

# Synthesis and Characterization of Ni (II) Complexes With Benzothiazole Derivatives

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**Abstract:** Ni (II) ion forms a large no. of complexes encompassing coordination number four, five and six and all the main structural types viz, octahedral, trigonal bipyramidal, square pyramidal, tetrahedral and square planar etc. Moreover, a characteristic feature of Ni (II) complexes are that they often exhibit equilibria, between these structural type which are generally temperature dependent and sometimes concentration dependent. In this paper we present Synthesis and Characterization of Ni (II) Complexes With Benzothiazole Derivatives.

**Keywords:** Ni (II), Pyramidal, Benzothiazole, Trigonal bipyramid.

## 1. Introduction

For the vast majority of four coordinated Ni (II) complexes, planar geometry is preferred. This is a natural consequence of the d<sup>8</sup> configuration since the planar ligands sets causes one of the d-orbitals viz dx<sup>2</sup> - y<sup>2</sup> to be uniquely high in energy and the eight electrons can occupy the outer four d-orbitals leaving the strongly antibonding orbital (dx<sup>2</sup> - y<sup>2</sup>) vacant. In tetrahedral coordination on the other hand occupation of antibonding orbitals is unavoidable. As important examples of square planar complexes, we may mention yellow [Ni (CN)<sub>4</sub>]<sup>2-</sup>, red bis (dimethylglyoximate) Nickel (II), the red keto enolate complexes. The yellow to brown Ni(CR<sub>3</sub>)<sub>2</sub>X<sub>2</sub> compounds in which alkyl and complexes containing homologue of the ligands in which the substituents on carbon are small, [Ni X<sub>4</sub>]<sup>-</sup>, [Ni X<sub>3</sub>L]<sup>-</sup>, (NiL<sub>2</sub>X<sub>2</sub>) and [Ni(L-L)<sub>2</sub>]<sup>+2</sup> when X represent a halogen, L a neutral ligand such as a phosphine, phosphine oxide or arsine and (L-L) is one of several type of bidentate ligand are the example of tetrahedral stereochemistry Pentacoordination in complexes have attracted the attention of chemists in recent past Furlani<sup>1</sup> reviewed the subject quite extensively. Orioli<sup>2</sup> however, confined himself in reviewing the cases of Ni (II) penta coordination only. The geometries that are frequently encountered are-

- (a) Trigonal bipyramid (D<sub>3h</sub> symmetry) (XXXVI)
- (b) Intermediate geometry (C<sub>2v</sub> symmetry) (XXXVII)
- (c) Square pyramid C<sub>4v</sub> (XXXVIII)

## 2. Experimental

Nickel(II) Chloride hexahydrate (1.419 gms, 0.005 mole) was dissolved in distilled water and ammonium hydroxide was added till a clear solution was obtained and to this a solution of ligand (0.005 mole) in N, N-dimethyl formamide was added. The pH of reaction mixture was found to be 9-10. The reaction mixture was refluxed on small flame or on water bath for 7-8 hours. The pH of reaction mixture was checked time to time and maintained by adding few drops of sodium bicarbonate. The coloured precipitate of the complexes thus obtained were filtered in hot washed with very dil. HCl, water and finally with benzene to remove unreacted metal salts and ligands. All the complexes were carefully recrystallised with nitrobenzene, dried over fused calcium chloride. Absence of free ligand in each case was ascertained in routine way by tic. Almost all complexes were found to be insoluble in water and common organic solvents.

**2.1 Preparation of Ligands:**

The ligand were prepared by the method available in the literature. [3, 4] 2-Acetoimidothiazole  
In accordance with the general procedure 2-Acetoimidothiazole was prepared by acetylation of  
2-aminothiazole (0.5 grs, .005 mole) with dil. Acetic acid and acetic anhydride in 91% yield. Yellow  
crude product was recrystallised from glacial acetic acid.

