Platinum(II) Complexes of ON Donor Schiff Bases Derived from Aniline & Salicylaldehyde or Substituted Salicylaldehydes

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New platinum(II) complexes of the Schiff bases derived from aniline and salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 3-ethoxysalicylaldehyde and 2-hydroxy-1-naphthaldehyde have been synthesized. The complexes have been characterized on the basis of elemental analyses, electrical conductance, magnetic susceptibility, infrared and electronic spectral measurements. The Schiff bases behave as monobasic bidentate ON donors. The complexes are of the type PtL₂ (where LH = bidentate monobasic Schiff base). The complexes are nonelectrolytes and diamagnetic in nature, and these have been assigned four-coordinated square-planar structures.

Although there has been considerable interest in the study of coordination complexes of Schiff bases with first transition series metal ions, relatively less work has appeared on the complexes of Schiff bases with higher transition series metal ions. A survey of literature indicates that there is no report on the platinum(II) complexes of the simple Schiff bases derived from salicylaldehyde or substituted salicylaldehydes and aniline. We report here the syntheses and characterisation of such new complexes.

General method of preparation of the complexes
To an aqueous solution (8 ml) of potassium tetrachloroplatinate(II) (0.42 g, 0.001 mol) was added an aqueous solution (2 ml) of KOH (0.11 g, 0.002 mol). The resultant solution was added to an ethanolic solution (10 ml) of the appropriate Schiff base (0.002 mol). The mixture was refluxed on a water-bath for 2 hr. The solid compound was obtained after partial evaporation of the solvent under a fan. The compound was recrystallized from 1:1 water-ethanol mixture, filtered, washed with 1:1 water-ethanol mixture followed by petroleum ether and dried in vacuo at room temperature; yield, ~ 50%

The metal content in the complexes was determined gravimetrically by igniting the complexes and weighing as Pt. Carbon, hydrogen and nitrogen analyses were done microanalytically. The analytical data are given in Table 1. The conductance measurements were carried out in acetone (10⁻³ M) with the help of a Toshniwal conductivity bridge (model CL 01-02A) and a dip-type cell calibrated with aqueous KCl solutions. The infrared spectra were recorded in nujol-mull using a Beckman IR-20 infrared spectrophotometer calibrated with polystyrene. The magnetic susceptibility measurements were done by the Gouy method using Hg[Co(NCS)₄] as the standard and diamagnetic corrections were also applied. The electronic absorption spectra were recorded in acetone on a VSU2-P Carl Zeiss spectrophotometer.

The analytical data show that complexes are of the type PtL₂ (where LH = Schiff base, 1). The electrical conductance values of the complexes in acetone are consistent with their non-electrolytic nature (Λₗ = 7-11 ohm⁻¹ cm² mol⁻¹). The complexes are diamagnetic as expected for the 5d⁷ platinum(II) ion. The Schiff bases exhibit an IR band around 2800 cm⁻¹ which is assigned to the intramolecularly hydrogen bonded ν(OH). The absence of this band in the complexes as well as the absence of anions in the complexes indicate deprotonation, consequent coordination and monobasic behaviour of the Schiff bases.

The free Schiff bases exhibit in the IR spectra a strong band at 1615-1625 cm⁻¹ which is assigned to the ν(C = N) mode. This band shifts to lower energy side by 5-30 cm⁻¹ in the complexes indicating coordination of nitrogen to the metal ion. The ν(C-O) (phenolic) mode is observed in the IR spectra of free ligands in the region 1515-1535 cm⁻¹ (ref. 8); this relatively higher energy value is due to the partial double bond character of the C-O bond because of the

Potassium tetrachloroplatinate(II) and 5-chlorosalicylaldehyde were synthesized according to published procedures. Salicylaldehyde was obtained from Sarabhai M. Chemicals Co. 3-Ethoxysalicylaldehyde was purchased from Aldrich Chemical Co. (U.S.A.). 2-Hydroxy-1-naphthaldehyde was procured from Fluka AG (Switzerland). The Schiff bases were prepared according to reported procedures.
Table 1—Analytical Data of Platinum(II) Complexes of Schiff Bases

<table>
<thead>
<tr>
<th>Complex/ Stoichiometry (Colour)</th>
<th>Found (calc.) %</th>
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<tbody>
<tr>
<td>Pt (sal-aniline)$_2$ (Yellow)</td>
<td>Pt 33.16 N 4.88 C 53.06 H 3.24</td>
</tr>
<tr>
<td>C$<em>{26}$H$</em>{20}$O$_2$N$_2$Pt</td>
<td>(33.23) (4.77) (53.15) (3.41)</td>
</tr>
<tr>
<td>Pt (5-chlorosal-aniline)$_2$ (Brown)</td>
<td>29.61 4.10 47.08 2.59</td>
</tr>
<tr>
<td>C$<em>{26}$H$</em>{16}$O$_2$N$_2$Cl$_2$Pt</td>
<td>(29.73) (4.27) (47.56) (2.74)</td>
</tr>
<tr>
<td>Pt (5-nitrosal-aniline)$_2$ (Yellow)</td>
<td>28.89 7.96 46.38 2.81</td>
</tr>
<tr>
<td>C$<em>{26}$H$</em>{16}$O$_2$N$_2$Pt</td>
<td>(28.80) (8.27) (46.09) (2.66)</td>
</tr>
<tr>
<td>Pt (3-ethoxysal-aniline)$_2$ (Brown)</td>
<td>28.65 4.10 52.99 4.42</td>
</tr>
<tr>
<td>C$<em>{30}$H$</em>{26}$O$_2$N$_2$Pt</td>
<td>(28.89) (4.15) (53.33) (4.15)</td>
</tr>
<tr>
<td>Pt (nap-aniline)$_2$ (Yellow)</td>
<td>27.76 7.96 59.01 3.27</td>
</tr>
<tr>
<td>C$<em>{34}$H$</em>{24}$O$_2$N$_2$Pt</td>
<td>(28.39) (4.08) (59.38) (3.49)</td>
</tr>
</tbody>
</table>

Abbreviations: sal = salicylaldehyde, 5-chlorosal = 5-chlorosalicylaldehyde, 3-ethoxysal = 3-ethoxysalicylaldehyde, nap = 2-hydroxy-1-naphthaldehyde

neighbouring benzene ring. Thus, the ν(C-O) (alcoholic) mode should occur at a lower energy than the ν(C-O) (phenolic) mode. On complexation the ν(C-O) (phenolic) mode shifts to higher energy side by 5-10 cm$^{-1}$ indicating coordination of phenolic oxygen of the schiff bases. This positive shift is due to the maintenance of a ring current arising out of electron delocalisation in the chelate ring. Thus, the IR, analytical data and valence requirement of the metal ion indicate that the ligands are behaving as monobasic bidentate ligands. The complexes are four-coordinated and square planar.

The schiff bases exhibit electronic spectral bands around 48000, 38000, 32000 and 29000 cm$^{-1}$ due to $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*_{2,3}$, $\pi \rightarrow \pi^*_{1}$ and $n \rightarrow \pi$ transitions respectively. On complex formation the $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*_{2}$ and $\pi \rightarrow \pi^*_{1}$ transitions move to lower energy side and $n \rightarrow \pi^*$ transition shifts to higher energy side. This is due to the increase in energy of $\pi$ levels relative to $n$ level and is indicative of the involvement of the schiff bases in coordination. The $d-d$ bands of platinum(II) could not be located as these are overlapped by the ligand bands which have very high molar extinction coefficients ($5110-13540$ litre mol$^{-1}$ cm$^{-1}$).

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References