

Synthesis and Characterisation of Some Novel Ni(II) Complexes of Semicarbazones derived from Heterocyclic Aldehydes

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Abstract:

Some novel complexes of Ni(II) with ligands 3-hydroxyindole-2-carbaldehyde semicarbazone (L_1H) and 5-hydroxyimidazole-2-carbaldehyde semicarbazone (L_2H) have been synthesised in acidic (pH=2.0), neutral (pH=7.0) and alkaline (pH=10.0) media in order to investigate the pH dependent coordination behaviour of the selected ligands. The synthesised complexes have been characterised on the basis of elemental analyses, determination of molar masses, molar conductance and magnetic susceptibility measurements, UV and IR spectral studies. In acidic (pH=2.0) and neutral (pH=7.0) media, both L_1H and L_2H behave as neutral tridentate ligands while in alkaline medium (pH=10.0), they behave as monoanionic tridentate ligands. The complexes are found to be monomeric as indicated by their observed molar masses and have molecular formula $[Ni(L_1H)_2]Cl_2$ and $[Ni(L_2H)_2]Cl_2$ in both acidic and neutral media. However, they have been formulated as $[Ni(L_1)_2]$ and $[Ni(L_2)_2]$ in alkaline medium. The complexes synthesised in acidic and neutral media have 1 : 2 electrolytic nature whereas those synthesised in alkaline medium are non-electrolytes as indicated by their molar conductance values. Octahedral geometry has been suggested for all the complexes on the basis of magnetic moment values as well as the number and positions of electronic spectral bands. The nature of metal-ligand bonding has been established by infrared spectral studies.

Key words: Schiff base, semicarbazones, indole, imidazole, tridentate ligands.

1. Introduction:

Schiff bases have been the domain of research works for inorganic and bioinorganic chemists since their discovery by Hugo Schiff in 1964 [1]. They are prepared by the condensation of primary amines with carbonyl compounds [2]. They are nitrogen analogues of carbonyl compounds where the carbonyl group ($>C=O$) is replaced by azomethine ($>C=N-$) group [3]. The biological activities of Schiff bases are due to the presence of azomethine group ($>C=N-$) in them. Semicarbazones belong to the family of Schiff bases having structural unit $>N-N=C<$ where the azomethine group is adjacent to another nitrogen atom. This additional nitrogen atom, adjacent to azomethine group, modifies biological activities of semicarbazone drastically. The biological activities of semicarbazones are due to the presence of lone pair of electrons in sp^2 hybrid orbital of azomethine

nitrogen [4-6]. Semicarbazones containing an azomethine proton ($-\text{NH}-\text{N}=\text{CH}-$) is therapeutically important for the development of new drugs [7]. The additional donor site $> \text{C}=\text{O}$ of aroyl, acyl and heteroaroyl semicarbazone Schiff bases makes semicarbazones an excellent polydentate chelating ligand which can coordinate with various transition and inner transition metal ions in a number of ways[8]. Semicarbazones and their metal complexes show varied applications as antifungal, antibacterial, anti-oxidant, and in cytotoxic studies[9]. Schiff bases having chelating donor sites like nitrogen, oxygen and sulphur when coordinated to metal ions exhibit enhanced biological activities[10].

Keeping in view the diverse applications of semicarbazones and their metal complexes, we report the synthesis and characterization of some novel complexes of Ni(II) with semicarbazone ligands containing heterocyclic moieties. The complexes have been synthesized in acidic, neutral and alkaline media to investigate the pH dependent coordination behaviour of ligands.

