



Spectral Characterization and Magnetic properties of Ni (II) complexes with Naphthylbiguanide as a Ligand

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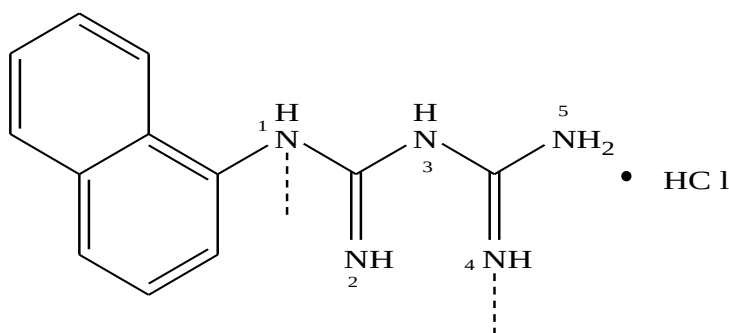
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Abstract: Complexes of Ni(II) with Naphthylbiguanide $[C_{12}H_{13}N_5 \cdot HCl]$ of the molecular composition $[Ni(C_{12}H_{13}N_5)_2] \cdot H_2O$, $[Ni(C_{12}H_{13}N_5)_2] \cdot 2.5H_2O$, $[Ni(C_{12}H_{13}N_5)_2] \cdot 2H_2O$, $[Ni(NaphBigH^+)_2]SO_4 \cdot H_2O$ and $[Ni(NaphBigH^+)_2]Cl_2 \cdot 2H_2O$ have been prepared and characterized by the IR, UV and magnetic studies. The complexes of Ni(II) are found to be diamagnetic which indicates the low spin square planar structure of Ni(II) complexes.

Keywords: Nickel, Complexes, Naphthylbiguanide, IR, UV

I. Introduction

Naphthylbiguanide hydrochloride $[C_{12}H_{13}N_5 \cdot HCl]$ (Fig. 1) is a bidentate chelating ligand and its complexes have not been studied extensively.



Two molecules of this ligand coordinate with the metal ion through N (2) and N (4) of both the biguanide substituent groups to form a six membered chelate ring. The complexes of a number of biguanides and substituted biguanides with different metal ions have been studied extensively.^{1,2,3,4}

To determine the chelating behavior of Naphthylbiguanide hydrochloride ligand, we have prepared and characterized the complexes of Ni (II) with this ligand.

II. Materials and Methods

Materials: Naphthylamine, Dicyandiamide and all other chemicals required were available commercially and used as such.

Physical Measurements: The results of C, H and N were obtained from Central Drug Research Institute, Lucknow. The anions and metal ions were estimated by standard methods⁵. Magnetic properties were measured as reported earlier¹.

The result of U-V spectra were recorded on Carry 5000 UV-VIS-NIR spectrophotometer at SAIF STIC and the IR spectra were recorded on Perkin Elmer at Central Drug Research Institute, Lucknow. And the magnetic measurements (VSM) were done from IIT Guwahati.

Synthesis of Ligand and Complexes⁶

Naphthylbiguanide hydrochloride [$C_{12}H_{13}N_5.HCl$]

Naphthylbiguanide hydrochloride was prepared by refluxing alcoholic solution of both Naphthylamine hydrochloride $C_{10}H_7NH_2.HCl$ and dicyandiamide $C_2H_4N_4$ in round bottom flask on water bath. This process continues for about two hours. The crystals get deposited on cooling the mixture obtained. The crystals were filtered and recrystallized with hot water. Found C =53.709; N =25.349.

Preparation of Complexes

a) α -Variety: An ammoniacal solution of $NiSO_4$ in slight excess was added to that of naphthylbiguanide in hot dil. Ammonia. After sometime the precipitate was filtered and washed several times with water till free from sulphate. The product was dried on a porous plate and then over alkali to a constant weight.

Found: N = 26.61%; Ni = 11.13%

$[Ni(C_{12}H_{12}N_5)_2] \cdot H_2O$ requires:

N = 26.48%; Ni = 11.10%

The substance forms flesh coloured crystals, insoluble in water. It can displace NH_3 from boiling NH_4Cl solution. It is sparingly soluble in alcohol, but dissolves in pyridine giving red solution. When heated at $110^\circ C$ for about 12 hours it lost whole of its water (3.407; cal. 3.417) and formed the anhydro base without any change of colour.

Found:

Ni = 11.50%

$[Ni(C_{12}H_{12}N_5)_2]$ requires:

Ni = 11.49%

b) β -Variety: It was obtained as insoluble yellow crystals by adding a large excess of naphthylbiguanide solution drop by drop to that of nickel chloride at the boiling temperature. The crystals were washed several times with hot water and dried as before. The substance dissolves in pyridine and warm alcohol to a yellow solution.

