

Studies of Spectral and Magnetic Behavior of Nickel(II) Complexes with Tridentate Schiff Base

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Abstract : The complexes of the type $[\text{Ni}(\text{L})(\text{B})_3]$ have been prepared in presence of bases having nitrogen and oxygen atoms as their donor sites. In the general formula of the complexes, M=Nickel(II), L=2(2-hydroxy benzyldine) imino benzohydroxamic acid and B=bases such as water, ammonia, phenyl-isocyanide, quinoline, pyridine and different picolines. On the basis of characterisation by elemental analysis, measurement of electrical conductance, magnetic moment, electronic and IR spectra, all the complexes have been found to be non-electrolyte, mono-meric, paramagnetic and octahedral in geometry.

Keywords - Schiff base, tri-dentate, characterisation, magnetic moment, electrical conductance, complex, ligand, donor site, solution, solvent, filtrate, filtration, precipitate.

I. INTRODUCTION

Much work on divalent transition metal chelates has been carried out with Schiff bases obtained by the condensation of primary amine and a carbonyl compound. But at least work has been reported about formation of chelates of divalent transition metals with such Schiff bases which contain derivative of hydroxamic acid as functional group in its moiety. Therefore, in this paper, I report the formation of some chelates of divalent Nickel metal due to their wide application in the field of medicines, antimicrobial, industry and fertilisers.

II. PREPARATION OF LIGAND

This Schiff base compound has been prepared by the condensation reaction of 2-hydroxy benzaldehyde (salicylaldehyde) and 2-amino benzohydroxamic acid at reflux temperature.

Procedure: 12.4g (0.1 mole) of 2-hydroxy benzaldehyde was completely dissolved in minimum volume of ethyl alcohol and 17.4g (0.1 mole) of 2-amino benzohydroxamic acid was dissolved in glacial acetic acid. Both the solutions were mixed together gradually and the resulting solution was vigorously and continuously stirred until a brownish yellow precipitate appeared in the solution. This was then refluxed for half an hour.

A clear brownish yellow solution was obtained which on cooling produced brownish crystals of Schiff base. The compound was separated by filtration, washed with cold water, followed by a little alcohol and then recrystallized with methyl alcohol. The compound was found to be soluble in acetone and the melting point of the compound was recorded and found to be 130°C.

The compound was further analysed and found to contain carbon=65.24%, hydrogen=4.66% and nitrogen=10.95% which corresponds the molecular formula $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$.

The identification of the compound was confirmed by I.R. and ^1H NMR spectroscopy.

Preparation of Ni(II) Complexes:

0.23g (0.001 mole) of Nickel(II) chloride hexahydrate was completely dissolved in aqueous-ethanolic solution and 0.272g (0.001 mole) of the ligand was dissolved in ethyl alcohol. Both the solution were mixed together gradually with regular shaking. The resulting solution was then refluxed for 40-50 minutes on water-bath at room temperature. The colour of the solution was gradually changed and crystals having faint-green, in some cases dirty green colour, was separated out by allowing the solution to stand overnight. The product was separated by filtration, washed with a small amount of acetone and dried over KOH pellets placed in desiccator.

The complexes of Ni(II) cations were prepared separately keeping the metal-ligand ratio as 1:1 respectively in each case in presence of bases like water, ammonia, phenyl isocyanide, quinoline, pyridine, α -, β - and γ -picolines.