2. Experimental

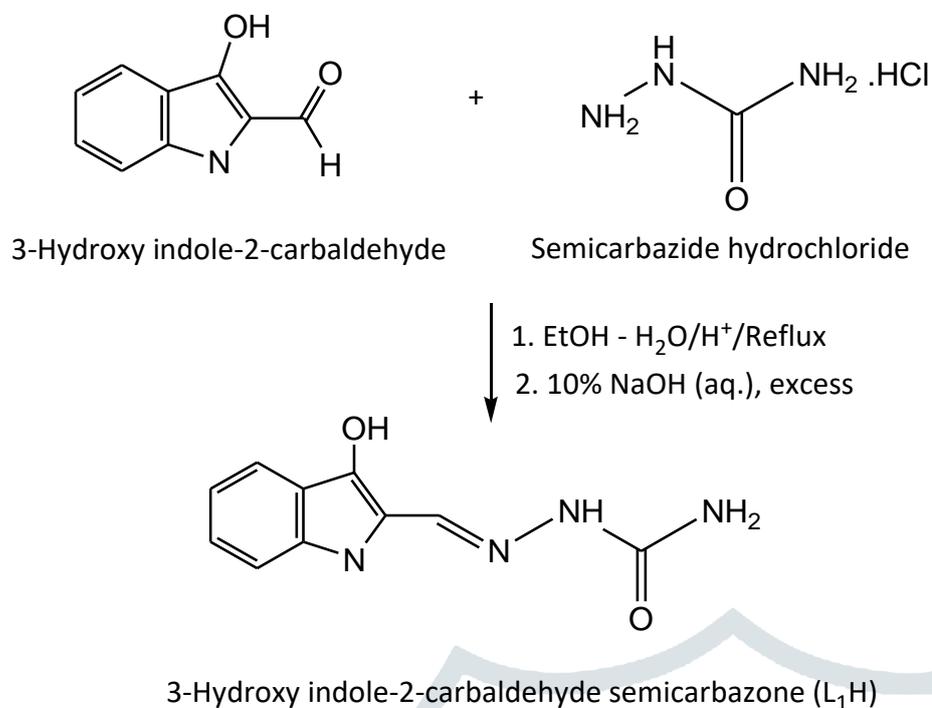
2.1 Materials and Methods:

All chemicals used were of analytical grade purchased from Sigma Aldrich and E. Merk. They were used as received without further purification. The microanalysis of C, H and N in ligands and complexes was done by elemental analyser Euro EA (Model PAR 155). Molar conductance of complexes was determined using digital conductivity meter (HPG system, G-3001). Metal in complexes was estimated as dimethyl glyoximate in slightly alkaline solution. The IR spectra of ligands and complexes were recorded in the range of $4000-400 \text{ cm}^{-1}$ using Agilent Technologies FT-IR spectrophotometer (Cary 630). Electronic spectra of ligands and complexes were recorded on Hitachi 300 spectrophotometer. Molar masses of complexes were determined by cryoscopic method.

2.2 Preparation of the ligand 3-hydroxyindole-2-carbaldehyde semicarbazone (L_1H):

Procedure: 0.1 mole (16.10g) of 3-hydroxyindole-2-carbaldehyde was dissolved in ethanol-water (60 : 40 w/w) mixture. 0.1 mole (11.15g) of semicarbazide hydrochloride was dissolved in minimum volume of water. The two solutions were mixed with constant stirring. It was then filtered and mixed with 20 mL of bench hydrochloric acid solution. The solution was refluxed in a 500 mL round bottom flask using water condenser for about 2 hours. This solution was allowed to cool in ice-cold water and excess of 10% NaOH aqueous solution was added to it. This resulted in the precipitation of a white solid which was filtered, washed with water and crystallised in ethanol. It was dried over anhydrous CaCl_2 in a desiccator. Its m.p. was recorded to be 125°C . The yield was approximately 80%.

