

## Physicochemical studies on preparation, structure and bonding of Ni(II) complexes with N,O and S containing ligands

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### Abstract

Transition metal complexes of Nickel (II) with nitrogen, Oxygen, and sulphur donors such as thiocarbohydrazido, thio-cyanato, thiosemicarbazido and water are characterized based on structural, magnetic, and spectral data. These complexes have been thoroughly investigated using the physicochemical method. The present work deals mainly with the study of preparation, bonding, and structures with magnetic and spectral properties in Nickel (II) complexes. The bonding is based on the valence bond theory. The magnetic susceptibility of these complexes is observed using Gou balance methods and spectral properties are based on NMR Spectro metre.

**Keywords:-** Nitrogen, Sulphur, complexes, Nickel chloride, Magnetic properties, Structure. Spectral.

### Introduction

Nowadays, Coordination chemistry is a fundamental tool to elucidate the nature of bonding, structures, and magnetic and spectral properties. For this purpose, various theories are expected such as valence bond theory, Crystal field theory, ligand field theory, etc. At present work, the bonding and structures of Nickel (II) complexes of Nitrogen, Sulphur and oxygen-containing ligands are assigned. Such ligands are thiosemicarbazido, thiocyanato, hydroxo, etc. The bonding and structure in the Nickel (II) complexes with such ligands are characterised by magnetic and structural data.

### Preparation of Nickel (II) Complexes

#### 1. Bis –(thiocarbohydrazido) bis thiocyanato Ni (II) dihydrate: -

NiCl<sub>2</sub>.6H<sub>2</sub>O was dissolved in water and treated with an excess of KCN solution. This mixture was treated with a hot aqueous solution of the ligand such that Ni: ligand = 1:2. A precipitate obtained was digested in the water bath for 3 hours. It was then filtered, washed with hot water, ethanol and ether and dried at about 90°C for 3 hours. The complex analysed was  
$$\text{Ni}[(\text{H}_2\text{N.NHCSNHNH}_2)_2(\text{CNS})_2].2\text{H}_2\text{O}$$

#### 2. Bis –(thiosemicarbazido) bis aqua Ni (II): -

An aqueous solution of Nickel chloride was mixed with a hot aqueous solution of ligand such that Ni: ligand = 1:2. The pH of the solution was adjusted at 8 by adding 2N NaOH solution. The precipitate

obtained was digested in the water bath for about 1 hour and then filtered, washed with hot water, alcohol and ether and dried at about 90°C for 3 hours. The complex analysed was



3. **Bis –(thiosemicarbazido) bromohydroxo Ni (II) complex: -**

Nickel chloride was dissolved in water and a few c.c. of NaOH was added to it. The precipitate obtained was dissolved in a minimum quantity of HBr. The ligand was dissolved in the hot water and mixed into the above solution. The precipitate obtained was digested in the water bath for about 1 hour and then filtered, washed with hot water, alcohol & ether and dried at about 90°C for 3 hours. The complex analysed was



4. **Bis –(thiosemicarbazido) bisqua Ni (II) hydroxide complex: -**

Nickel chloride was dissolved in water and a few c.c. of NaOH was added to it. The precipitate obtained was dissolved in a minimum quantity of Conc. H<sub>2</sub>SO<sub>4</sub>. The ligand was dissolved in the hot water and mixed into the above solution. The precipitate obtained was digested in a water bath for about 1 hour and then filtered, washed with hot water, alcohol & ether and dried at about 90°C for 3 hours. The complex analysed was



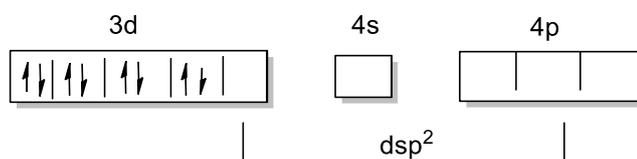
5. **Bis –(thiosemicarbazido) bisthio-cyano Ni (II) tetrahydrate complex: -**

In this case, the reaction was carried out in a formamide medium in place of an aqueous medium and the procedure was like method 1. The complex analysed was