**M.P. – 113°C**

**Elemental analysis:**

	Found	Calculated for C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> OS
N	19.70	19.71 %
S	22.50	22.53 %
C	42.31	42.25 %

**Major IR Spectral bands:** 820 cm<sup>-1</sup>, 1520 cm<sup>-1</sup>, 1540 cm<sup>-1</sup>, 2957 cm<sup>-1</sup>

**U.V. Spectral bands :** 280 nm

**2-Acetoimidobenzathiazole**

This was also obtained by general method described above by the acetylation of 2-amino  
benzothiazole (0.75g, 0.005 mole) with dil acetic acid and acetic anhydride. It gives  
2-acetoimidobenzothiazole in 90% yield. The brown crude product was recrystallised from glacial  
acetic acid.

**M.P. = 120°C**

**Elemental analysis:**

	Found	Calculated for C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> OS
N	14.60	14.58
S	16.68	16.66
C	56.27	56.25

**Major IR Spectral bands:** 825 cm<sup>-1</sup>, 1525 cm<sup>-1</sup>, 1535 cm<sup>-1</sup>, 2960 cm<sup>-1</sup>

**U.v. Spectral bands :** 275 nm

**6-methyl 2-acetoimidobenzothiazole**

This was also obtained by general method described above by the acetylation of 6-methyl-  
aminobenzothiazole (0.82g, 0.005 mole) with dil. Acetic acid and acetic anhydride. It gives  
6-methyl-2 acetoimidobenzothiazole in 85% yield. The deep brown crude product was recrystallised  
from glacial acetic acid.

**M.P. = 125°C**

**Elemental analysis:**

	Found	Calculated for C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> OS
N	13.62	13.59
S	15.54	15.53
C	58.21	58.25

**Major IR Spectral bands:** 822 cm<sup>-1</sup>, 1540 cm<sup>-1</sup>, 1565 cm<sup>-1</sup>, 2965 cm<sup>-1</sup>

**U.V. Spectral bands:** 270 nm

**4-mythyl 2-acetoimidothiazole**

Following the usual procedure 4-mythyl, 2-acetoimidothiazole was prepared by acetylation of  
4-methyl-2-aminothiazole (0.57 gra, 0.005 mole) with dil. Acetic acid and acetic anhydride in 92%.  
The light yellow crude product was recrystalised from glacial acetic acid.

**M.P. - 115°C**

**Elemental analysis:**

	Found	Calculated for C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> OS
N	18.00	17.94
S	20.53	20.51
C	46.13	46.15

**Major IR Spectral bands:** 830 cm<sup>-1</sup>, 1510 cm<sup>-1</sup>, 1535 cm<sup>-1</sup>, 2968 cm<sup>-1</sup>

**U.V. Spectral bands :** 275 nm

**5 [thiazole-2-azo] thiobarbutyric acid**

In accordance with the general procedure 5-[thiazole-2-azo-] thiobarbutyric acid was prepared by  
coupling of diazotized solution of 2-amino thiazole (0.5g, 0.005 mole) with thiobarbutyric acid

(1.27g, 0.005 mole) in 80% yield. The light brown crude product was recrystallised from glacial acetic acid.

**M.P. – 110°C**

**Elemental analysis:**

	Found	Calculated for C <sub>7</sub> H <sub>5</sub> N <sub>5</sub> O <sub>2</sub> S <sub>2</sub>
N	27.43	27.45
S	25.07	25.09
C	28.21	28.23

**Major IR Spectral bands:** 786 cm<sup>-1</sup>, 830 cm<sup>-1</sup>, 1049 cm<sup>-1</sup>, 1610 cm<sup>-1</sup>, 3125 cm<sup>-1</sup>

**U.V. Spectral bands :** 280 nm

#### **5 [thiazole-4-mythyl-2-azo-] thiobarbutyric acid**

In accordance with the general procedure 5-[thiazole-4-mythyl-2-azo] thiobar butyric acid was prepared by coupling of diazotized solution of 2-amino- 4-methylthiazole (.57g, 0.005 mole) with thiobarbutyric acid (1.34g, 0.005 mole) in 85% yield. The yellow crude product was recrystallised from ethanol.