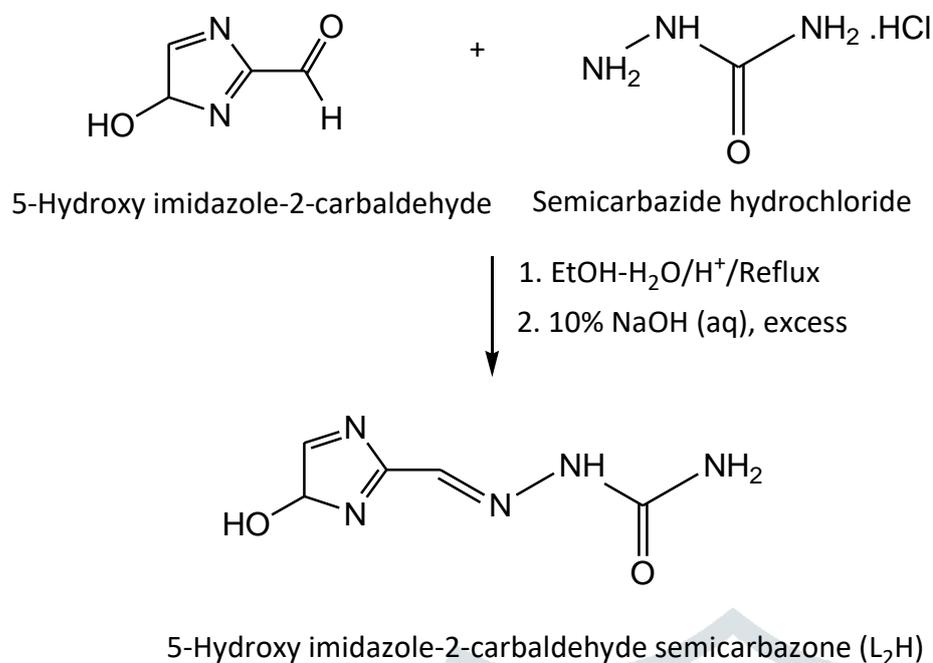
The Scheme of preparation of the ligand is shown in Fig. 1.



(Fig. 1)

2.3. Preparation of 5-hydroxyimidazole-2-carbaldehyde semicarbazone (L₂H):

Procedure: 0.10 mole (11.20 g) of 5-hydroxy imidazole-2- carbaldehyde was dissolved in minimum volume of aqueous-ethanolic (60:40 w/w) mixture. 0.1 mole (11.15 g) of semicarbazide hydrochloride was dissolved in minimum volume of water. The two solutions were mixed with constant stirring. It was then mixed with 20 mL of 2N HCl solution. The solution was then refluxed in a round bottom flask using water condenser for about 2 hours. It was than allowed to cool in ice-cold water. To this solution was added an excess of 10% NaOH aqueous solution when white crystalline solid separated out. The solid was filtered, washed twice with cold water, recrystallized in ethanol and then dried over anhydrous CaCl₂ in a desiccator. The m.p. of solid was recorded to be 118.5°C. The yield was approximately 75%. The scheme of preparation of the ligand LH₂ is given in Fig. 2.



(Fig. 2)

2.4 Preparation of complexes of Ni(II) with 3-hydroxy indole-2-carbaldehyde semicarbazone (L₁H) in acidic (pH=2.0), neutral (pH=7.0) and alkaline (pH=10.0) media:

Procedure:

0.02 mole (4.36 g) of the ligand 3-hydroxyindole-2-carbaldehyde semicarbazone (L₁H) was dissolved in minimum volume of ethanol. To this solution was added an aqueous solution of 0.01 mole (2.38 g) of nickel (II) chloride hexahydrate. The pH of the solution was adjusted to 2.0/7.0/10.0 using dil. HCl and NH₄OH solutions in three separate round bottom flasks. The solution was refluxed on a water bath using water condenser for about 4 hours. The solution was allowed to cool over night when coloured solid separated out. It was filtered, washed twice with water and then with acetone. The solid was found insoluble in water and common organic solids such as benzene, toluene, CCl₄, CHCl₃, acetone, ether, ethanol and methanol. It was, however, soluble in DMF and DMSO. The solid was recrystallized in DMF and dried over anhydrous CaCl₂ in a desiccator. The m.p. of compound was recorded. The yield was approximately 55 to 60%.

2.5 Preparation of complexes of Ni(II) with 5-hydroxy imidazole-2-carbaldehyde semicarbazone (L₂H) in acidic (pH=2.0), neutral (pH=7.0) and alkaline (pH=10.0) media:

Procedure:

0.02 mole (3.08 g) of the ligand 5-hydroxyimidazole-2-carbaldehyde semicarbazone (L₂H) was dissolved in minimum volume of ethanol. To this solution was added an aqueous solution of 0.01 mole of nickel (II) chloride

hexahydrate in a round bottom flask. The pH of the solution was adjusted to 2.0/7.0/10.0 in three separate flasks using dil. HCl and dil. NH_4OH solutions. The solution was then refluxed on a water bath using water condenser for about 4 hours. It was then allowed to cool over night at room temperature when coloured precipitate separated out. The precipitate was washed with water and then with ethanol. It was found insoluble in common organic solvents but soluble in DMF and DMSO. The precipitate was recrystallized in DMF and washed with acetone. It was dried over anhydrous CaCl_2 in a desiccator. Its m.p. was recorded. The yield was approximately 60-62%.

