

# Synthesis and Characterisation of Some Novel Ni(II) Complexes with Dithiocarbamate Ligand at different pH

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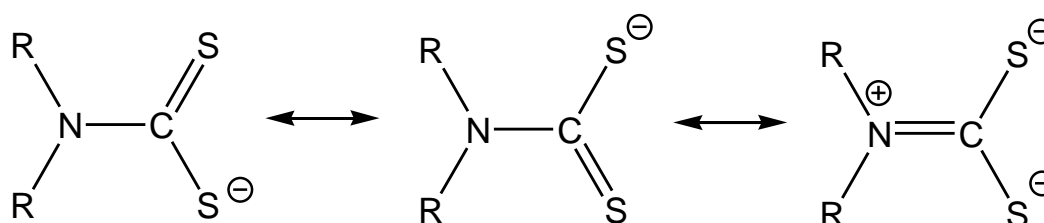
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**Abstract :** Some novel complexes of Ni(II) with 5-cyano-3-formyl-1H-indole-1-dithiocarbamate ion (L) have been synthesised in acidic (pH=2.0), neutral (pH=7.0) and alkaline (pH=10.0) media to investigate the pH dependent coordination behaviour of the ligand. The complexes have been characterised on the basis of elemental analysis, molar mass determination, molar conductance and magnetic moment measurements, uv and IR spectroscopic studies. Complexes synthesised in acidic and neutral media have been formulated as  $[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]$  while that synthesised in alkaline medium is formulated as  $[\text{Ni}(\text{L})_2(\text{NH}_3)_2]$ . All the complexes are non-electrolytes as their molar conductance values fall in the range  $18\text{--}24\text{ohm}\text{--}1\text{cm}^2\text{mol}^{-1}$ . They are found to be paramagnetic with octahedral geometry. The ligand behaves as monoanionic bidentate ligand and its coordination behaviour is found to be independent of the pH of the reaction medium.

**Keywords:** Dithiocarbamate, pH dependent coordination behaviour, spectroscopic studies, monoanionic bidentate ligand.

## I. INTRODUCTION

Metal complexes have been the domain of research work for inorganic and bioinorganic chemists in recent years because a number of biological processes significant to life are controlled by metal ions and their complexes[1,2]. A large number of metal complexes have been found to possess remarkable biological properties such as analgesic [2], antibacterial [3, 4], antimalarial [5,6] anti-cancer[7,8], antidiabetic [9,10], antiviral [11,12], anti-HIV [13,14] and plant growth regulating activities [15]. Dithiocarbamates constitute an important class of ligand system with exceptional coordination behaviour of forming stable metal complexes. They have general formula  $\text{R}_2\text{NCS}_2^-$  which usually exists in three different resonating forms as shown in Fig. 1.



(Fig. 1)

This ligand is expected to exhibit diverse coordination behaviour at different pH.

Keeping in view the diverse applications of metal complexes of dithiocarbamates, we report herein the synthesis and characterisation of some novel complexes of Ni(II) with 5-cyano-3-formyl-1H-indole-1-dithiocarbamate ion(L) at different pH.

