



## Structural studies of nickel (II) complexes with tetradentate Schiff base ligand

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### Abstract

Ni(II) complexes with a tetradentate Schiff base ligand have been synthesized from the condensation reaction of 2,6-diacetyl pyridine with 2-amino acetohydroxamic acid in an alcoholic medium at room temperature. The Schiff base and its synthesized nickel complexes were characterized by elemental analysis, molar conductivity measurements, magnetic moment measurements, IR, NMR and UV-Vis spectral data investigations. The lower molar conductance value of the synthesized nickel (II) complexes in DMF solution indicates that the complexes are non-electrolytic in nature. The synthesized metal chelates have the general formula  $[M(L)(B)_2]$ , where M = Ni, L is a Schiff base, and B represents a base such as ammonia, water, pyridine, phenyl-isocyanide, or  $\alpha$ -picoline. All synthesized Ni (II) complexes are paramagnetic because they contain unpaired electrons. IR spectra of the Schiff base indicate that the ligand acts as a biantionic tetradentate and is coordinated by two nitrogen atoms of the hydroxamic acid group and two nitrogen atoms of the azomethine group to nickel ions. On the basis of elemental analysis, magnetic behavior, and spectral data, we suggest an octahedral geometry for the nickel(II) complexes.

**Keywords:** Tetradentate, Schiff base, 2,6-diacetyl pyridine, nickel- complexes

### Introduction

Schiff bases are a versatile class of organic compounds in chemical research. The Schiff bases are the bridge between basic organic synthesis, coordination chemistry and materials science. The Schiff base is also known as azomethine or imine due to the presence of a double bond between carbon and nitrogen ( $-C=N-$ ). The nitrogen atom of azomethine is  $sp^{[2]}$  hybridized and attached with an aryl or alkyl group. The presence of azomethine bonds, which also affect biological, physical, and chemical properties [1-5]. The Schiff bases are generally synthesized by the condensation reaction of aldehydes or ketones with a primary amine under suitable conditions. The aromatic carbonyl compounds are more reactive than aliphatic due to the effective conjugation system often found in the Schiff bases of aromatic compounds. Schiff bases and their metal complexes play an important role in pharmaceutical and analytical chemistry [6-11]. Inhibition of urease in the bivalent nickel centers of bacterial and plant urease systems is a primary target for substrate analogues such as hydroxamic acid. Hydroxyamic derivatives are key targets for matrix metalloproteinase targeting in the anti-metastatic oncology diagnostic assay. The acidic nature of the hydroxamic acid is similar to that of carboxylic acid. Schiff base metal complexes provide a suitable surface area, so they are used as homogeneous catalysts in different industries. Salenic and related complexes of the Schiff base tetradentate ligands are well known for their asymmetric synthesis, epoxidation, polymerization and selective oxidation reactions [12-18]. The nitrogen and oxygen atoms in the Schiff base play an important role in the chemistry of the biological and the coordination [19-21]. Transition metal Schiff base complexes are also used in anti-bacterial, anti-fungal, anti-cancer, anti-oxidant, anti-diuretic, dyes, polymer and industrial areas. In

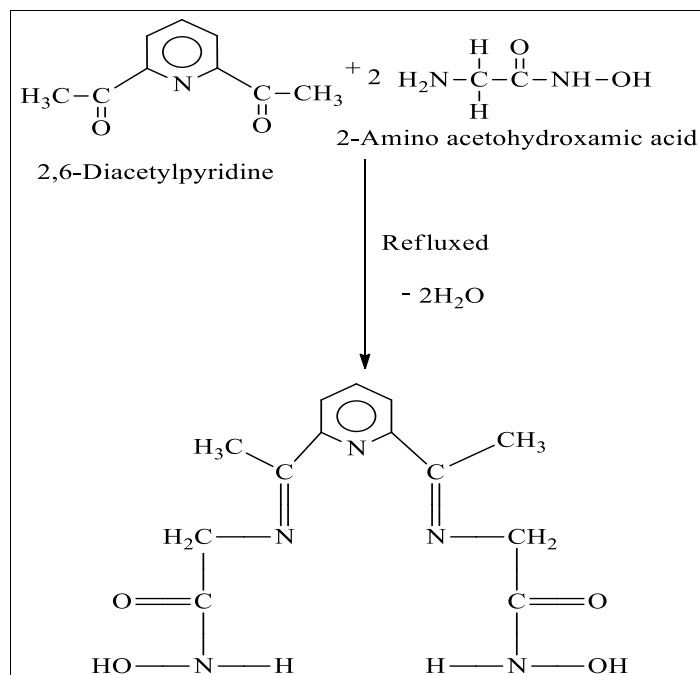
this paper we have synthesized and characterized Ni(II) complexes derived from 2-aminoacetohydroxamic acid.

