

Preparation of Some Complexes of Divalent Nickel(II) and Iron(II) Metals with Tri-dentate Schiff Base

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Abstract : Some complexes of divalent Nickel and Iron metals have been prepared with tri-dentate Schiff base, 5-bromo salicylaldehyde-o-hydroxyhydrazone in presence of bases which have nitrogen and oxygen atoms as their donor sites. On characterisation of the ligand and the complexes by usual physico-chemical methods, all the complexes of Ni(II) and Fe(II) metals were found to be non-electrolyte, mono-meric, paramagnetic octahedral in nature with general molecular formula $[M(L)(B)_3]$ where M = Ni(II) and Fe(II) cations, L = Ligand and B = bases.

KEY WORDS: divalent transition metals, oxidation state, complex, ligand, solution, cation, paramagnetic, octahedral geometry.

I. INTRODUCTION

In absence of Schiff bases as ligand, the field of formation of complex compounds is shortened. A considerable amount of research work has been carried for the formation of coordination compounds with such bases which don't have o-hydroxy phenyl hydrazine in its moiety. So, in this paper, I report the formation of complexes of divalent of Nickel and Iron metals with tridentate Schiff base, which contains o-hydroxy phenyl hydrazine in its moiety. Such complexes have their major application in the field of industry, pharmacology and fertilisers.

Preparation of the ligand: 12.4g (0.01 mole) of o-hydroxy phenyl hydrazine hydrochloride was completely dissolved in ethanol. A minimum volume of 10% solution of sodium acetate was added to the solution to neutralise the solution. After that, an ethanolic solution containing 18.5g (0.1 mole) of 5-bromo salicylaldehyde was added gradually to neutral solution containing o-hydroxy phenyl hydrazine with regular shaking. The resulting solution was then heated on water-bath for about three hours under suitable conditions. After that, the solution was cooled under tap-water, followed by ice-bath. On cooling the solution, light yellowish solid was obtained. The solid was separated by filtration under suction. Then it was washed with cold water and a little ether. The compound was found to be soluble in organic solvents but more soluble in ethyl alcohol. The compound was recrystallized with ether and dried over in an oven. The melting point of the compound was recorded and found to be ± 2 , 187°C.

The compound was further analysed and found to contain carbon = 53.26%, hydrogen = 3.78%, nitrogen = 9.70% and bromine = 27.20% which corresponds to the molecular formula $C_{13}H_{11}N_2OBr$.

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

Preparation of the complexes: 0.24g (0.001 mole) of Nickel(II) chloride hexahydrate was completely dissolved in minimum volume of water. Similarly, 6.3g (0.001 mole) of the ligand was completely dissolved in ethanolic solution. Both the solutions were gradually mixed together and shaken well. Then the resulting solution was refluxed on water-bath for about an hour at room temperature. During the course of the reflux, the colour of the solution gradually changed and crystals of light and dirty green colour were obtained by allowing the solution to stand over-night in the cub-board. The compound was separated by filtration and then washed with acetone and dried over KOH placed in a desiccator.

Similar procedure was adopted for the preparation of the complexes of Fe(II) metals. The complexes of Fe(II) and Ni(II) metals with the ligand have been prepared separately in presence of bases like ammonia, quinoline, phenyl isocyanide, pyridine. In each case, the ratio of metal and ligand was always kept 1:1 respectively. In case of Fe(II) metal, the complex was obtained with slight variation of colour.

Analytical Table of Nickel(II) and Fe(II) Complexes

Found→% (Calculated→%)