**M.P. – 122°C**

**Elemental analysis:**

	Found	Calculated for C <sub>8</sub> H <sub>7</sub> N <sub>5</sub> S <sub>2</sub> O <sub>2</sub>
N	26.00	26.02
S	23.74	23.79
C	31.20	31.22

**Major IR Spectral bands:** 780 cm<sup>-1</sup>, 825 cm<sup>-1</sup>, 1040 cm<sup>-1</sup>, 1390 cm<sup>-1</sup>, 1450 cm<sup>-1</sup>, 1540 cm<sup>-1</sup>, 1615 cm<sup>-1</sup>, 3137 cm<sup>-1</sup>

**U.V. Spectral bands:** 280 nm

## **2.2 Preparation of Nickel Complexes with Ligands Nickel(II) Complexes with 2-acetoimidothiazole:**

In accordance with the general procedure, purple coloured complex was obtained by using 2 mole of 2-acetoimidothiazole (1 gms, 0.01 mole) as a ligand in 70% yield. The paramagnetic complex (meff = 3.10 B.M.) was finally decomposed at 265°C.

**Elemental analysis:**

	Found	Calculated for NiC <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>
Ni	15.38	15.42
N	14.85	14.89
S	17.00	17.02
C	31.88	31.91

**Major IR Spectral bands:** 812 cm<sup>-1</sup>, 1512 cm<sup>-1</sup>, 1553 cm<sup>-1</sup>, 3430 cm<sup>-1</sup>, 3440 cm<sup>-1</sup>

**Electronic Spectral bands:** 405nm, 640nm

#### **Nickel (II) Complexes with 2-acetoimidobenzothiazole**

Again black coloured paramagnetic complex (meff =3.05 B.M) was prepared by the general method described above using 2-mole of (2-acetoimidobenzothiazole) (1.5 gm, 0.01mole) as a ligand in 60% yield. The final decomposition point of the complex was found to be 275° C

**Elemental Analysis:**

	Found	Calculated for NiC <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>
Ni	12.15	12.18
N	11.73	11.76
S	45.36	45.37
C	13.41	13.44

**Major IR Spectral bands:** 815 cm<sup>-1</sup>, 1518 cm<sup>-1</sup>, 1547 cm<sup>-1</sup>, 3442 cm<sup>-1</sup>, 3450 cm<sup>-1</sup>

**Electronic Spectral bands:** 410 nm, 645 nm

#### **Nickel (II) complexes 6-methyl 2-acetoimidobenzothiazole**

This complex was obtained by the general method described above from 2 mole of 6-methyl 2-acetoimidobenzothiazole (1.64gm, 0.01 mole) in 55%yield. The brown coloured paramagnetic complex (meff = 3.01 B.M) decomposed above 272° C.

**Elemental Analysis:**

	Found	Calculated for C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>
Ni	11.45	11.50
N	11.07	11.11
S	12.60	12.63
C	47.59	47.61

**Major IR Spectral bands:** 810 cm<sup>-1</sup>, 1530 cm<sup>-1</sup>, 1570 cm<sup>-1</sup>, 3428 cm<sup>-1</sup>, 3433 cm<sup>-1</sup>

**Electronic Spectral bands:** 395 nm, 650 nm

**(iv) Nickel (II) Complexes with 4-methyl 2-acetoimidothiazole**

Following the usual procedure using 2 mole of 4- methyl 2-acetoimidothiazole (1.14gm, 0.01mole) complex was prepared in yield 85% yield. The deep brownish red complex was found to be paramagnetic with ( $\mu_{eff}$  =3.03 B.M). The complex decomposes above 270° C.

**Elemental analysis:**

	Found	Calculated for NiC <sub>12</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>
Ni	14.34	14.35
N	13.80	13.86
S	15.80	15.84
C	35.63	35.64

**Major IR Spectral bands:** 815 cm<sup>-1</sup>, 1507 cm<sup>-1</sup>, 1550 cm<sup>-1</sup>, 2960cm<sup>-1</sup>, 3431cm<sup>-1</sup>, 3436 cm<sup>-1</sup>

**Electronic Spectral bands:** 407 nm, 655 nm

**(v) Ni (II) complexes with 5-(thiazole-2-azo) thiobarbutyric acid**

In accordance with the general procedure complex was prepared from Nickel(II) acetate (1.76gms, 0.0mole) and 5-(thiazole-2-azo-)thiobarbutyric acid (2.25gm mole, 0.01mole) in 80% yield. The brownish black complexes was paramagnetic ( $\mu_{eff}$  =3.45 B.M) and decomposed finally above 271°C.

