

Synthesis and Characterization of Complexes of Pd(II) with Schiff base Ligand

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Abstract:

A novel series of Pd(II) complexes with Schiff bases derived from pyridine-2-carbaldehyde and 2-aminopyrazine and 2-methylaniline have been synthesized. The metal complexes were characterized by micro elemental analysis, molar conductivity, magnetic susceptibility, FTIR, and electronic absorption spectra. The Pd (II) complexes are colored and stable in air. In the metal complexes the metal -ligand ratio found to be 1:2. The sharp band appeared at 1650-1660 cm^{-1} is characteristics of the azomethine group present in the Schiff base ligands. This band was shifted to lower frequency (1640 – 1645 cm^{-1}) in all the Pd (II) complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes. A broad band at 3400- 3650 cm^{-1} is present in metal complexes but absent in ligands, which indicates coordination of water molecules to the metal ion. The higher molar conductivity data of the complexes in DMF solution indicates they are electrolytic in nature. The spectral data indicate that the Schiff base ligand behaves as bidentate and coordinated with metal ion by azomethine nitrogen and pyridine nitrogen atom to the metal ion. On the basis of elemental analysis, magnetic susceptibility and electronic spectral data, geometry of complexes was proposed to be square planar in nature.

Keywords: Pyridine-2-carbaldehyde, 2-methylaniline, Pd-salt, 2-aminopyrazine.

1. INTRODUCTION

Schiff bases are the most important class of organic compounds synthesized from the condensation of a primary amine with active carbonyl compounds. Schiff bases may be represented as $\text{R}-\text{CH}=\text{N}-\text{R}'$ where R and R' may be alkyl, aryl or heterocyclic¹⁻⁴. Schiff bases of aromatic aldehydes are more stable than aliphatic aldehydes due to effective conjugation. The presence of azomethine group, which is responsible for stability, reactivity and biological activity of Schiff bases and their metal complexes. Schiff bases and their metal complexes are used in catalyst, antimicrobials, antioxidants, dyes optical materials and analytical chemistry. Due to chelation transition metal Schiff base complexes are more stable and have wide applications in antibacterial, antifungal, antiviral, anticancer, and anti-inflammatory⁵⁻⁸. Pyrazines are most important classes of heterocyclic compounds that can be obtained naturally or can be synthesized chemically. Pyrazine is a weaker base than pyridine and pyrimidine. Pyrazine and alkyl pyrazine are flavour and aroma compound found in baked and roasted goods. Pyrazines gained attention from the food industry as important ingredients in raw and roasted foods⁹⁻¹². Pyridine is one of the simplest known heterocyclic compounds since its discovery in 1844 by Thomas Anderson. Pyridine is monodentate ligand which bind to metal ion in different proportion. Pyridine is a unique ligand in coordination chemistry due to presence of nitrogen and lone pair of electrons¹³⁻¹⁷. Schiff bases played an important role as ligands even a century after their discovery in chemistry. Schiff base metal complexes derived from pyridine-2-carbaldehyde and its derivatives have wide range of applications in bioinorganic and medicinal chemistry. In this work, we report the synthesis and characterization of Pd (II) complexes of Schiff base ligands derived from condensation reaction of pyridine-2-carbaldehyde with 2-amino pyrazine and 2-methyl aniline.

2. MATERIALS AND METHODS

The chemicals used in the present work were of Anal-R grade and were used without further purification. The elemental analysis (C, H and N) data was obtained using 2400 CHN Perkin-Elmer elemental analyzer. The molar conductivity of the complexes in DMF solution (10^{-3}M) were measured by using DI-909 digital conductivity meter. The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR spectrophotometer using KBr disc. The magnetic susceptibility data were measured by Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. The electronic spectra of the complexes were recorded by using Shimadzu model UV-1601 spectrophotometer in DMSO solution.

Synthesis of Schiff base Ligand (L_1)

The Schiff base ligand 2-(pyridine-2'-carboxaldehydimino) pyrazine was prepared by adding 2 mmol of pyridine-2-carboxaldehyde in 25 ml ethanol to 2 mmol of 2-aminopyrazine in 25 ml ethanol. The resulting solution was refluxed for 3-4 h. On cooling the reaction mixture, the yellow crystalline solid was formed. The precipitate is washed with ethanol and diethyl ether several times and is then recrystallized with ethanol to obtain the required Schiff base(L_1).

