

Studies of Spectral and Magnetic Behaviour of Some Complexes of Divalent Nickel and Iron Metals with Polydentate Schiff base as Ligand

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Abstract—First of all in 1869, H. Schiff a product obtained by the condensation of a primary amine and a carbonyl compound. In order to perpetuate the name of discoverer the product was later on known as Schiff base. We have prepared a Schiff base, Bis (O-benzophenone) di-amino propane by the condensation of 1,3 di-amino propane and (O-hydroxy phenone) under suitable condition. On the characterization, the ligand molecule has been found to be bi-anionic tetradentate. The complexes of Nickel (II) and Iron (II) have been prepared separately with this ligand in presence of bases containing Nitrogen and Oxygen atoms as their donor sites. By the characterization of the complexes by usual physico chemical methods, all the complexes have been found to be non-electrolyte, mono-metric, paramagnetic with octahedral geometry.

Index Terms—Magnetic, Structural studies, Spectral, ligand, derivative, condensation, donor site, paramagnetic geometry, filtration, Schiff base, tetradentate etc.

I. INTRODUCTION

A considerable amount of research work has been carried out for the formation of complexes of divalent transition metals with polydentate ligands containing Oxygen, Nitrogen and Sulphur atoms as their donor sites, But a least work has been done with the Schiff base derived by the condensation of o-hydroxy benzophenone and 1,3-diamino propane. Therefore, we have undertaken to report the formation of complexes of divalent Nickel and Iron metals with bis(o-hydroxy benzophenone) di-imino propane which has been derived from 1,3-diamino propane and O-hydroxy benzophenone.

Preparation of the ligand: It has all ready been given in paper-I

Preparation of the Complexes:

Procedure:-0.001 mole (0.24 gram) of Nickel (II) chloride hexa hydrate was dissolved in aqueous-ethnolic solution and similarly 0.001 mole (0.434 gram) of the ligand was completely dissolved in minimum volume of ethyl alcohol. Both the solutions were mixed together gradually with regular shaking. A minimum volume of ammonia was added to the resulting solution to make it alkaline. Then the resulting solution was filtered and filtrate was collected in small round bottom flask. After that the filtrate was refluxed under reflux for two and half an hour. Then faint green crystalline solid was separated in the solution. The crystalline solid was separated by filtration and the solid was washed with a small amount of acetone followed by ether. Then the product was dried over KOH pellets placed in a desiccators. The metal and the ligand ratio was always kept 1:1. Similarly the complexes of Nickel (II) metal has been prepared separately presence of bases like Ammonia, Phenylisocyanide, quinoline, and pyridine. There are slight variation in the colour of the complexes and time of reflux.

The Similar procedure was adopted for the preparation of Iron(II) complexes with the same ligand and the bases with slight variation of time and colour of the complexes obtained.

In case of Iron(II) complex formation, freshly prepared solution of Iron heptahydrate was taken as precautions to prevent the oxidation of divalent Iron to Tri-valent iron.

Table No. 1
Elemental analysis of Nickel(II) & Iron (II) Complexes
Found and (Calculated)

Compounds	Metal	Carbon	Hydrogen	Nitrogen
[Ni (C ₂₉ H ₂₄ N ₂ O ₂)(H ₂ O) ₂]	10.96 (11.14)	65.80 (66.07)	5.32 (5.30)	5.34 (5.32)
[Ni (C ₂₉ H ₂₄ N ₂ O ₂)(NH ₃) ₂]	11.00 (11.18)	66.06 (66.32)	5.72 (5.71)	10.70 (10.67)
[Ni (C ₂₉ H ₂₄ N ₂ O ₂)(C ₆ H ₅ NC) ₂]	8.14 (8.42)	73.78 (74.06)	4.90 (4.88)	8.10 (8.03)
[Ni (C ₂₉ H ₂₄ N ₂ O ₂)(C ₉ H ₇ N) ₂]	7.62 (7.84)	75.13 (76.33)	5.10 (5.07)	7.50 (7.47)
[Ni (C ₂₀ H ₂₄ N ₂ O ₂)(C ₅ H ₅ N) ₂]	11.78 (11.99)	65.48 (65.72)	5.68 (5.66)	10.60 (10.57)
[Cu (C ₂₉ H ₂₄ N ₂ O ₂)(H ₂ O) ₂]	10.68 (10.32)	66.41 (65.82)	5.36 (5.34)	5.40 (5.34)
[Cu (C ₂₉ H ₂₄ N ₂ O ₂)(NH ₃) ₂]	10.10 (10.72)	66.40 (66.66)	5.76 (5.74)	10.80 (10.72)
[Cu (C ₂₉ H ₂₄ N ₂ O ₂)(C ₆ H ₅ NC) ₂]	7.82 (8.06)	73.78 (74.35)	4.90 (4.89)	8.10 (8.06)
[Cu (C ₂₉ H ₂₄ N ₂ O ₂)(C ₉ H ₇ N) ₂]	7.12 (7.50)	75.10 (75.60)	5.10 (5.09)	7.56 (7.50)
[Cu (C ₂₀ H ₂₄ N ₂ O ₂)(C ₅ H ₅ N) ₂]	8.30 (8.66)	71.80 (72.44)	5.30 (5.26)	4.70 (8.66)