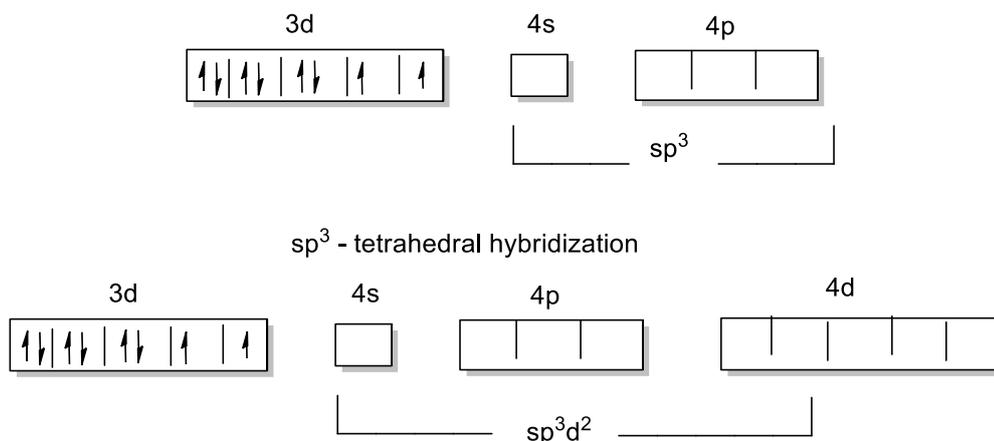
**Bonding, Structure & Exp. Data in Ni (II) complex: -**

Bivalent Ni (II) is a d<sup>8</sup> system and can form octahedral, tetrahedral, or square planar complexes involving sp<sup>3</sup>d<sup>2</sup>, sp<sup>3</sup> or dsp<sup>2</sup> hybridization respectively. In a square planar complex, all the electrons in 3d orbitals of the Nickel (II) ion are paired up and hence such complexes of the Nickel (II) ion are diamagnetic.



dsp<sup>2</sup> - Square planer hybridization

In tetrahedral or outer orbital octahedral Ni complexes, there will be two unpaired electrons and hence they would have a paramagnet, having magnetic moment 2.83 B.M. or above



sp<sup>3</sup>d<sup>2</sup> - outer orbital octahedral hybridization

It appears that the ligand is coordinated through terminal nitrogen atoms forming a six-membered ring and the monodentate CNS group is coordinated through nitrogen according to Tramer<sup>i</sup>. The central nickel (II) ion in Ni[(H<sub>2</sub>N.NHCSNH<sub>2</sub>)<sub>2</sub>(CNS)<sub>2</sub>].2H<sub>2</sub>O. Since the compound is soluble in dimethyl formamide, the following structure for this complex was suggested.

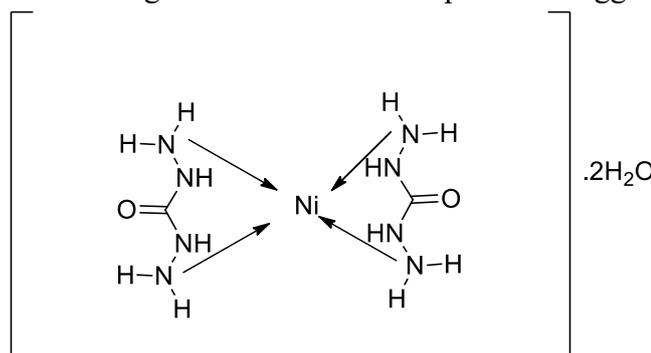


Fig 1.

The normal co-ordinate analysis of thiocarbonylhydrazide was carried out by Burns.<sup>ii</sup> In Ni[(H<sub>2</sub>N.NHCSNH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex each H<sub>2</sub>N.NHCSNH<sub>2</sub> is coordinated through two nitrogen atoms forming five-membered rings and the monodentate H<sub>2</sub>O molecules are coordinated through an O-atom to Nickel(II) ion. Thus, the structure of this Complex was suggested as

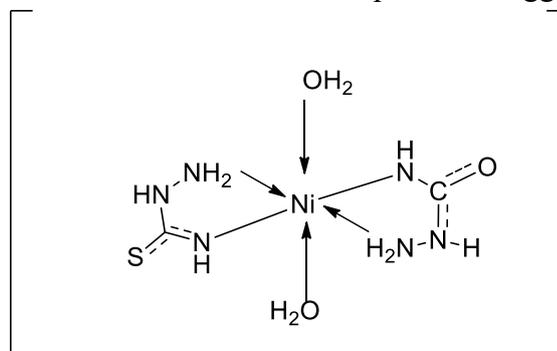


Fig 2.

The metal-oxygen Bond is sufficiently covalent<sup>iii</sup> and the presence of these bonds in aqua complexes was first suggested by Fujita et.al<sup>iv</sup>.

The infrared spectrum of  $\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{OH})\text{Br}]$  is almost like that of  $\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{OH})_2(\text{H}_2\text{O})_2]$  except that the  $\delta$  M-OH band in the former case is observed at about  $1150\text{ cm}^{-1}$ .