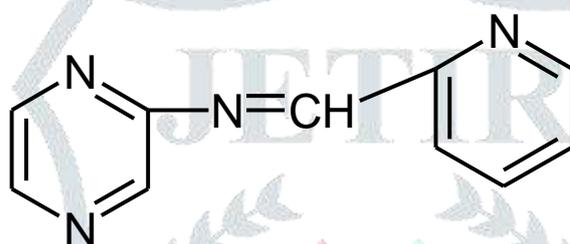


Figure1. Synthesis of Schiff base ligand(L_1)

Synthesis of Schiff base Ligand (L_2)

The Schiff base ligand N-(2-methyl phenyl)-1-pyridine-2-yl-methanimine was prepared by adding 0.01 mol of pyridine-2-carboxaldehyde in 20 ml ethanol to 0.01 mol of 2-methyl aniline in 20 ml ethanol. The resulting solution was refluxed for 4-5 h and then left overnight in refrigerator. The solid brown colored product obtained was filtered, washed with ethanol and acetone and dried over CaCl_2 in a desiccator.

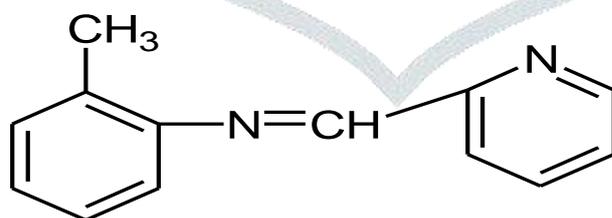
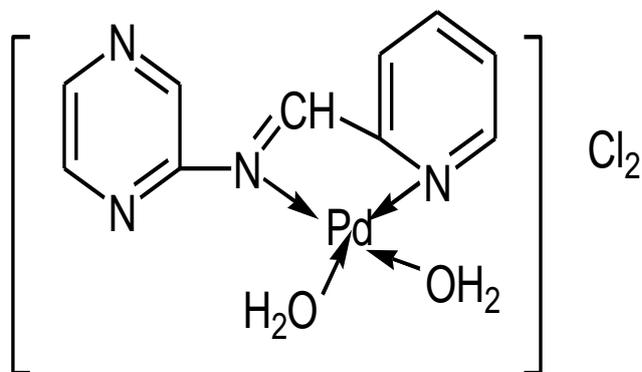
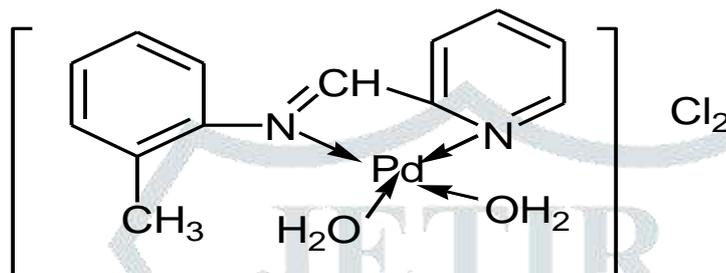


Figure2. Synthesis of Schiff base ligand(L_2)

Synthesis of Pd(II) complexes

The palladium (II) complexes were prepared by mixing (50 ml) ethanolic solution of Pd(II) chlorides with the (50 ml) ethanolic solution of Schiff base in a metal-ligand ratio 1:1. The resulting mixture was refluxed on water bath for 2-3 h. The complex obtained in each time was cooled, filtered and washed with acetone and recrystallized with ethanol and dried over anhydrous KOH in a desiccator.

Figure3. Proposed structure of $[Pd(L_1)(H_2O)_2] Cl_2$ complexFigure4. Proposed structure of $[Pd(L_2)(H_2O)_2] Cl_2$ complex

3. RESULTS AND DISCUSSION

The analytical and physical properties of Schiff bases and their palladium (II) complexes are given in Table-1. All palladium (II) complexes are coloured and stable in air. The metal ligand ratio in all the metal complexes have 1:1.

Table 1. Physical Properties and Analytical data of Schiff bases and their Pd(II) Complexes

| Compounds | Color | % Analysis Found (Calc) | | | |
|------------------------------|--------------|-------------------------|----------------|------------------|------------------|
| | | C | H | N | M |
| Schiff base(L ₁) | Yellow | 62.45 (62.43) | 4.22 (4.19) | 30.36 (30.29) | — |
| Schiff base(L ₂) | Brown | 79.31 (79.49) | 6.02 (6.11) | 14.17 (14.26) | — |
| $[Pd(L_1)(H_2O)_2]Cl_2$ | Brick red | 30.23 (30.21) | 3.12 (3.09) | 14.26 (14.21) | 26.83 (26.78) |
| $[Pd(L_2)(H_2O)_2]Cl_2$ | Light yellow | 38.09 (38.04) | 3.93 (3.90) | 6.87 (6.82) | 25.91 (25.85) |

