

# Synthesis and characterization of complexes of platinum( II) with bidentate Schiff base ligands

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## Abstract

A novel series of platinum (II) complexes derived from Schiff base ligands 2-(pyridine-2'-carboxaldehydeimino) pyrazine and 2,6-diacetyl pyridine bis (semicarbazone) have been synthesized and characterized by micro elemental analysis, molar conductivity, magnetic susceptibility, FTIR, and electronic absorption spectra. The Pt (II) complexes are colored and stable in air. In the metal complexes the metal -ligand ratio found to be 1:2. 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, pyridine nitrogen atom and oxygen atom of semicarbazone 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, 2,6-diacetyl pyridine, Pt-salt, 2-aminopyrazine, semicarbazide.

## 1. INTRODUCTION

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first synthesized by Hugo Schiff in 1864. These compounds containing a general formula  $RCH = N - R^1$  where R and  $R^1$  are alkyl, aryl, cycloalkyl or heterocyclic groups are also known as anils, imines or azomethines. Schiff bases are the condensation products of an amine and carbonyl compounds, and are important class of ligand that coordinates to metal ions via azomethine nitrogen (C=N). The carbonyl group of the aldehyde gives aldimines while that of ketone gives ketoimines, and these provided binding site for the metal ions through non-bonding electrons of the nitrogen. They also have many other hetero-elements like oxygen and sulphur which provided binding sites through non-bonding electrons. They are crystalline solids which are feebly basic, but at least some form insoluble salts with strong acids. They also offer a versatile and flexible Series of ligand capable of binding with various metal ions to gives complexes with suitable properties for theoretical or practical applications. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable, while those of aromatic aldehydes having effective conjugation are more stable in general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehydes are less sterically hindered than that of ketones. The extra carbon of ketones donates electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehydes. Schiff bases are generally bidentate, tridentate, tetradentate and polydentate ligands capable of forming very stable complexes with transition metals. They can only act as coordinating ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reaction with a metal ion. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields like biological, inorganic and analytical chemistry. Schiff bases are used in optical and electrochemical sensors, as well as in various chromatographic methods to enable detection of enhanced selectivity and sensitivity. Schiff bases are widely applicable in analytical determination using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial and anticancer applications. Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. These complexes have also applications in clinical, analytical and

industrial in addition to their important roles in catalysis and organic synthesis. 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. Schiff base metal complexes derived from pyridine-2-carbaldehyde and its derivatives have wide range of applications in bioinorganic and medicinal chemistry. In the present paper, we report here the synthesis and characterization of Pt (II) complexes of Schiff base ligands derived from condensation reaction of pyridine-2-carbaldehyde with 2-amino pyrazine and 2,6-diacetyl pyridine with semicarbazide.

## 2. MATERIALS AND METHODS

### Chemicals and Reagents :-

All the starting materials 2-amino pyrazine, pyridine-2-carbaldehyde, semicarbazide, metal salts and solvents used in this research were of analytical grade and were used in reaction as received without further purification. 2-amino pyrazine, pyridine-2-carbaldehyde, semicarbazide and 2,6-diacetyl pyridine obtained from Sigma-Aldrich. Metal salts and solvents were obtained from Merck.

### Physical Measurements: -

The percentage (%) of metal was determined by EDTA complexometric titration. The elemental analysis of C, H and N was performed by using a Perkin-Elmer 2400 elemental analyzer. The melting point of all compounds were determined using Griffin melting point apparatus. The molar Conductivity were determined by using DMSO as a solvent in digital conductivity meter at 25<sup>o</sup>c. The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR-8400 spectrophotometer using KBr disc. The magnetic susceptibility was determined on Gouy balance at room temperature using Hg [Co (SCN)<sub>4</sub>] as a calibrant. The absorption spectra were recorded by using Shimadzu model UV-1601 spectrophotometer at room temperature in DMF solution.

### Synthesis of Schiff base Ligand (L<sub>1</sub>): -

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<sub>1</sub>).

