, 125.25d, 113.62d and 113.05 d ppm are assigned respectively to four sets of protonated carbons (3',5'), (5,6), (2',6') and (4,7). The other four resonances observed as a singlet at 154.07, 149.92, 131.26 and 107.66 ppm are assigned respectively to the quaternary carbons 2, 4', (8, 9) and 1', respectively.

The $^1$H 4Q-SQ correlated spectra of the complexes (Figs. 9 and 10) were recorded using appropriate pulse sequence [37-39]. The 4Q-SQ spectrum for palladium(II) chloro complex distinctly differentiated the overlapped sub-spectra of two coupled groups of protons, arising from benzimidazole and amino-phenyl rings. Thus, 4Q dimension showed only two peaks at the cumulative additive values of the chemical shifts of coupled protons. The 4Q chemical shifts pertaining to each cross section are marked in the spectrum. The cross section taken along F2

### Table-3

$^{13}$C NMR Spectral Data of SAPbzlH, 4-APbzlH and Palladium(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>1'</th>
<th>2', 6'</th>
<th>4'</th>
<th>3', 5'</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAPbzlH</td>
<td>150.7t</td>
<td>111.2br</td>
<td>122.5br</td>
<td>121.7br</td>
<td>116.6d (161.0)</td>
<td>143.9s</td>
<td>135.0s</td>
<td>149.1s</td>
<td>122.0d (162.0)</td>
<td>128.6s</td>
<td>127.5d (162.0)</td>
</tr>
<tr>
<td>4-APbzlH</td>
<td>151.0s</td>
<td>114.0d (160.0)</td>
<td>121.7d (160.0)</td>
<td>121.7d (160.0)</td>
<td>114.0d (160.0)</td>
<td>138.3s</td>
<td>138.3s</td>
<td>152.1s</td>
<td>113.5d (157.9)</td>
<td>115.8s</td>
<td>128.0d (158.0)</td>
</tr>
<tr>
<td>[Pd(C$<em>{13}$H$</em>{11}$N$_3$)$_2$Cl$_2$]-2HCl</td>
<td>154.0s</td>
<td>113.0d (167.0)</td>
<td>125.1d (162.0)</td>
<td>125.1d (162.0)</td>
<td>113.0d (167.0)</td>
<td>131.3s</td>
<td>131.3s</td>
<td>1074.7s</td>
<td>113.5d (165.0)</td>
<td>149.8s</td>
<td>129.7d (158.9)</td>
</tr>
<tr>
<td>[Pd(C$<em>{13}$H$</em>{11}$N$_3$)$_2$Br$_2$]-2HBr</td>
<td>154.0s</td>
<td>113.0d (167.0)</td>
<td>125.2d (162.0)</td>
<td>125.2d (162.0)</td>
<td>113.0d (167.0)</td>
<td>131.2s</td>
<td>131.2s</td>
<td>107.6s</td>
<td>113.6d (165.0)</td>
<td>149.9s</td>
<td>129.6d (165.0)</td>
</tr>
</tbody>
</table>

*Spectra have been recorded in DMSO-$d_6$; coupling constant in Hz are given in parentheses.*
Mechanistic studies: Palladium(II) chloride in ethanol in the presence of dilute HCl reacts with Schiff base in 1:2 molar ratio to produce PdCl₂(SAPbzH)₂ (IA; Scheme-I) [40] in which SAPbzH molecules are bound to Pd(II) ion through tertiary nitrogens of imidazole ring. The coordinated SAPbzH molecules undergo hydrolysis at uncoordinated nitrogens of -N=CH− bonds. The electrophilic attack of protons on N atoms makes the latter electrophilic (IB, IC) and this gets transferred to the carbon atoms (IC). Nucleophilic attack of H₂O molecules (ID) on carbo cations react in the cleavage of N-C bond (IE). Thus, aldehyde (IF) is formed by acid hydrolysis of each of the coordinated SAPbzH, latter being converted into an amine.
Conclusion

The present studies suggest that the hydrolysis at -\text{N}=\text{CH}- of 2-salicylidene-4-aminophenyl benzimidazole (SAPbzlH) takes place only in the presence of \text{Pd}^{2+} ions. The formation of amine has been conclusively proved by detailed \text{H} and \text{C} NMR studies. The amine formed coordinates to palladium through imidazole nitrogen. The complexes have been assigned a square planar structure.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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