

# Synthesis and Characterisation of Complexes of Cobalt(II) and Nickel(II) Metals with Tetradentate Schiff Base

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**Abstract :** The complexes of Cobalt(II) and Nickel(II) metals with tetradentate Schiff base have been prepared in presence of bases having nitrogen and oxygen atoms as their donor sites. On the characterisation of the ligand and the complexes, all the complexes have been found to be non-electrolyte, monomeric, paramagnetic and octahedral in geometry with molecular formula  $[M(L)(B)_2]$  where M=divalent Cobalt and Nickel metals, L=ligand and B=bases.

**IndexTerms** - Divalent transition metal, donor, ligand, complex, characterisation, octahedral geometry, solution, filtration, filtrate, precipitate.

## I. INTRODUCTION

Much work has been done on the formation of complexes of divalent transition metals with Schiff bases, but at least work has been carried out with such Schiff bases which contain *p*-methoxy-*o*-hydroxy acetophenone in its moiety. Therefore, in this paper, I report the formation of complexes of divalent Cobalt and Nickel metals with tetradentate Schiff base 1,2-di-imino-*bis*(*p*-methoxy-*o*-hydroxy acetophenonyl) ethane-1,2-dione in presence of bases like water, ammonia, phenyl isocyanide, quinoline and pyridine.

## II. PREPARATION OF THE LIGAND

The Schiff base ligand 1,2-di-imino-*bis*(*p*-methoxy-*o*-hydroxy acetophenonyl) ethane-1,2-dione has been prepared by the condensation of *p*-methoxy-*o*-hydroxy acetophenone (2 moles) and ethane-1,2-diamide (1 mole) at room temperature.

**Procedure:** A suspension of 1.70g (0.001 mole) of *p*-methoxy-*o*-hydroxy acetophenone (2 moles) and 0.8g (0.001 mole) of ethane-1,2-diamide was dissolved in minimum volume of ethyl alcohol and the solution was diluted up to 20ml by the addition of aqueous alcoholic solution. The resulting mixture-solution was heated on water-bath for 3 hours when a crystalline cream colour solid began to separate. It was heated further for half-an hour for the occurrence of complete reaction. Then it was cooled, filtered, washed with aqueous-ethanolic solution, dried and crystallised with methyl alcohol as cream colour solid was obtained with melting point 216°C. The compound was further analysed and found to contain Carbon=61.85%, Hydrogen=5.20% and Nitrogen=7.40% which corresponds to the molecular formula  $C_{20}H_{20}N_2O_6$ .

The identification of the compound was confirmed by IR and  $^1H$ NMR spectroscopy.

## III. PREPARATION OF CO(II) AND NI(II) COMPLEXES

A suspension of 0.4g (0.001 mole) of the ligand and 0.23g (0.001 mole) of Cobalt(II) chloride hexahydrate was also dissolved in aqueous-ethanolic solution and it was diluted up to 20ml. the molar ratio of the metal and the ligand was always kept into 1:1 ratio respectively. The resulting solution was heated under reflux on a hot water-bath for about two and half hour when a light brown crystalline solid was obtained which was separated by filtration. The crystalline solid was washed with small quantity of alcohol followed by ether and dried over KOH pellets placed in a desiccator.

Complexes of Co(II) cations were separately prepared in presence of aqueous and non-aqueous medium. Similar procedure was undertaken for the preparation of Nickel(II) complexes with the ligand and different Schiff bases with slight variation in time of reflux. The colour of crystals obtained in case of Nickel(II) complexes were found to be faint, light and dirty green and in some cases brownish green colour also.