### Materials and Methods

All the chemicals used in the synthesis of Schiff base ligand and its nickel(II) complexes were of analytical grade. All solvents have been used without further cleaning. The melting points of the synthesized nickel complexes were recorded with the Digital 9100 melting point apparatus. The elemental analysis of the investigated Schiff base and its complexes was performed with the Perkin-Elmer 2400 elemental analyzer. Molar conductivity of the synthesized nickel complexes was measured in  $10^{-3}$  M DMF solution on Elico conductive cells. The infrared spectra of the ligand and synthesized complexes were recorded on a Shimadzu infrared spectrophotometer with KBr discs in the range  $4000 - 400 \text{ cm}^{-1}$ . The electronic spectra of the complexes studied were recorded on a Perkin-Elmer UV spectrophotometer. Magnetic susceptibility of complexes has been measured on a Gouy balance using  $Hg[Co(SCN)_4]$  as standard.

### Synthesis of Schiff base Ligand (L)

The Schiff base ligand 2,6-bis(2-imino acetohydroxamic acid) di-acetyl pyridine was synthesized by the condensation of 1.632 g (0.01 mol) of 2,6-diacetylpyridine with 1.802 g (0.02 mol) of 2-amino acetohydroxamic acid in ethanol (20 ml). The resulting mixture was left under reflux for 3-4 hours and monitored by thin layer chromatography. After cooling, a yellowish solid was obtained and separated by filtration. The solid product was washed with ethyl alcohol and recrystallized with dimethyl ketone and dried in a vacuum over anhydrous  $CaCl_2$ . The M.P. of the yellowish solid was found to be  $192^\circ\text{C}$ .



**Fig1:** Synthesized Schiff base Ligand

### Synthesis of the Nicke(II) complexes

The NiCl<sub>2</sub>.6H<sub>2</sub>O was dissolved in aqueous ethanol solution. The Schiff base 2,6-bis (2-imino acetohydroxamic acid) diacetyl pyridine solution in ethanol was added with regular shaking. The ligand: metal molar ratio was always kept 1:1 respectively. The synthesized Ni (II) complexes were prepared with the Schiff base in presence of different co-ligands such as water, ammonia etc. The resulting solution was filtered and the filtrate was refluxed on water bath for 2-3 hours. The resultant coloured solid product was collected by filtration and washed with cold ethanol, and finally dried over anhydrous CaCl<sub>2</sub> in a desiccator.

### Results and discussion

The general formula for the synthesized complexes was found to be [M(L)(B)<sub>2</sub>], where M = Ni, L is a Schiff base, and B represents a base such as ammonia, water, pyridine, phenyl-isocyanide, and α-picoline. The experimental data show good agreement with those calculated from the suggested formula. The micro analytical data of Schiff base and complexes are presented in Table 1. The synthesized complexes were variously coloured, stable in air at room temperature and soluble in DMF and DMSO. The molar conductance data of complexes are presented in Table 2. The lower molar conductance (11-24 cm<sup>2</sup> mol<sup>-1</sup>) data, suggested non-electrolytic nature of complexes.