S.N.	Compounds	Metal	Carbon	Hydrogen	Nitrogen	Bromine
1.	[Ni(C ₁₃ H ₉ N ₂ O ₂ Br)(H ₂ O) ₃]	13.76 (14.05)	35.82 (37.34)	4.01 (3.59)	6.76 (6.70)	18.90 (19.15)
2.	[Ni(C ₁₃ H ₉ N ₂ O ₂ Br)(NH ₃) ₃]	13.82 (14.15)	37.10 (37.61)	4.36 (4.34)	16.96 (16.87)	19.00 (19.29)
3.	[Ni(C ₁₃ H ₉ N ₂ O ₂ Br)(C ₆ H ₅ NC) ₃]	8.54 (8.72)	66.20 (60.65)	3.60 (3.56)	10.48 (10.40)	11.50 (11.89)
4.	[Ni(C ₁₃ H ₉ N ₂ O ₂ Br)(C ₉ H ₇ N) ₃]	7.48 (7.81)	63.52 (63.94)	4.01 (3.99)	9.40 (9.32)	10.32 (10.65)
5.	[Ni(C ₁₃ H ₉ N ₂ O ₂ Br)(C ₅ H ₅ N) ₃]	9.44 (9.77)	55.48 (55.93)	4.00 (3.99)	11.70 (11.65)	13.02 (13.31)
6.	[Fe(C ₁₃ H ₉ N ₂ O ₂ Br)(H ₂ O) ₃]	13.12 (13.49)	37.20 (37.59)	3.64 (3.61)	6.52 (6.46)	18.96 (19.27)
7.	[Fe(C ₁₃ H ₉ N ₂ O ₂ Br)(NH ₃) ₃]	13.30 (13.59)	37.44 (37.86)	4.40 (4.36)	17.10 (16.99)	19.04 (19.41)
8.	[Fe(C ₁₃ H ₉ N ₂ O ₂ Br)(C ₆ H ₅ NC) ₃]	8.10 (8.35)	60.40 (60.89)	3.60 (3.58)	10.50 (10.44)	11.60 (11.94)
9.	[Fe(C ₁₃ H ₉ N ₂ O ₂ Br)(C ₉ H ₇ N) ₃]	7.16 (7.48)	63.80 (64.17)	4.04 (4.01)	9.46 (9.35)	10.40 (10.69)
10.	[Fe(C ₁₃ H ₉ N ₂ O ₂ Br)(C ₅ H ₅ N) ₃]	9.08 (9.36)	55.82 (56.18)	4.04 (4.01)	11.80 (11.70)	13.06 (13.37)

The elemental data of Nickel(II) and Iron(II) complexes indicate mono-meric nature with molecular formula [M(L)(B)₃] where M = Nickel(II) and Iron(II) cation, L = ligand and B = bases.

II. ANALYTICAL METHOD

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 glyoximato method.
- (ii) **Iron:** Iron is volumetrically estimated by dichromate titration method.
- (iii) **Carbon, Hydrogen and Nitrogen** have been estimated by semimicro combustion method.

ELECTRICAL CONDUCTIVITY: Electrical conductivity of the solution of the complexes has been measured by conductivity meter bridge manufactured by WissTechenWearchStathen type-LBR at room temperature.

I.R.: Perkin Elemer 577 spectrophotometer has been used to measure infra-red spectra of the ligand and the complexes.

U.V.-VISIBLE SPECTROPHOTOMETRIC MEASUREMENT: The electronic spectra of the complexes have been recorded by using Hitachi-320 spectrophotometer.

MAGNETIC SUSCEPTIBILITY: Magnetic susceptibility of the complexes has been measured by Gouy's method.

III. RESULTS AND DISCUSSION

The values of electrical conductivity for Nickel(II) and Iron(II) complexes have been obtained in the range of 12-18 and 8-14ohm respectively which indicate non-electrolyte nature of complexes of Nickel(II) and Iron(II) cations. The values of magnetic moment of Nickel(II) complexes obtained in the range of 3.30-3.40BM indicates octahedral geometry for all the complexes. The values of magnetic moment of Iron(II) complexes obtained in the range of 4.98-5.10BM indicates octahedral geometry for all the complexes.

ELECTRONIC SPECTRA OF THE COMPLEXES:In Iron(II) complexes, a broad and unsymmetrical band obtained in the range of 10,500-10,850 cm^{-1} due to ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition indicates octahedral geometry for all the complexes.

In case of Nickel(II) complexes, three electronic bands corresponding to $\nu_1 = {}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ at 8,050-8,160 cm^{-1} , $\nu_2 = {}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ at 15,400-16,100 cm^{-1} and $\nu_3 = {}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions have been obtained which clearly suggest octahedral geometry for all the complexes.

The value of B obtained on the basis of $\nu_3 + \nu_2 - 3\nu_1 = 15B$ equation has been found to be 1,040 cm^{-1} which also suggest octahedral geometry for all the complexes.

COMPARISON OF I.R. BANDS OF THE LIGAND AND THE COMPLEXES: The ligand molecule and the complexes have so many bands, most of which have no importance but some of them are very important to decide the bonding sites of the ligand and the structure of the complexes.

A strong and sharp band obtained at 3,450 cm^{-1} due to the vibration of combined (NH+OH) groups disappears in all the complexes suggesting the deprotonation of phenolic -OH group. The medium and sharp band obtained at 1,320 cm^{-1} due to the deformation vibration of phenolic -OH group disappears in the complexes supporting the deprotonation of phenolic (-OH) group. A sharp and medium band obtained at 1,530 cm^{-1} due to the vibration of phenolic (C-O) group has been shifted to 1,560 cm^{-1} in the complexes supporting the deprotonation of phenolic -OH group and participation of oxygen atom of phenolic -OH group in the bond formation with the metal cation.