3. Results and Discussion

3.1 Microanalytical data:

From microanalytical data (Table-1), the stoichiometries of complexes have been determined. The observed molar masses of complexes proved their monomeric nature.

Sl.No.	Ligand/complex	Colour	M.P.	% found (% caculated)					Molar mass calculated found
				C	H	N	Cl	Ni	
1.	L_1H	White	125°C	55.04 (55.12)	4.58 (4.61)	25.68 (25.72)	-	-	2.18 (216.5)
2.	L_2H	White	118.5°C	38.96 (39.12)	3.89 (3.76)	36.36 (36.38)	-	-	154 (155.4)
3.	$[\text{Ni}(\text{L}_1\text{H})_2]\text{Cl}_2$ pH=2.0	Green	210°C	42.42 (42.55)	3.45 (3.48)	19.79 (19.84)	12.55 (12.62)	10.38 (10.42)	565.7 (567)
4.	$[\text{Ni}(\text{L}_1\text{H})_2]\text{Cl}_2$ pH=7.0	Green	210°C	42.42 (42.36)	3.45 (3.34)	19.79 (19.86)	12.55 (12.41)	10.38 (10.28)	565.7 (567)
5.	$[\text{Ni}(\text{L}_1)_2]$ pH=10.0	Bluish Green	207°C	48.71 (48.80)	3.65 (3.48)	22.73 (22.68)	-	11.91 (11.84)	492.7 (494)
6.	$[\text{Ni}(\text{L}_2\text{H})_2]\text{Cl}_2$ pH=2.0	Yellowish green	214°C	27.41 (27.52)	2.74 (2.68)	25.58 (25.62)	16.22 (16.46)	13.41 (13.44)	437.7 (438.8)
7.	$[\text{Ni}(\text{L}_2\text{H})_2]\text{Cl}_2$ pH=7.0	Yellowish green	214°C	27.41 (27.45)	2.74 (2.66)	25.58 (25.42)	16.22 (16.34)	13.41 (13.37)	437.7 (435)
8.	$[\text{Ni}(\text{L}_2)_2]$ pH = 10.0	Bluish Green	208°C	32.90 (33.12)	2.74 (2.73)	30.71 (30.75)	-	16.09 (16.14)	364.7 (365)

L_1H = 3-Hydroxyindole-2-carbaldehyde semicarbazone

L_1 = deprotonated 3-hydroxy indole-2- carbaldehyde semicarbazone

L_2H =5-Hydroxy imidazole-2-carbaldehyde semicarbazone

L_2 = deprotonated 5-hydroxyimidazole-2-carbaldehyde semicarbazone

The microanalytical data and observed molar masses are in good agreement with proposed formula of respective complexes.

3.2 Molar conductance

The molar conductance values of complexes of Ni(II) with L₁H and L₂H in acidic and neutral media were in the range 164-182 ohm⁻¹ cm² mol⁻¹ indicating 1 : 2 electrolytic nature of these complexes [11]. The complexes of L₁H and L₂H with Ni (II) prepared in alkaline medium exhibited molar conductance values in the range 18-24 ohm⁻¹ cm² mol⁻¹ indicating their non-electrolytic nature [11].

3.3 Magnetic susceptibility:

All the complexes were found to be paramagnetic with magnetic moment values in the range of 2.92 to 3.10 BM indicating octahedral nature of Ni(II) complexes.