Table 2. Molar Conductance and Magnetic Moment data of Pd(II) Complexes

| Compounds | Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) | μ_{eff} (B.M) | Magnetic nature |
|--|---|--------------------------|-----------------|
| $[\text{Pd}(\text{L}_1)(\text{H}_2\text{O})_2]\text{Cl}_2$ | 170 | — | Diamagnetic |
| $[\text{Pd}(\text{L}_2)(\text{H}_2\text{O})_2]\text{Cl}_2$ | 178 | — | Diamagnetic |

Molar Conductance and Magnetic Moment

Molar conductance and magnetic moment data of palladium (II) complexes are given in Table 2. The higher molar conductance values of palladium (II) complexes in DMF solution indicate their electrolytic in nature. All Pd (II) complexes are diamagnetic in nature due to paired electrons present in d-orbital of palladium (II) ion.

IR Spectra

The I.R spectral data of Schiff base ligands and Pd(II) complexes are given in Table 3. The band appeared at 1660 cm^{-1} is characteristics of the azomethine group present in the Schiff base ligands. This band was shifted to lower frequency ($1640 - 1645\text{ cm}^{-1}$) in all the palladium (II) complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes. A broad band at $3400- 3650\text{ cm}^{-1}$ is present in metal complexes but absent in ligands, which indicates coordination of water molecules to the metal ion. The band due to $\nu(\text{C}=\text{N})$ pyridine ring appears at $1621-1630\text{ cm}^{-1}$ in the Schiff bases, which shifted to lower frequency ($1610 - 1620\text{ cm}^{-1}$) in all the Pd (II) complexes, which indicates the coordination of the pyridine nitrogen to metal ion in complexes. The appearance of new band at $375-400\text{ cm}^{-1}$ due to $\nu(\text{M}-\text{N})$ in all the metal complexes.

Table 3. IR spectral data of Schiff base ligands and their metal complexes

| Compounds | $\nu(\text{C}=\text{N})$ (imine) | $\nu(\text{C}=\text{N})$ (pyridine) | $\nu(\text{M}-\text{N})$ |
|------------------------------|----------------------------------|-------------------------------------|--------------------------|
| Schiff base(L ₁) | 1660 | 1630 | — |
| Schiff base(L ₂) | 1650 | 1621 | — |
| $[\text{Pd}(\text{L}_1)_2]$ | 1645 | 1620 | 375 |
| $[\text{Pd}(\text{L}_2)_2]$ | 1640 | 1610 | 400 |

Electronic absorption spectra:

The electronic spectra of palladium complexes were recorded in DMSO solution between 200- 600 nm at room temperature. The absorption bands at 275 nm assigned to $\pi \rightarrow \pi^*$ transition and at 390 nm assigned to $n \rightarrow \pi^*$ transition. The bands at 390-470 nm assigned to LMCT. The bands observed at 575 and 538 nm assigned to ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_1(\text{F})$ and ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ respectively. The magnetic moment values of palladium complexes show they are diamagnetic in nature, due to absence of unpaired electron in d- orbital of

palladium ion. On the basis of electronic spectral data and magnetic moment values, which suggests square planar geometry of palladium complexes.

4. CONCLUSION

The Schiff bases derived from pyridine-2-carbaldehyde and 2-aminopyrazine and 2-methylaniline have been synthesized. The metal complexes were characterized by micro elemental analysis, molar conductivity, magnetic susceptibility, FTIR, and electronic absorption spectra. The Pd (II) complexes are colored and stable in air. In the metal complexes the metal -ligand ratio found to be 1:2. The sharp band appeared at 1660 cm^{-1} is characteristics of the azomethine group present in the Schiff base ligands. This band was shifted to lower frequency ($1640 - 1645\text{ cm}^{-1}$) in all the Pd (II) complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes. The band due to $\nu(\text{C}=\text{N})$ pyridine ring appears at $1621-1630\text{ cm}^{-1}$ in the Schiff bases, which shifted to lower frequency ($1610 - 1620\text{ cm}^{-1}$) in all the Pd (II) complexes, which indicates the coordination of the pyridine nitrogen to metal ion in complexes. The appearance of new band at $375-400\text{ cm}^{-1}$ due to $\nu(\text{M}-\text{N})$ in all the metal complexes. The higher- molar conductivity data of the complexes in DMF solution indicates they are electrolytic nature. The spectral data indicate that the Schiff base ligand behaves as bidentate and coordinated with metal ion by azomethine nitrogen and pyridine nitrogen atom to the metal ion. On the basis of elemental analysis, magnetic susceptibility and electronic spectral data, geometry of complexes was proposed to be square planar in nature.

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