This may be accounted for the linking of the OH group to the central metal ion as

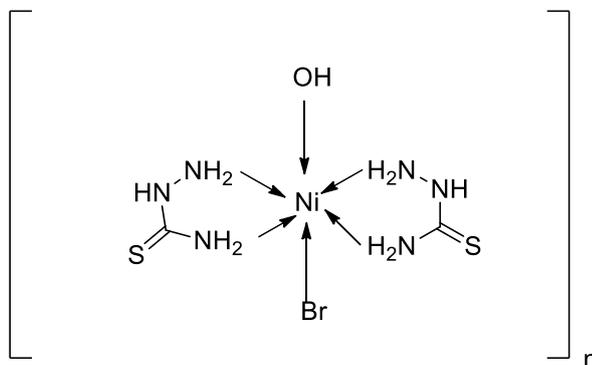


Fig 3.

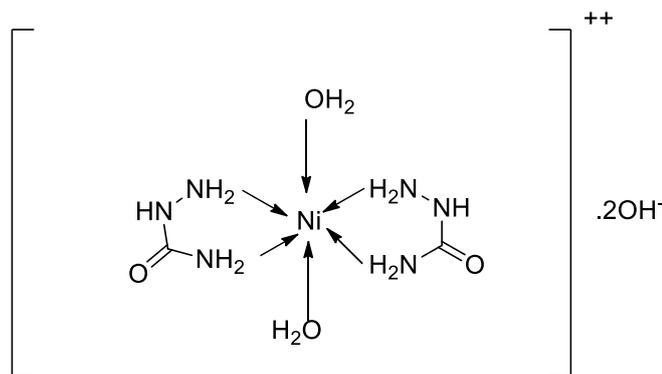


Fig 4.

This complex is completely insoluble in water and organic solvents and does not give the test of the  $\text{OH}^{-1}$  ion.

Hence the polymeric structure may be assigned to the complex in which the unit shown in the given figure 3 is present.

### Magnetic property

The spin-only formula indicates a magnetic moment of 2.83 BM for two unpaired electrons. The experimental value of the magnetic moment of nickel (II) complex are: -

Sl. No.	Complex	Effective Magnetic Moment
1	$\text{Ni}[(\text{H}_2\text{N.NHCSNHNH}_2)_2(\text{CNS})_2].2\text{H}_2\text{O}$	3.35 B.M.
2	$\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{H}_2\text{O})_2]$	3.18 B.M.
3	$\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{OH})\text{Br}]$	2.90 B.M.
4	$\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{OH})_2(\text{H}_2\text{O})_2]$	2.90 B.M.
5	$\text{Ni}[(\text{H}_2\text{N.NHCSNHNH}_2)_2(\text{CNS})_2].4\text{H}_2\text{O}$	3.52 B.M.

Table 1.

### Spectral Property

The electronic bands of the complexes are found in  $\text{cm}^{-1}$  are given in table 2.

Sl. No.	Complex	Electronic Bands (in $\text{cm}^{-1}$ )
1	$\text{Ni}[(\text{H}_2\text{N.NHCSNHNH}_2)_2(\text{CNS})_2].2\text{H}_2\text{O}$	10200, 11000, 15400, 18000, 26300
2	$\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{H}_2\text{O})_2]$	10800, 11400, 18200, 19700, 27800
3	$\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{OH})\text{Br}]$	10500, 11700, 15400, 17600, 26300
4	$\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{OH})_2(\text{H}_2\text{O})_2]$	10200, 11000, 15200, 16900, 24300
5	$\text{Ni}[(\text{H}_2\text{N.NHCSNHNH}_2)_2(\text{CNS})_2].4\text{H}_2\text{O}$	10200, 11000, 14300, 17600, 24400

Table 2.

### Colour

The colour of the complexes is given in this table 3.

Sl. No.	Complex	Colour
1	$\text{Ni}[(\text{H}_2\text{N.NHCSNHNH}_2)_2(\text{CNS})_2].2\text{H}_2\text{O}$	Light Green
2	$\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{H}_2\text{O})_2]$	Light Green
3	$\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{OH})\text{Br}]$	Light Green
4	$\text{Ni}[(\text{H}_2\text{N.NHCSNH}_2)_2(\text{OH})_2(\text{H}_2\text{O})_2]$	Yellowish Green
5	$\text{Ni}[(\text{H}_2\text{N.NHCSNHNH}_2)_2(\text{CNS})_2].4\text{H}_2\text{O}$	Light Green

Table 3.

### Discussion and result

From the above observation, it is conclusive that Nickel complexes with nitrogen sulphur and nitrogen-containing legging are octahedral tetrahedral and the square planar geometry is also found that most of them are paramagnetic in nature the magnetic moment of the complex discussed are given in Table 1 the spectral banks and the colour are also given in table 2 and table 3.

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## References:-

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