### Analytical Table of Cobalt(II) and Nickel(II) Complexes

Found→% (Calculated→%)

S.N.	Compounds	Metal	Carbon	Hydrogen	Nitrogen
1.	[Co(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(H <sub>2</sub> O) <sub>2</sub> ]	12.10 (12.35)	50.08 (50.32)	4.66 (4.61)	6.00 (5.87)
2.	[Co(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(NH <sub>3</sub> ) <sub>2</sub> ]	12.08 (12.40)	50.10 (50.53)	5.08 (5.05)	11.90 (11.79)
3.	[Co(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ]	8.10 (8.42)	64.90 (65.24)	4.60 (4.57)	8.10 (8.01)
4.	[Co(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ]	8.80 (9.10)	62.74 (63.07)	4.34 (4.32)	8.90 (8.85)
5.	[Co(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	9.28 (9.60)	59.70 (60.11)	4.70 (4.67)	9.42 (9.35)
6.	[Ni(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(H <sub>2</sub> O) <sub>2</sub> ]	11.90 (12.13)	50.10 (50.34)	4.64 (4.61)	5.90 (5.87)
7.	[Ni(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(NH <sub>3</sub> ) <sub>2</sub> ]	12.08 (12.36)	50.14 (50.55)	5.10 (5.05)	11.90 (11.79)
8.	[Ni(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ]	8.12 (8.40)	64.90 (65.26)	4.61 (4.57)	8.10 (8.01)
9.	[Ni(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ]	8.82 (9.07)	62.74 (63.08)	4.36 (4.32)	8.72 (8.65)
10.	[Ni(C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> )(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	9.60 (9.80)	59.76 (60.13)	4.70 (4.67)	9.40 (9.35)

#### IV. ANALYTICAL METHODS

Cobalt was estimated volumetrically by oximato method and Nickel was gravimetrically estimated by dimethyl glyoximato method. Carbon, hydrogen and nitrogen was estimated semi-micro combustion method.

The magnetic moment of Cobalt(II) and Nickel(II) complexes has been measured by using Gouy's method. The values of magnetic moment of Cobalt(II) and Nickel(II) complexes have been found in the range of 4.90-5.10BM and 3.34-3.48BM respectively indicating octahedral geometry for all the complexes.

Electronic spectra of cobalt(II) and Nickel(II) complexes have been recorded with Hitachi-320 spectrophotometer. A broad and unsymmetrical band has been obtained in the range of 21,400-22,100cm<sup>-1</sup> due to <sup>4</sup>T<sub>1g</sub>(F)→<sup>4</sup>T<sub>1g</sub>(P) transition indicating distorted octahedral geometry for Co(II) complexes.

In case of Nickel(II) complexes, three bands around 8,250-8340cm<sup>-1</sup>, 15,350-15,950cm<sup>-1</sup> and 20,200-20,900cm<sup>-1</sup> have been obtained due to <sup>3</sup>A<sub>2</sub>(F)→<sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>A<sub>2</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) transition respectively which suggest octahedral geometry for Nickel(II) complexes.

I.R. spectra of the ligand and the complexes of both the metal cations have been recorded on Perkin Elmer-577 spectrophotometer using KBr pellets in the range of 4,000-400cm<sup>-1</sup>.

The ligand molecule displays highest IR band at near 3,430cm<sup>-1</sup> which may be due to the vibration of OH bond. In the ligand molecule, two bands obtained around 1,690cm<sup>-1</sup> and 1,640cm<sup>-1</sup> are attributed due to ν<sub>(C=O)</sub> and ν<sub>(C=N)</sub> frequencies respectively. The band obtained at 1,480cm<sup>-1</sup> is attributed due to ν<sub>(C-N)</sub> frequency. The two bands around 1,430cm<sup>-1</sup> and 1,150cm<sup>-1</sup> are obtained due to □<sub>(C-O)</sub> phenolic group and deformation of phenolic (C-O) group.

It has been found that in the Schiff base ligand, two hydroxy (OH) of the ligand molecule will be deprotonated forming bi-negative tetradentate molecule.

In this case, two protons of the phenoxy (OH) groups are lost producing bivalent ions. The resulting ligand act as tetradentate molecule which coordinate through two deprotonated phenolic oxygen atoms and two aldimino (azomethine) nitrogen atoms.

In all the complexes, the highest band obtained in the ligand molecule at  $3,430\text{cm}^{-1}$  due to phenolic (OH) frequency disappears in all the complexes supporting the deprotonation of phenolic (OH) and coordination of phenolic oxygen to the bond formation with the metal ion. The  $\nu_{(\text{C-O})}$  vibration of phenolic (C-O) group shifts to the higher frequency in the complexes suggesting increase of bond order of (C-O) group in the complexes.