On the basis of elemental analysis of the ligand and the complexes, the general molecular formula of the complexes has been found to be [(M(L)(B)₂]. Where M=Nickel(II) and Iron (II) Metals L=Ligand and B=Bases. The complexes has been found to be Monomeric.

Chemical required: Acetates/ Chlorides of Nickel (II) and Iron (II) metals, Dimethylformamide, ethyl alcohol, 1,3-Di-amino propane ammonium hydroxyde, O-hydroxy benzophenone, ammonia, quinoline, phenyl, isocyanide and pyridine. All chemicals obtained either from E.Merk or B.D.H. (A.R.) quality has been used without further purification.

II. ANALYTICAL METHODS

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

- (i) Nickel :- Nickel has been gravimetrically as dimethyleoximate method.
- (ii)Iron:- Iron has been estimated volumetrically .
- (iii) Hydrogen, Carbon and Nitrogen:- Hydrogen, Carbon and Nitrogen was estimated by semi-macro-duma's method.

III. CONDUCTIVITY MEASUREMENT

The measurement of electrical conductivity of the solutions of the complexes has been done by conductivity meter bridge manufactured by Wiss-Techen Wearch Stathen type-LBR-at room temperature . The cell constant has been measured by using N/10 and N/100 KCl solutions . Pure DMF and conductivity water has been used as solvents.

U.V. –Visible spectra photometric Measurement:- Hitachi-320 spectrophotometer has been used to record the electronic absorption spectra of the complexes.

I.R. Spectra:- Perkin Elemer 577 spectrophotometer has been used to record the infra-red spectra of the complexes and the ligand in nujol mull.

During the course of recording the infrared spectra of the ligand of the complexes in Nujol mull, three peaks has been obtained in the range of 2960 cm⁻¹ to 2800 cm⁻¹ and at 1460 cm⁻¹ to 1380cm⁻¹ and a small peak at about 700 cm¹ has been excluded while recording the I.R. spectra for the determination of structure of the ligand and the complexes.

MAGNETIC SUSCEPTIBILITIES:

The measurement of the magnetic susceptibilities of the complexes has been done by Gouy's method by using Mercury tetra thio cyanato cobaltate, (Hg Co (SCN)₄) as celebrant.

IV. RESULTS AND DISCUSSION

The values of electrical conductance of Nickel (II) and Iron (II) complexes have been found in the range of 30-40 Am and 36-46 Am respectively which indicate non-electrolyte nature of the complexes of both the metals.

The values of magnetic moments of Nickel (II) and Iron (II) complexes have been obtained in the range of 3.16–3.34 BM and 5.36 – 5.54 BM respectively indicating the paramagnetic character of all the complexes.

In case of Nickel (II) Complexes, three electronic bands have been obtained due to the following :

$$1 = {}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) = 8110 - 8230 \text{ cm}^{-1} (e=1.3)$$

$$2 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) = 15600-16400 \text{ cm}^{-1} (e=2.96)$$

and

$$3 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) = 21500 = 21700 \text{ cm}^{-1} (e=4.4)$$

transitions which indicate octahedral or distorted octahedral spin free octahedral geometry for Nickel (II) complexes.