3.4 Electronic spectra:

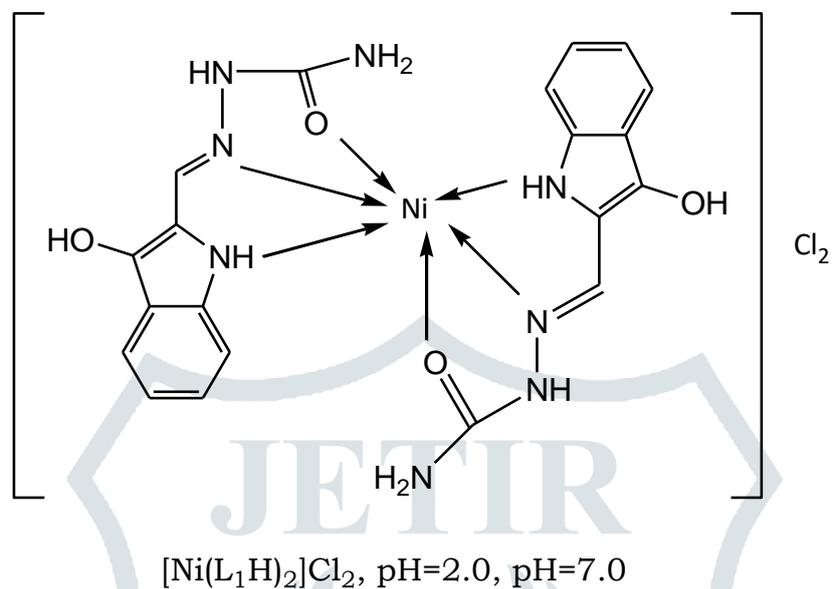
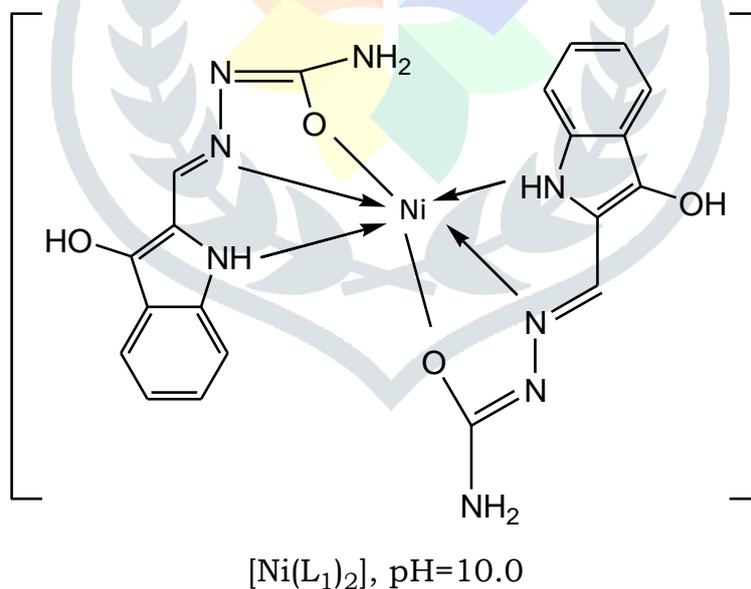
The electronic spectra of all the complexes displayed three d-d transition bands in the range 9500 – 10400 cm⁻¹, 14150 – 19880 cm⁻¹ and 22425 – 23700 cm⁻¹ which were assigned to ³A_{2g}(F) → ²T_{2g}(F), ³A_{2g}(F) → ³T_{1g}(F) and ³A_{2g}(F) → ³T_{1g}(P) respectively. The number and positions of electronic spectral bands indicated octahedral geometry for all the complexes.

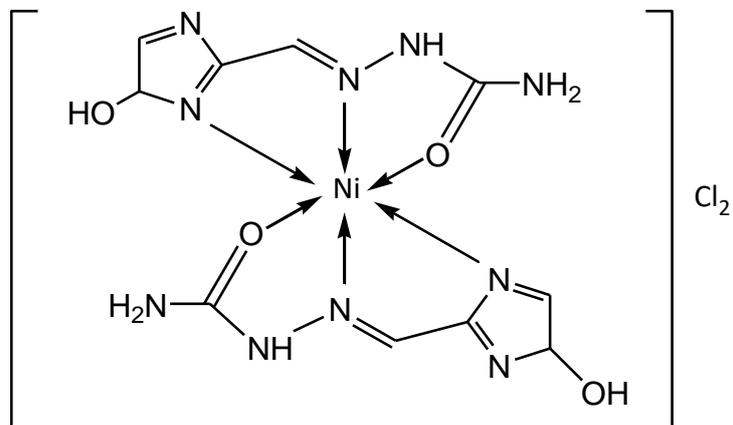
3.5 Infrared spectra:

The medium band at 1680 cm⁻¹ and 1685 cm⁻¹ in infrared spectra of L₁H and L₂H respectively due to azomethine (>C= N-) group got red shifted by 10-15 cm⁻¹ in the infrared spectra of all the complexes indicating the participation of nitrogen atom of azomethine group in bonding to the metal ion. The strong and sharp band at 1650 cm⁻¹ and 1630 cm⁻¹ in spectra of L₁H and L₂H respectively due to ν_{C=O} mode of vibrations got red shifted by

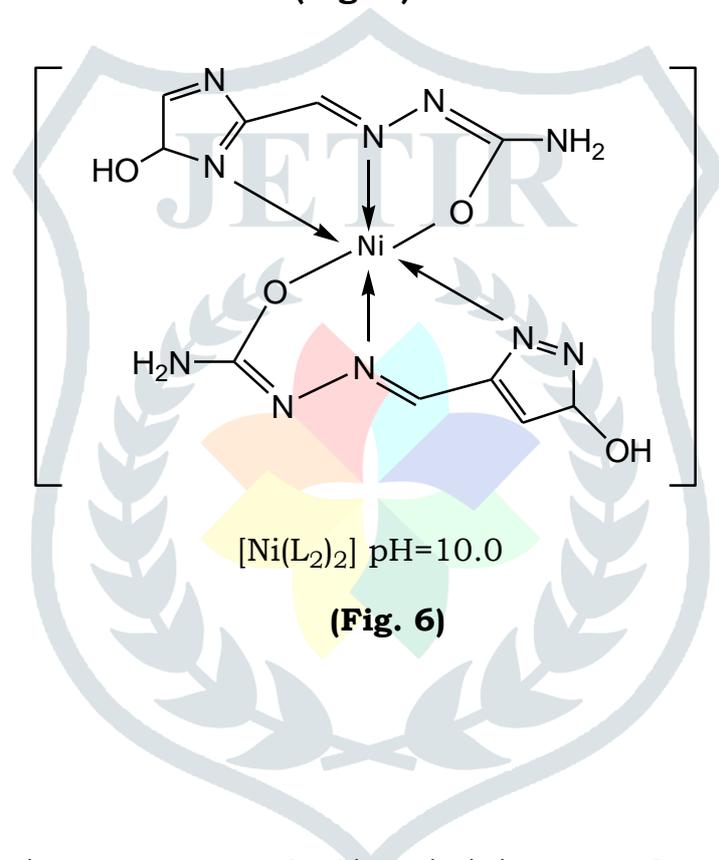
20-25 cm⁻¹ in the spectra of complexes prepared in acidic and neutral media. This indicated the participation of >C=O group in bonding to the metal ion. On the other hand, these infrared bands of ligands disappeared in infrared spectra of complexes prepared in alkaline medium and a new band at 1110 cm⁻¹ appeared which may be assigned to ν_{C-O} mode of vibrations. This indicated the deprotonation of the enol form of the ligand and its participation in bonding to the metal ion through oxygen atom of deprotonated -OH group. Two new bands appeared in the region 480–495 cm⁻¹ and 425–435 cm⁻¹ in infrared spectra of complexes which may be assigned to ν_{Ni-O} and ν_{Ni-N} modes of vibrations respectively. This further indicated the bonding of ligands to Ni(II) through nitrogen and oxygen atoms.

On the basis of elemental analysis, determination of molar masses, molar conductance and magnetic moment measurements, uv and IR spectral studies, the following octahedral structures have been established for the complexes [Fig. 3 to Fig. 6]:

**(Fig. 3)****(Fig. 4)**



(Fig. 5)



(Fig. 6)

4. Conclusion:

All the newly synthesized complexes are paramagnetic with octahedral geometry. Complexes synthesized in acidic and neutral media are 1: 2 electrolytes while those synthesized in alkaline media are non-electrolytes. Ligands L_1H and L_2H behave as neutral tridentate ligands in acidic and neutral media but they behave as monoanionic tridentate ligands in alkaline medium. The deprotonated enolic form of ligands L_1H and L_2H take part in bonding.

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