**Table 1:** Microanalytical data of Ni(II) complexes

Compounds	M.P (°C)	Colour	Found (Calculated) %			
			C	H	N	M
Ligand(L)	192	Yellowish	50.72(50.81)	5.52(5.58)	22.74(22.79)	-
[Ni(L)(H <sub>2</sub> O) <sub>2</sub> ]	240	Green	38.93(39.03)	4.72(4.79)	17.48(17.51)	14.62(14.67)
[Ni(L)(NH <sub>3</sub> ) <sub>2</sub> ]	252	Greenish white	39.18(39.23)	5.26(5.32)	24.54(24.63)	14.72(14.75)
[Ni(L)(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	260	Dark green	52.86(52.90)	4.80(4.83)	18.68(18.78)	11.20(11.24)
[Ni(L)(C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ]	265	Pale green	56.82(56.87)	4.32(4.42)	17.12(17.19)	10.23(10.29)
[Ni(L)(C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ]	258	Olive green	59.76(59.83)	4.65(4.70)	15.72(15.76)	9.41(9.43)
[Ni(L)(C <sub>5</sub> H <sub>4</sub> NCH <sub>3</sub> ) <sub>2</sub> ]	290	Green	54.52(54.57)	5.28(5.31)	17.74(17.82)	10.62(10.67)

**Table 2:** Molar conductance data of Ni(II) complexes

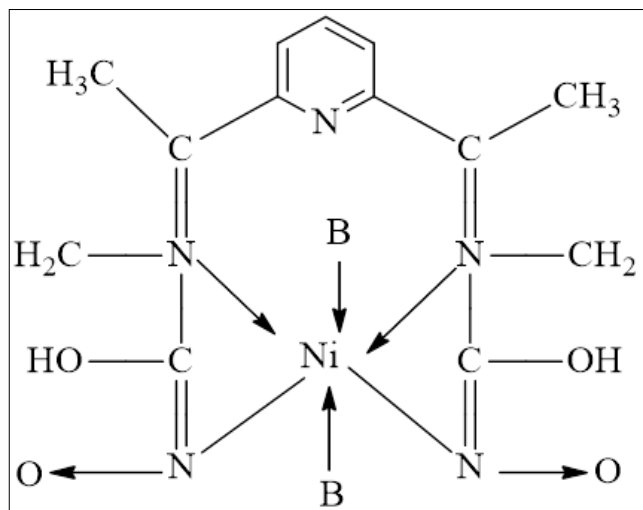
Compounds	Solvent	Molar Conductance (Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
[Ni(L)(H <sub>2</sub> O) <sub>2</sub> ]	DMF	15
[Ni(L)(NH <sub>3</sub> ) <sub>2</sub> ]	DMF	17
[Ni(L)(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	DMF	11
[Ni(L)(C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ]	DMF	20
[Ni(L)(C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ]	DMF	22
[Ni(L)(C <sub>5</sub> H <sub>4</sub> NCH <sub>3</sub> ) <sub>2</sub> ]	DMF	24

**Table 3:** Magnetic moment data of Ni(II) complexes

Compounds	(B.M)	Magnetic behaviour
[Ni(L)(H <sub>2</sub> O) <sub>2</sub> ]	3.16	Paramagnetic
[Ni(L)(NH <sub>3</sub> ) <sub>2</sub> ]	3.14	Paramagnetic
[Ni(L)(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	3.08	Paramagnetic
[Ni(L)(C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ]	3.01	Paramagnetic
[Ni(L)(C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ]	3.02	Paramagnetic
[Ni(L)(C <sub>5</sub> H <sub>4</sub> NCH <sub>3</sub> ) <sub>2</sub> ]	3.06	Paramagnetic

**Table 4:** Electronic absorption spectral data of Ni(II) complexes

Compounds	$\nu_1$ (cm <sup>-1</sup> )	$\nu_2$ (cm <sup>-1</sup> )	$\nu_3$ (cm <sup>-1</sup> )	Geometry
[Ni(L)(H <sub>2</sub> O) <sub>2</sub> ]	9890	15740	24890	Octahedral
[Ni(L)(NH <sub>3</sub> ) <sub>2</sub> ]	10130	16280	25520	Octahedral
[Ni(L)(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	10540	16960	26330	Octahedral
[Ni(L)(C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ]	11435	19060	28980	Octahedral
[Ni(L)(C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ]	10820	17790	27180	Octahedral
[Ni(L)(C <sub>5</sub> H <sub>4</sub> NCH <sub>3</sub> ) <sub>2</sub> ]	10650	17250	26680	Octahedral