In our present investigation, one broad and unsymmetrical band obtained in the range of 15220-13440 cm^{-1} indicates distorted octahedral geometry of Iron (II) complexes.

Comparison of I.R. spectra of the ligand and the complexes to decide the bonding sites of the ligand and the structure of the complexes:-

The bands obtained in the free ligand molecule due to the vibrations of hydroxy-OH and azomethine (>C=N) groups have been appreciably changed after complex formation. A sharp and strong band obtained in the range of 3640-3670 cm^{-1} due to vibration of free hydroxy-OH group in the ligand molecule disappeared in all the complexes. The disappearance of the strong band present in the ligand molecule and appearance a new band around at 1360-1380 cm^{-1} in the complexes further suggests the deprotonation of hydroxyl group present in the benzophenone ring. The sharp and broad band obtained in the range of 1640-1660 cm^{-1} in

the ligand molecule has been reduced to 1540-1560 cm^{-1} in all the complexes. This reduction in the band position indicates the participation of Nitrogen atom of azomethine group in the bond formation with the metal cations.

By the comparison of I.R. spectra of the ligand and the complexes, it has been obtained that two nitrogen atoms of two azomethine groups and two oxygen atoms of deprotonated hydroxy (-OH) group attached to benzophenone moiety, are the bonding sites of the ligand molecule. Thus the ligand molecule behaves as bi-anionic tetra-dentate molecule.

In aquo complexes no separate band has been obtained to indicate the coordination of Oxygen atom of Water molecule and Nitrogen atom of ammonia. A strong and broad band has been obtained in the range of 3360-3410 cm^{-1} due the vibrations of combined (OH + NH) groups. A sharp and medium band has been obtained in the range of 740-770 cm^{-1} in a aquo-complexes due to rocking mode of coordinated water molecule.

I.R. spectra of free phenyl isocyanide molecule has a band obtained at 2180 cm^{-1} has been increased to 2220-2230 cm^{-1} in the complexes. This increase in band position indicates the participation of Nitrogen atom of isocyanide group of phenyl isocyanide.

In quinoline complexes, a band has been obtained at 1370-1410 cm^{-1} in due to the vibration of quinoline ring indicates the participation of Nitrogen atom of quinoline in the complex formations.

In pyridine, a number of bands are obtained in finger print and far infra-red region. A band obtained in the range 1070-1080 cm^{-1} due to breathing mode of pyridine ring has been regarded as the characteristic vibrations of the coordinated pyridine.

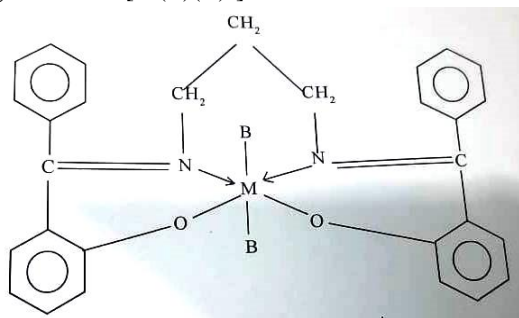
A sharp and medium band obtained in the range of 510-530 cm^{-1} in the complexes due to the vibration of (M - O) bond further confirms the participation of Oxygen atom in bond formation with the metal cation. A sharp and medium band obtained in the range of 370-420 cm^{-1} in the complexes due to the vibration of (M-N) bond further confirms the participation of Nitrogen atom in bond formation with the metal cation.

The frequency obtained due to the vibrations of (M-O) bond is greater than that of (M-N) bond because (M-O) bond is more ionic than (M-N) bond.

On the basis of elemental analysis, measurement of electrical conductance, magnetic moment, electronic and I.R. spectra of the ligand and the complexes,

octahedral geometry has been suggested for the complexes of Nickel (II) and Iron (II) cation formed with 2(O-hydroxy benzophenone) Di-imino propane in presence of bases like water, ammonia, phenyl-isocyanide, quinoline, pyridine and α -picoline.

The general formula for all the complexes has been suggested to be $[M(L)(B)_2]$ as shown below.



Where

M = Nickel (II) and Iron (II) metals

L = Bis(O-hydroxy benzophenone) Di-imino Propane.

B = water , ammonia , quinoline, phenyl -isocyanide, and pyridine.

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