Found:

N = 25%; Ni = 10.59%

$[Ni(C_{12}H_{12}N_5)_2] \cdot 2.5 H_2O$ requires:

N = 25.20%; Ni = 10.56%

On heating the substance at $140^\circ C$ for about 12 hours it lost all of its H_2O and forms anhydro base without any change in colour.

Found:

H_2O = 8.00%; Cal. H_2O = 8.00%

c) γ -Variety: It was obtained by dissolving the hydrated α -form in the minimum quantity of cold HCl and then adding an excess of caustic soda solution. The light buff coloured crystalline precipitate was filtered, washed with cold water free from chloride and then dried as before.

N = 25.70%; Ni = 10.71%

$[Ni(C_{12}H_{12}N_5)_2] \cdot 2 H_2O$ requires:

N = 25.61%; Ni = 10.74%

The substance melts when boiled with H_2O . It is sparingly soluble in alcohol but dissolves in pyridine giving a yellow solution.

d) Nickel α -Naphthylbiguanidinium sulphate: It was obtained as a buff colored crystalline precipitate by adding a solution of $NiSO_4$ in slight excess to that of α -Naphthylbiguanide. The substance is sparingly soluble in pyridine, acetone and alcohol.

Found:

SO_4 = 15.30%; Ni = 9.37%

$[Ni(NaphBigH^+)_2]SO_4 \cdot H_2O$ requires:

SO_4 = 15.32%; Ni = 9.36%

e) Nickel α -Naphthylbiguanidinium chloride: A solution of naphthylbiguanide was added to a hot solution of Nickel chloride in calculated amount. The mixture was filtered from any precipitated β -base. The filtrate on cooling, gave light yellow crystals of the complex chloride. The substance dissolves completely in hot water as well as in pyridine, acetone and warm alcohol.

N = 22.58%; Ni = 9.50%; Cl = 11.98%

[Ni(NaphBigH⁺)₂]Cl₂·2H₂O requires:

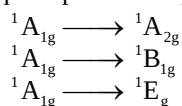
N = 22.59%; Ni = 9.47%; Cl = 11.96%

III. Results and Discussion

Similar to biguanide, ethylene dibiguanide and phenyl biguanide, naphthyl biguanide also act as chelating molecule and coordinates with bivalent metal ions to form bischelates⁷. The complex base of Ni (II) with naphthylbiguanide has been isolated in three different varieties: α , β and γ which differ in degree of hydration and colour. The α -form is flesh coloured and crystallizes with one molecule of water which is lost at 110°C without any change in colour. It is insoluble in water and dissolves in pyridine to give a red solution. The β -variety forms a bright yellow colour crystal and contains 2.5 molecules of water which is lost at 140°C without change in colour. The γ -form has light buff colour and dissolves in pyridine to give yellow solution. The α and β forms may be regarded as cis and trans isomers of the square planar Ni (II) complexes.

Electronic Spectra

Ni (II) has ³F ground state term. In excited state three states are spin allowed and three are spin forbidden transition in low spin square planar complexes of d⁸ system. The spin allowed transitions are:



The electronic band⁷ at ${}^1A_{1g} \longrightarrow {}^1B_{1g}$ occurs in visible region. The complexes of Naphthylbiguanide show one broad band near 465-480 nm attributed to ${}^1A_{1g} \longrightarrow {}^1B_{1g}$ transition. The strong absorption band about 300 nm in almost all nickel (II) complex salts are attributed to charge transfer transition.

IR Spectra^{9,10}

In the free ligand naphthylbiguanide, the various modes of vibration of =NH, N and NH₃⁺ lies between 3400 cm⁻¹ to 1385 cm⁻¹. The peak at 3400.8 cm⁻¹ shows stretching of N – H and NH₂ bond. N – H def. is obtained at 1633.54 cm⁻¹.

For aromatic compounds, C=C stretching absorption occurs at 1650-1450 cm⁻¹ and C – H def vibrations at 900-700 cm⁻¹. The band at 1069 cm⁻¹ shows in plane bending in C – H bond of aromatic ring. The band at 760 cm⁻¹ shows out of plane bending of the ring C – H bond.

The N – H stretching decreases on complex formation with metal as observed in the complex. The peak at 3019 cm⁻¹ to 3392 cm⁻¹ shows stretching of N – H, NH₂ and OH groups. Strong bands are observed for C=N at 1600-1640 cm⁻¹. C – H stretching vibration is observed at 3019cm⁻¹. C=C and C – N stretching vibration occurs at about 1520 and 1595 cm⁻¹. The I.R. spectrum was not recorded in far I.R. region hence the ν (Ni – N) vibrations were not indicated in the complex.

The diamagnetic behavior and electronic absorption pattern suggest square planar geometry for Ni (II) complexes¹¹.

IV. Conclusion

From the stoichiometry, spectral studies (IR & electronic absorption) and physico-chemical properties the probable structure of the complexes must be square planar.

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VI. References

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