Analytical Data of Nickel(II) ComplexesFound \rightarrow % (Calculated \rightarrow %)

S.N.	Compounds	Metal	Carbon	Hydrogen	Nitrogen
1.	[Ni(C ₁₄ H ₁₀ N ₂ O ₃)(H ₂ O) ₃]	15.62 (16.00)	45.40 (45.81)	4.40 (4.36)	7.70 (7.63)
2.	[Ni(C ₁₄ H ₁₀ N ₂ O ₃)(NH ₃) ₃]	15.96 (16.31)	45.76 (46.19)	5.24 (5.22)	19.30 (19.24)
3.	[Ni(C ₁₄ H ₁₀ N ₂ O ₃)(C ₆ H ₅ NC) ₃]	9.14 (9.44)	67.15 (67.55)	4.44 (4.02)	11.30 (11.25)
4.	[Ni(C ₁₄ H ₁₀ N ₂ O ₃)(C ₉ H ₇ N) ₃]	8.10 (8.38)	69.96 (70.31)	4.44 (4.43)	10.10 (10.00)
5.	[Ni(C ₁₄ H ₁₀ N ₂ O ₃)(C ₅ H ₅ N) ₃]	10.32 (10.67)	62.92 (63.30)	4.60 (4.54)	12.82 (12.73)
6.	[Ni(C ₁₄ H ₁₀ N ₂ O ₃)(C ₅ H ₄ NCH ₃) ₃] α -picoline	9.40 (9.92)	64.44 (64.89)	5.24 (5.23)	11.90 (11.83)
7.	[Ni(C ₁₄ H ₁₀ N ₂ O ₃)(C ₅ H ₄ NCH ₃) ₃] β -picoline	9.44 (9.92)	64.48 (64.89)	5.26 (5.23)	11.92 (11.83)
8.	[Ni(C ₁₄ H ₁₀ N ₂ O ₃)(C ₅ H ₄ NCH ₃) ₃] γ -picoline	9.56 (9.92)	64.56 (64.89)	5.22 (5.23)	11.88 (11.83)

On the basis of elemental data of Nickel(II) complexes with the ligand, in the presence of bases, have been found to be mono-meric with molecular formula [Ni(L)(B)₃] where L=ligand and B=bases.

CHEMICALS REQUIRED: 2-amino benzo hydroxamic acid, salicylaldehyde, DMF, ethyl alcohol, ammonia, phenyl isocyanide, quinoline, pyridine and different picolines.

ANALYTICAL METHODS: The estimation of metals and non-metals present in the ligand and the complexes has been done by standard methods-

- (i) Nickel: Nickel has been estimated gravimetrically by dimethyl glyoximate method.
- (ii) Hydrogen, Carbon and Nitrogen have been estimated by semi-micro combustion method.

III. RESULT AND DISCUSSION

The values of electrical conductivity for Nickel(II) complexes have been obtained in the range of 12-18hm which indicate non-electrolyte nature of complexes of Nickel(II) cations. The values of magnetic moment of Nickel(II) complexes obtained in the range of 3.10-3.30BM indicates octahedral geometry for all the complexes.

ELECTRONIC SPECTRA OF THE COMPLEXES: In case of Nickel(II) complexes, three electronic bands corresponding to $\nu_1=^3A_{2g}(F)\rightarrow^3T_{2g}(F)$ at $8,150\text{cm}^{-1}$, $\nu_2=^3A_{2g}(F)\rightarrow^3T_{1g}(F)$ at $15,200\text{-}15,900\text{cm}^{-1}$ and $\nu_3=^3A_{2g}(F)\rightarrow^3T_{1g}(P)$ at $20,600\text{-}21,200\text{cm}^{-1}$ transitions have been obtained which clearly suggest octahedral geometry for all the complexes.

The value of B obtained on the basis of $\nu_1+\nu_2-\nu_3=15B$ equation has been found to be $1,040\text{cm}^{-1}$ which also suggest octahedral geometry for all the complexes.

COMPARISON OF I.R. BANDS OF THE LIGAND AND THE COMPLEXES: From the comparison of IR spectral data of the ligand and the complexes, it is concluded that there are appreciable changes in the frequency of enolic (OH), azomethine (C=N) and hydroxamic acid part (C=N-O).

In free ligand, a strong and sharp band due to H-bonded (OH) group has been obtained at $3,260\text{cm}^{-1}$.