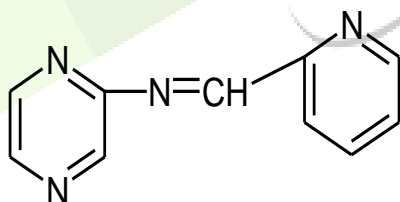
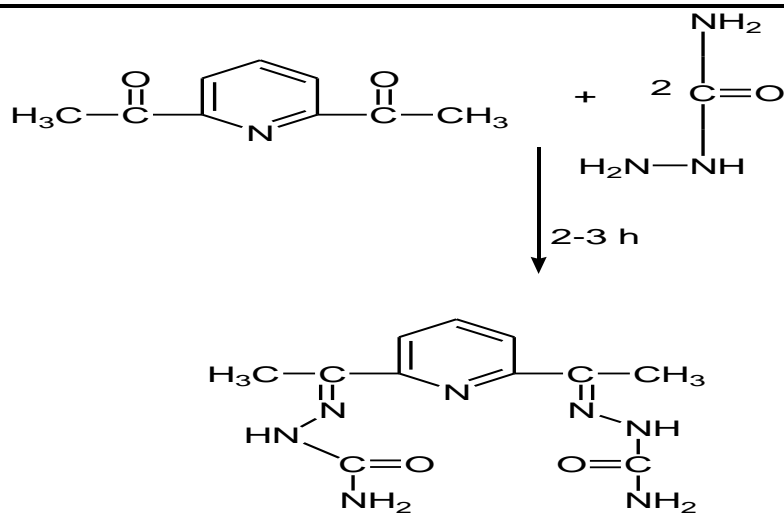


Figure1. Synthesis of Schiff base ligand(L<sub>1</sub>).

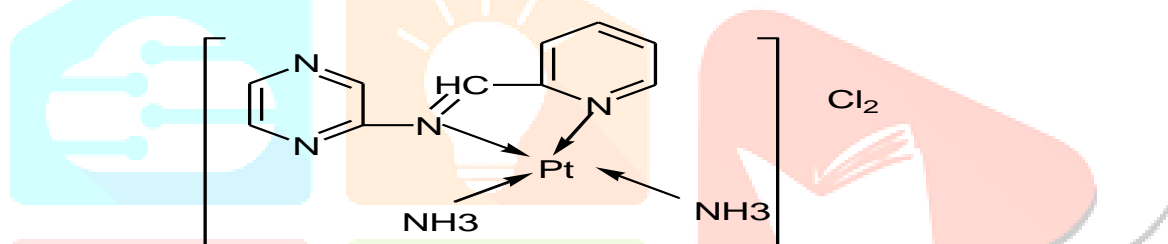
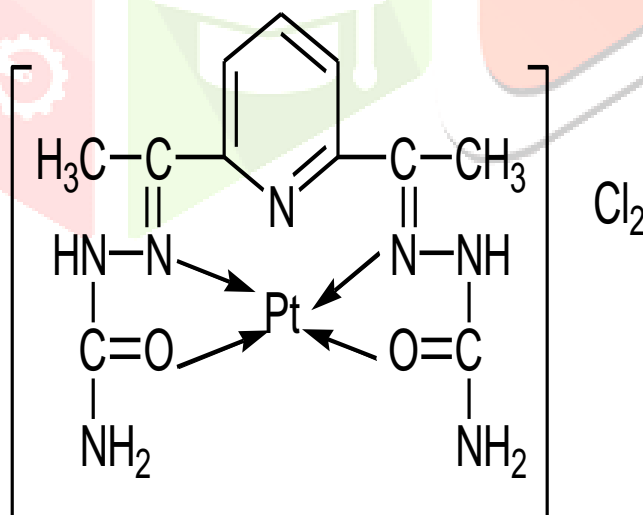
### Synthesis of Schiff base Ligand (L<sub>2</sub>): -

The Schiff base ligand 2,6-diacetyl pyridine bis(semicarbazone) was prepared by adding 1.502 g (0.02 mol) of semicarbazide in 25 ml ethanol and 1.632 g (0.01 mol) of 2,6-diacetyl pyridine in 25 ml ethanol. The resulting solution was refluxed for 2-3 h. On cooling the reaction mixture, the cream colour crystalline solid was formed. The precipitate is washed with distilled water and ethanol several times and is then recrystallized with ethanol to obtain the required Schiff base ligand.

Figure 2. Synthesis of Schiff base ligand(L<sub>2</sub>).

### Synthesis of Pt(II) complexes

The platinum (II) complexes were prepared by mixing (50 ml) ethanolic solution of Pt(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.