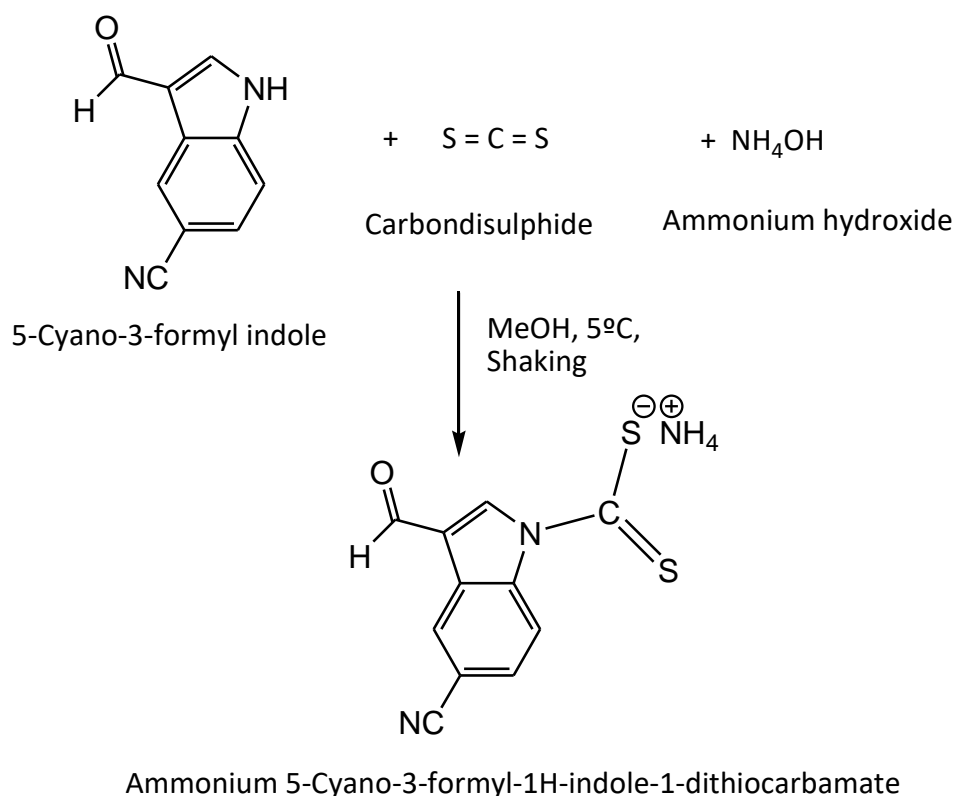
## II. EXPERIMENTAL

### 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 the ligand and complexes was done by elemental analyser Euro EA (Model 3000). The magnetic moment of complexes was determined using vibrating sample magnetometer (Model PAR 155). Molar conductance values of complexes were determined using digital conductivity meter (HPG system, G-3001). Nickel in complexes was estimated as nickel dimethyl glyoximate in slightly ammoniacal solution. The IR spectra of ligand and complexes were recorded in the range of 4000-400  $\text{cm}^{-1}$  using Agilent Technologies FT-IR spectrophotometer (Cary 630). Electronic spectra of ligand and complexes were recorded on Hitachi 300 spectrophotometer. Molar masses of complexes were determined by cryoscopic method..

### 2.2 Preparation of the ligand, ammonium 5-cyano-3-formyl-1H-indole-1-dithiocarbamate:

**Procedure:** 0.1 mole (17.0g) of 5-cyano-3-formylindole was dissolved in minimum volume of methanol in a round bottom flask. It was then placed in a vessel containing crushed ice and allowed to cool for 15 minutes. 0.1 mole (13.88 mL,  $d=0.9 \text{ g mL}^{-1}$ , 28% (w/w) of conc. ammonium hydroxide (ice-cold) was added to the methanolic solution of 5-cyano-3-formyl indole with constant stirring. 0.1 mole (6mL,  $d=1.263 \text{ g mL}^{-1}$ ) of carbon disulphide was added very slowly to the ice-cold solution of ammoniacal 5-cyano-3-formyl indole with constant stirring under a fume cupboard. The mixture was stirred for half an hour maintaining the temperature of the mixture below 5°. It was then allowed to sand at room temperature for an hour when pale yellow crystals of ammonium 5-cyano-3-formyl-1H-indole-1-dithiocarbamate separated out. The crystals were filtered, washed with water and then with acetone. The precipitate was recrystallised in ethanol and dried over anhydrous  $\text{CaCl}_2$  in a desiccator. Its m.p. was recorded to be 114.5°C. The scheme of preparation is shown in Fig. 2.



**(Fig. 2)**

### 2.3 Preparation of Ni(II) complexes of 5-cyano-3-formyl-1H-indole-1-dithiocarbamate in acidic (pH=2.0), alkaline (pH=10.0) and neutral (pH=7.0) media:

**Procedure:** 0.02 mole (5.94g) of ammonium 5-cyano-3-formyl-1H-indole-1-dithiocarbamate was dissolved in minimum volume of ethanol. To this solution was added an aqueous solution containing nickel (II) chloride hexahydrate in a round bottom flask. The pH of the solution was adjusted to 2.0/7.0/10.0 with the help of bench HCl and NH<sub>4</sub>OH solutions. The solution was refluxed for about 4 hours when a coloured precipitate separated out. It was filtered, washed with water and then with acetone and finally recrystallised in DMF. It was dried over anhydrous CaCl<sub>2</sub> and its m.p. was recorded. The yield was 60-65%.

## III. Results and Discussion

### 3.1 Micronalytical Data:

From microanalytical data (Table 1) and molar masses of complexes, the stoichiometry and molecular formula of complexes have been determined. Observed molar masses indicate monomeric nature of complexes.