A strong and sharp band around  $1,690\text{cm}^{-1}$  obtained in the ligand molecule has been found to be intact in the complexes indicating that condensation of (C=O) group of the ligand molecule could not take place during the course of complex formation with the ligand.

A strong and sharp band obtained around  $1,640\text{cm}^{-1}$  due to  $\nu_{(\text{C=N})}$  vibrations has been reduced to  $1,590\text{cm}^{-1}$  suggesting the coordination of azomethine nitrogen (aldimino) atoms in the bond formation with the metal cation.

A medium and sharp band obtained around  $1,480\text{cm}^{-1}$  due to  $\nu_{(\text{C-N})}$  vibrations has been reduced to  $1,450\text{cm}^{-1}$  suggesting the coordination of amide II nitrogen in the bond formation with the metal cation.

In case of aquo-complexes, separate band for coordinated  $\text{H}_2\text{O}$  has not been obtained as it is overlapped by  $\nu_{(\text{OH})}$  vibration. The frequencies obtained in the range of  $700\text{-}800\text{cm}^{-1}$  in aquo-complexes may be assigned due to rocking mode of coordinated water. In quinoline complexes, a sharp and medium band obtained around  $1,420\text{cm}^{-1}$  in the complexes indicates the support of N-atom of quinoline in the complex formation.

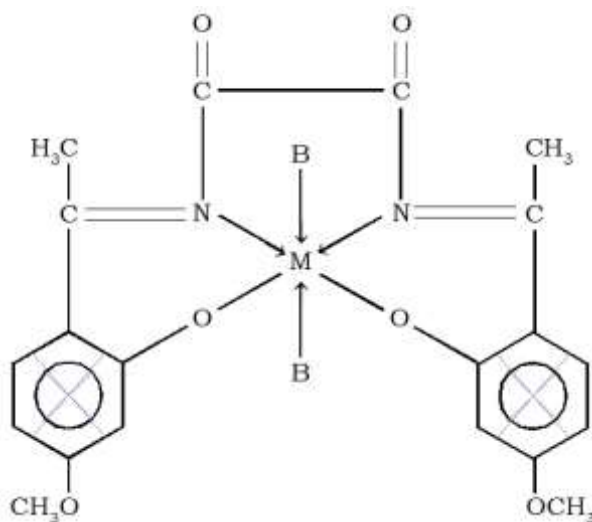
The pyridine ring breathing mode of vibration located at  $940\text{-}1,090\text{cm}^{-1}$  in complexes have been regarded as the characteristic vibrations of the coordinated pyridine. The IR band at  $570\text{-}590\text{cm}^{-1}$  in the complexes are also characteristic of presence of pyridine molecule in the complexes. A sharp and weak band around  $2,230\text{cm}^{-1}$  indicates the presence of phenyl isocyanide in the complexes.

The coordination through oxygen atom of phenolic group (-OH) has been further confirmed by the appearance of a band at  $560\text{-}590\text{cm}^{-1}$  in the complexes due to  $\nu_{(\text{M-O})}$  vibrations.

The coordination through aldimino (azomethine) nitrogen has been further confirmed by the appearance of a band about  $420\text{-}410\text{cm}^{-1}$  in the complexes due to  $\nu_{(\text{M-N})}$  vibrations.

Thus from the above discussion, it is proposed that two oxygen atoms in the phenolic -OH group and two nitrogen atoms of (azomethine group) are the bonding sites of the Schiff base ligand 1,2-di-imino-bis(*p*-methoxy-*o*-hydroxy acetophenonyl) ethane-1,2-dione. On the basis of elemental analysis and measurement of electrical conductance, all the complexes have been found to be monomeric and non-electrolyte in nature.

Thus on the basis of elemental analysis, measurement of magnetic moment, electrical conductance, electronic spectra and IR spectra of the ligand and the complexes and bonding sites of the ligand, the probable structure of all the complexes having general molecular formula  $[\text{M}(\text{L})(\text{B})_2]$  has been suggested to be octahedral in nature as shown below:



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