A sharp and medium band obtained at 3,510 cm^{-1} in the ligand molecule remains intact after complex formation. This indicates that imino hydrogen atom is not deprotonated and imino nitrogen don't take part in the bond formation with metal cation.

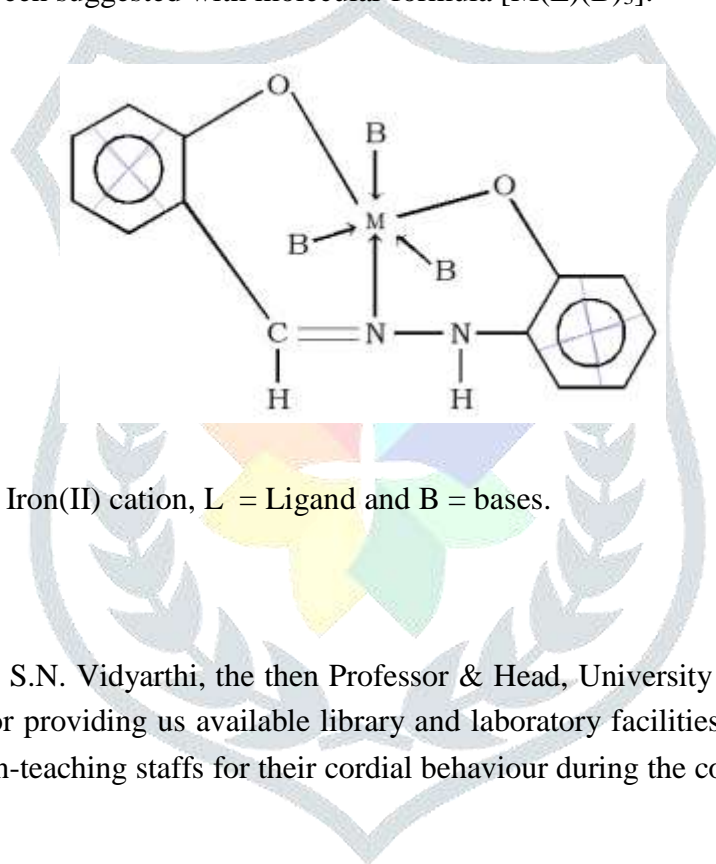
A strong and sharp band obtained at 1,640 cm^{-1} in the ligand molecule due to the vibration of azomethine group (>C=N-) has been reduced to 1,580 cm^{-1} in the complexes. This reduction indicates the participation of aldimino or azomethino nitrogen atom in the bond formation with the metal cation. A medium and sharp band obtained at 670 cm^{-1} due to the vibration of (N-N) group in the ligand molecule has been reduced to 620 cm^{-1} in the complex, supporting the participation of aldimino nitrogen in the complex formation. Thus, two oxygen atoms of phenolic -OH groups and one nitrogen atom of azomethine group are the bonding sites of the ligand molecule. Thus ligand molecule behaves as bi-anionic tridentate.

The new bonds obtained around 440 cm^{-1} and 540 cm^{-1} due to the vibrations of (M-N) and (M-O) bonds further confirms the participation of oxygen and nitrogen atoms in the bond formation with the metal cation.

For aquo and amine complexes, no separate band is obtained as it is overlapped by that of (OH) vibration. A sharp and medium band obtained at $3,360\text{cm}^{-1}$ due to the combined vibrations of (NH+OH) group indicates the presence of coordination of water ammonia molecules in the bond of formation with the metal.

A sharp and medium band due to phenyl isocyanide obtained at $2,180\text{cm}^{-1}$ and $2,220\text{cm}^{-1}$ in the ligand and the complexes respectively. This increase in the band position indicates the coordination of nitrogen atom of isocyanide group in the bond formation with the metal cations. In quinoline complexes, a medium and broad band obtained around $1,430\text{cm}^{-1}$ due to ring vibration indicates the involvement of N-atom of quinoline in the complex formation. Pyridine displays bands in finger print and far infra-red region. The bands obtained around $910-930\text{cm}^{-1}$ and $540-560\text{cm}^{-1}$ in the complexes are also special bands to indicate the presence of pyridine in the complexes.

Thus on the basis of elemental analysis, measurement of electrical conductance, magnetic moment, electronic and IR spectral behaviours of the ligand and Nickel(II) and Fe(II) complexes in presence of bases, octahedral geometry has been suggested with molecular formula $[\text{M}(\text{L})(\text{B})_3]$.



where M = Nickel(II) and Iron(II) cation, L = Ligand and B = bases.

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