Figure 3. Proposed structure of [Pt(L<sub>1</sub>)(NH<sub>3</sub>)<sub>2</sub>] Cl<sub>2</sub> complex.Figure 4. Proposed structure of [Pt(L<sub>2</sub>)] Cl<sub>2</sub> complex

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

Compounds	Color	% Analysis Found (Calc)			
		C	H	N	M
Schiff base(L <sub>1</sub> )	Yellow	65.31 (65.34)	4.22 (4.19)	30.36 (30.29)	—
Schiff base(L <sub>2</sub> )	Cream	47.55 (47.60)	5.32 (5.41)	35.31 (35.34)	—
[Pt(L <sub>1</sub> )(NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	Yellow	24.71 (24.76)	2.82 (2.89)	17.26 (17.31)	40.13 (40.18)
[Pt(L <sub>2</sub> )]Cl <sub>2</sub>	Brown	24.21 (24.29)	2.73 (2.76)	15.41 (15.45)	35.84 (35.90)

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

Compounds	Molar conductance (Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	μ <sub>eff</sub> (B.M)	Magnetic nature
[Pt(L <sub>1</sub> )(NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	172	—	Diamagnetic
[Pt(L <sub>2</sub> )]Cl <sub>2</sub>	105	—	Diamagnetic

### 3. RESULTS AND DISCUSSION

The analytical and physical properties of Schiff bases and their platinum (II) complexes are given in Table-1. All Pt (II) complexes are coloured and stable in air. The molar conductance values of metal complexes in DMSO solution reveal their electrolytic nature of the complexes. All compounds gave satisfactory micro elemental analysis.

**Infrared spectra:** - The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR-8400 spectrophotometer using KBr disc. On the basis of IR spectra important functional groups in the compound can be identified. The IR spectrum of the ligand was compared with spectra of Pt(II) complexes. The band appeared at 1660 cm<sup>-1</sup> is characteristics of the azomethine group present in the Schiff base ligands. This band was shifted to lower frequency 10-15 cm<sup>-1</sup> in all the Pt (II) complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes. The band due to ν(C=N) pyridine ring appears at 1620-1630 cm<sup>-1</sup> in the Schiff bases, which shifted to lower frequency 15-20 cm<sup>-1</sup> in all the Pt (II) complexes, which indicates the coordination of the pyridine nitrogen to metal ion in complexes. A band appears at 3445 cm<sup>-1</sup> indicate coordination of ammonia to the metal ion. The appearance of new band at 760 cm<sup>-1</sup> indicates coordination of senicarbazone oxygen to the metal ion.

**Electronic spectra and magnetic susceptibility:** - The electronic spectra have been identified with UV-Visible spectroscopy. The nature of ligand field around the metal ion and the geometry of complexes have been deduced from the electronic spectra. The absorption spectra were recorded by using Shimadzu model UV-1601 spectrophotometer at room temperature in DMF solution. The electronic spectra of the Schiff bases and their metal complexes were recorded in DMF solution. The spectra of the metal complexes show one strong band at 420 nm, which is assigned to the square planar <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>B<sub>1g</sub>. The hybridisation of Pt(II) complexes is dsp<sup>2</sup> and diamagnetic nature support the square planar geometry of the complexes.

**NMR spectra:** - The  $^1\text{H}$  nuclear magnetic resonance spectra of Schiff bases and their metal complexes were recorded in  $\text{DMSO-d}_6$ . Two methyl protons appeared at  $\delta$  2.32 ppm in the ligand 2 and no significance change in complexes. A sharp singlet at  $\delta$  6.57 ppm is due to  $-\text{NH}_2$  group in ligand. The position of this singlet remains same in the metal complexes, which suggest  $-\text{NH}_2$  group does not coordinated with metal ion. Signal due to azomethine proton appeared at  $\delta$  8.05 ppm in ligand, this signal shifted to  $\delta$  8.10-8.28 ppm on complexation suggest coordination of azomethine nitrogen to the metal ion. On the basis of above discussion, a square planar structure can be suggested for Pt(II) complexes.

#### 4. CONCLUSION

A novel series of platinum (II) complexes derived from Schiff base ligands 2-(pyridine-2'-carboxaldehydeimino) pyrazine and 2,6-diacetyl pyridine bis (semicarbazone) have been synthesized and characterizes by micro elemental analysis, molar conductivity, magnetic susceptibility, FTIR, and electronic absorption spectra. The Pt (II) complexes are colored and stable in air. The spectral data indicate that the Schiff base ligand behaves as bidentate and coordinated with metal ion by azomethine nitrogen, pyridine nitrogen atom and oxygen atom of semicarbazone to the metal ion. The spectra of the metal complexes show one strong band at 420 nm, which is assigned to the square planar  $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ . The hybridisation of Pt(II) complexes is  $\text{dsp}^2$  and diamagnetic nature support the square planar geometry of the complexes. On the basis of elemental analysis, magnetic susceptibility and electronic spectral data, geometry of complexes was proposed to be square planar.

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