A strong and sharp band obtained at $3,420\text{cm}^{-1}$ in the ligand molecule due to the vibration of phenolic -OH group, disappears in all the complexes indicating the deprotonation of phenolic -OH group. A medium and sharp band obtained at $1,510\text{cm}^{-1}$ has been assigned due to the vibration of phenolic C-O group in the ligand molecule. This band position has been shifted to $1,540\text{cm}^{-1}$ suggesting increase in bond order of (C-O) group in the complexes. This means that oxygen atom of phenolic -OH group takes part in the bond formation with the metal cations.

In all the complexes, hydrogen bonding between enolic (OH) and hydroxamic acid part (OH) is not completely broken but due to the deprotonation of (N-OH) part hydrogen, the hydrogen bond remains between enolic (OH) and oximino oxygen atom with lower strength. The band obtained at $3,260\text{cm}^{-1}$ due to (OH) group has been shifted to $3,340\text{cm}^{-1}$ in the complexes indicating the presence of at least one (OH) group even after complex formation.

In free ligand, a sharp and medium band obtained at $1,640\text{cm}^{-1}$ due to (C=N) vibrations has been reduced to $1,590\text{cm}^{-1}$ in the complexes. This reduction in (C=N) frequency indicates the coordination of azomethine nitrogen atom in bond formation with the metal cation. The sharp and medium band obtained at $1,080\text{cm}^{-1}$ due to (N-O) stretching vibration of the ligand has been increased to $1,130\text{cm}^{-1}$ indicating the participation of oximino nitrogen in the complex formation.

Thus the ligand 2(2-hydroxy benzylidene) imino benzo hydroxamic acid behaves as bi-anionic tridentate molecule. The azomethine or aldimino nitrogen and oximino nitrogen attached to the benzene nucleus are the donor sites of the ligand.

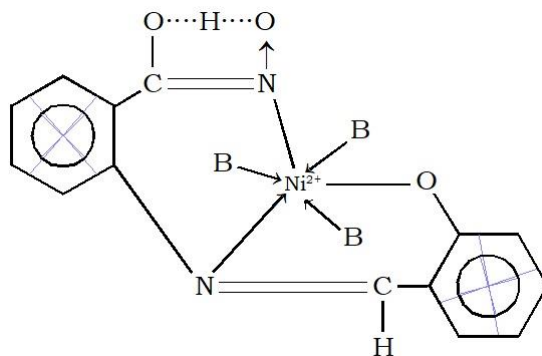
For aquo and amine complexes, no separated band is obtained as it is overlapped by that of (OH) vibrations. A sharp and medium band obtained at $1,020\text{cm}^{-1}$ in the complexes indicates the coordination of quinoline and pyridine in the complex formation. A sharp and medium band due to phenyl isocyanide obtained at $2,190\text{cm}^{-1}$ and $2,230\text{cm}^{-1}$ in free phenyl isocyanide and complexes respectively indicates the coordination of nitrogen atom of phenyl isocyanide in the bond formation with the metal cations.

Two new sharp and medium bands obtained at $440\text{-}450\text{cm}^{-1}$ and $520\text{-}540\text{cm}^{-1}$ due to (M-N) and (M-O) vibrations respectively further confirm the participation of nitrogen and oxygen atoms in complex formation.

The complexes, $[\text{Ni}(\text{L})(\text{B})_3]$ are quite stable at room temperature. They are stable even upto 140°C and neither change colour nor lose any weight indicating that bases like water, ammonia, phenyl isocyanide

and pyridine are bonded to the metal in these complexes. In the case of aquo complexes, the complexes retain water molecules even at 140°C suggesting the coordinated nature of H₂O. The electrical conductance of the complexes at room temperature falls in the range of 12-18 mho which indicates that these complexes are non-electrolyte in nature.

Thus on the basis of elemental analysis, magnetic moment and molar conductance measurements and spectral studies, it is suggested that Ni(II) cations forms octahedral complexes with the ligand 2-(2-hydroxy benzylidene) imino benzo hydroxamic acid in presence of the bases like water, ammonia, quinoline, phenyl isocyanide and pyridine.



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