**Table-1**  
**Microanalytical data of complexes**

Sl. No.	Complex & M.P.	pH	Mol. Mass calculated (found)	Colour	% found (% calculated)				
					C	H	N	S	Ni
1.	[Ni(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] m.p. =218°C	2.0	552.7 (550.0)	Green	47.76 (47.68)	1.63 (1.61)	10.13 (10.16)	23.15 (23.22)	10.62 (10.64)
2.	[Ni(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] m.p. = 218°C	7.0	552.7 (550.8)	Green	47.76 (47.68)	1.63 (1.61)	10.13 (10.22)	23.15 (23.24)	10.62 (10.66)
3.	[Ni(L) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] m.p. =220°C	10.0	550.7 (548.6)	Bluish Green	47.93 (47.81)	1.99 (1.96)	15.25 (15.28)	23.24 (23.22)	10.66 (10.62)

L=5-Cyano-3-formyl-1H-indole-1-dithiocarbamate ion

### 3.2. Molar conductance

The molar conductance of complexes were measured in 10<sup>-3</sup>M DMF solution at room temperature. The values of molar conductance were found in the range 18-24 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating non-electrolytic nature of complexes[16].

### 3.3 Magnetic moment

All the complexes were found to be paramagnetic with magnetic moment values in the range 2.94-2.98 BM indicating octahedral geometry for the complexes.

### 3.4 Electronic spectra

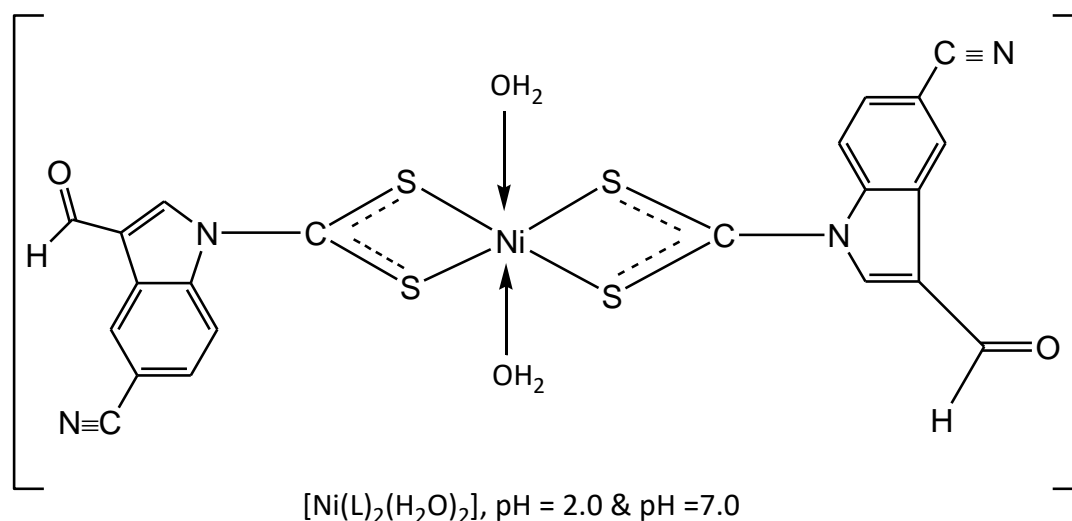
Electronic spectra of complexes displayed three d-d transition bands in each case in the range 9680-10200 cm<sup>-1</sup>, 14280 –19700 cm<sup>-1</sup> and 22540 –23540 cm<sup>-1</sup> which may be assigned to the transitions <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) respectively. The number and positions of electronic spectral bands also indicate octahedral geometry for the complexes.