B = Water, ammonia, pyridine, quinolone, phenyl isocyanide and  $\alpha$ -picoline

**Fig 2:** Synthesized Nickel(II) complexes

### IR spectra

The Schiff base ligand is highly sensitive to the enol form to form complexes. After deprotonating of two oxime (=N-O-H) groups and two azomethine groups participate in coordination with metal ion, suggested bi-anionic tetradentate nature of ligand. The broad and strong band located at 3260 cm<sup>-1</sup> due to vibrations of  $\nu$ (O-H) and  $\nu$ (N-H) of the ligand disappear in the complex formation and a new band appears around at 3430 cm<sup>-1</sup> in complexes confirming the presence of at least one free (O-H) group in complexes with weak H-bonding. The azomethine (>C=N) band at 1640 cm<sup>-1</sup> in Schiff base is also shifting to lower frequencies about at 45-60 in almost all metal complexes, which suggested the azomethine group participate in coordination with nickel ion. A strong band at 1240 cm<sup>-1</sup> in the Schiff base is disappearing in almost all complexes, suggested deprotonation of the (N-O-H) group. The two azomethine nitrogen atoms and two nitrogen atoms of deprotonated hydroxamic acid are the bonding sites of the ligand.

### Electronic absorption spectra and magnetic moment

The electronic spectral data of nickel complexes are presented in Table 4. The electronic spectra of ligand and nickel complexes were recorded at room temperature in DMSO. <sup>3</sup>A<sub>2g</sub> is the ground state term for nickel octahedral complexes. The nickel complexes show three absorption bands at 9890-11435 cm<sup>-1</sup>, 15740-19060 cm<sup>-1</sup> and 24890-28980 cm<sup>-1</sup>, corresponding to <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) transitions respectively. These data support the octahedral geometry of Ni(II) complexes. The magnetic moment data is presented in Table 3. The obtained magnetic moment data for nickel complexes in the range of 3.01 -3.16 B.M. These data suggested six coordinated high spin octahedral geometry of nickel complexes.

### NMR Spectra

The <sup>1</sup>H NMR spectra of the Schiff base and its Ni(II) complexes show characteristic signals due to azomethine, pyridyl, methyl, and methylene. Upon complexation, the signal of azomethine (8.46 ppm) shifted downfield to 8.55 - 8.64 in metal complexes, which suggested azomethine nitrogen atoms participate in coordination with nickel ion. In Schiff base, N-O-H and N-H signals are present but disappear in nickel complexes, which suggested deprotonation of the (N-O-H) group and coordinated through nitrogen atoms of hydroxamic acid. Additional signals also observed around 2.26-8.56 ppm due to co-ligands present in the complexes, which suggested formation of octahedral nickel (II) complexes.

### Conclusion

The present study reveals that the Schiff base 2,6-bis(2-iminoacetohydroxamic acid) diacetyl pyridine has been synthesized from the condensation reaction of 2,6-diacetyl pyridine with 2-amino acetohydroxamic acid in an alcoholic medium at room temperature. The Schiff base and its synthesized nickel complexes were characterized by elemental analysis, molar conductivity measurements, magnetic moment measurements, IR and UV-Vis spectral data investigations. The lower molar conductance value of the synthesized nickel(II) complexes in DMF solution indicates that the complexes are non-electrolytic in nature. The azomethine (>C=N) band at 1640 cm<sup>-1</sup> in Schiff base is also shifting to lower frequencies about at 45-60 cm<sup>-1</sup> in almost all metal complexes, which suggested the azomethine group participate in coordination with nickel ion. A strong band at 1240 cm<sup>-1</sup> in the Schiff base is disappearing in almost all complexes, suggested deprotonation of the (N-O-H) group. The two azomethine nitrogen atoms and two nitrogen atoms of deprotonated hydroxamic acid are the bonding sites of the ligand. The Schiff base behaves as biantionic tetradentate and coordinating through two nitrogen atoms of azomethine and two nitrogen atoms of deprotonated hydroxamic acid. On the basis of elemental analysis, magnetic moment measurements and different spectral data, octahedral geometry was proposed for nickel complexes.

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