### 3.5 Infrared spectra:

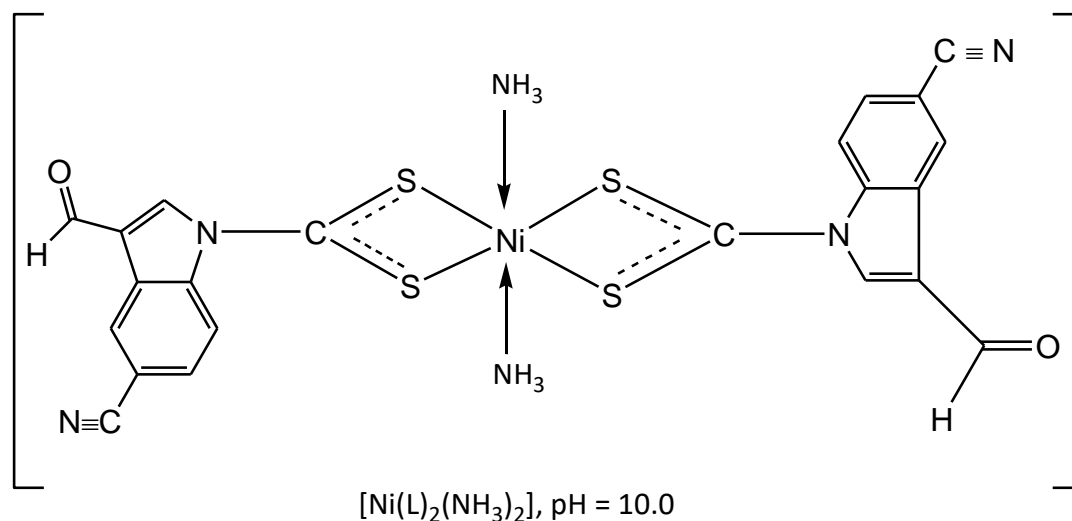
The weak infrared band at 2223 cm<sup>-1</sup> in the IR spectrum of the ligand assigned to  $\nu_{C\equiv N}$  stretching mode remained unchanged in position and intensity in infrared spectra of all the complexes. This indicated the non-participation of –C ≡ N group of the ligand in bonding to the metal ion. The sharp and strong band at 1715 cm<sup>-1</sup>

<sup>1</sup> in the spectrum of the ligand assigned to  $\nu_{\text{C=O}}$  stretching mode of  $-\text{CHO}$  group remained unchanged in position and intensity in the spectra of complexes. This indicated the non-participation of  $-\text{CHO}$  group of the ligand in bonding to the metal ion. The band at  $1460\text{ cm}^{-1}$  in the spectrum of the ligand assigned to  $\nu_{\text{N-CS}_2}$  mode of vibrations shifted towards lower frequency side at  $1420\text{ cm}^{-1}$  in the spectra of complexes. This indicated coordination of the ligand through sulphur atom to the metal ion weakening the  $\text{N-CS}_2$  bond. The bands at  $1010\text{ cm}^{-1}$  and  $920\text{ cm}^{-1}$  in the spectrum of the ligand due to  $\nu_{\text{CS}_2}$  antisymmetric and symmetric modes of vibrations respectively got shifted to  $925\text{ cm}^{-1}$  and  $820\text{ cm}^{-1}$  respectively in the infrared spectra of complexes. This also supported the coordination of the ligand to the metal ion through sulphur atoms. A new broad band centred at  $3480\text{ cm}^{-1}$  appeared in complex prepared in acidic and neutral media. This band may be assigned to  $\nu_{\text{OH}}$  mode of coordinated water molecules. This was also supported by the appearance of another new band at  $840\text{ cm}^{-1}$ , characteristic of the wagging mode of vibration of coordinated water molecule. The complex prepared in alkaline medium at  $\text{pH}=10.0$ , displayed new bands at  $3410\text{ cm}^{-1}$  and  $3380\text{ cm}^{-1}$  which may be assigned to antisymmetric and symmetric modes of vibrations respectively due to coordinated ammonia molecules. A new band in the region  $410\text{--}415\text{ cm}^{-1}$  appeared in all the complexes which may be assigned to  $\nu_{\text{Ni-S}}$  mode of vibration. This further supported the coordination of the ligand to metal ion through sulphur atom. Complexes prepared in acidic and neutral media displayed new bands in the region  $480\text{--}490\text{ cm}^{-1}$  which may be assigned to  $\nu_{\text{Ni-O}}$  mode of vibration. This supported the presence of water molecules in coordination sphere of complexes. The complex prepared in alkaline medium displayed a new band at  $465\text{ cm}^{-1}$  assignable to  $\nu_{\text{Ni-N}}$  mode of vibration. This supported the coordination of ammonia molecules to the metal ion in this complex.

On the basis of elemental analysis, determination of molar masses, molar conductance and magnetic moment measurements, uv and IR spectral studies, following octahedral structures have been established for the complexes (Fig. 3– Fig. 4):



**(Fig. 3)**



**(Fig. 4)**

#### IV. Conclusion

The complexes of Ni(II) with 5-cyano-3-formyl-1H-indole-1-dithiocarbamate prepared in acidic (pH =2.0), alkaline (pH=10.0) and neutral (pH=7.0) media have been found to have octahedral geometry. They are paramagnetic and non-electrolytic in nature. The coordination behaviour of the ligand has been found to be independent of the pH of the reaction medium. It behaves as monoanionic bidentate ligand in all the complexes.

#### V. Acknowledgement

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