**Elemental Analysis:**

	Found	Calculated for NiC <sub>7</sub> H <sub>5</sub> N <sub>5</sub> O <sub>3</sub> S <sub>2</sub>
Ni	17.60	17.62
N	21.25	21.27
S	19.43	19.45
C	25.51	25.53

**Major IR Spectral bands:** 784 cm<sup>-1</sup>, 820 cm<sup>-1</sup>, 830 cm<sup>-1</sup>, 1043 cm<sup>-1</sup>, 1526 cm<sup>-1</sup>, 1535 cm<sup>-1</sup>,1600cm<sup>-1</sup>, 3429 cm<sup>-1</sup>, 3434 cm<sup>-1</sup>,1392 cm<sup>-1</sup>

**Electronic Spectral bands:** 660nm

**(vi) Nickel (II) complexes with 5-(thiazole-4- methyl-2-azo)-thoibarbutyric acid**

In accordance with the general procedure complex was prepared from Nickel (II) acetate (1.76gm, 0.01mole) and 5-(thiazole-4 methyl-2-azo) thoibarbutyric acid (2.69gm, 0.01mole) in 82% yield. The light brown complex was paramagnetic ( $\mu_{eff}$  = 3.46BM) and decomposed finally above 273 °C.

**Elemental Analysis:**

	Found	Calculated for NiC <sub>8</sub> H <sub>7</sub> N <sub>5</sub> O <sub>3</sub> S <sub>2</sub>
Ni	16.91	16.90
N	20.38	20.40
S	13.97	13.99
C	27.96	27.98

**Major IR Spectral bands:** 780 cm<sup>-1</sup>, 815 cm<sup>-1</sup>, 825 cm<sup>-1</sup>, 1038 cm<sup>-1</sup>, 1389 cm<sup>-1</sup>, 1529 cm<sup>-1</sup>, 1532 cm<sup>-1</sup>, 1610c cm<sup>-1</sup>, 3432 cm<sup>-1</sup>, 3437 cm<sup>-1</sup>

**Electronic Spectral bands:** 665 nm

**3. Result and Discussion**

In the present investigation, the heterocyclic amines chosen for carrying out coupling reactions of diazotized solutions were 2-aminothiazole, 2-amino-4-methyl thiazole and thiobarbutyric acid was used for the coupling reactions. Further 2-amino thiazole, 2-amino benzothiazole, 6-(methyl)-2-aminobenzothiazole and 4-(methyl)-2-aminothiazoles were used for carrying out acetylation reactions. In this way the following six compounds have been synthesized.

1-aminothiazole + acetic anhydride->acetylation-> HL1

2-aminobenzothiazole + acetic anhydride->acetylation->HL2

3-[methyl-]2- aminobenzothiazole + acetic anhydride-> acetylation->HL3

4-[methyl]-2-aminothiazol + acetic anhydride->acetylation->HL4

5-aminothiazole + thiobarbutyric acid->diazotised->HL5

6-amino-4-[methyl] thiazole + thiobarbutyric acid ->diazotised->HL6

The problem of their structural assignment was concluded by carrying out several physiochemical measurements and thus finally tentative structures were proposed. These Ligands were subjected to the reaction with Nickel metal ion.

**Table-1: Physical Constants, magnetic Moment and analytical data of Cu(II) Complexes Metal & N-analysis**

Name of complexes	$\mu_{\text{eff}}$ at 298°K in B.M	decomposition temperature	Colour	Percentage yield	Elemental Analysis							
					Cu		N		S		C	
					Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
NiC <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	3.10	265°C	Purple	70%	15.38	15.42	14.85	14.89	17.00	17.02	31.8	31.91
NiC <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	3.05	275°C	Black	60%	12.15	12.18	11.73	11.76	13.41	13.44	45.36	45.37
NiC <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	3.01	272°C	Brown	55%	11.45	11.50	11.07	11.11	12.60	12.63	47.59	47.61
NiC <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	3.03	270°C	Deep brownish red	85%	14.34	14.35	13.80	13.86	15.80	15.84	35.63	35.64
NiC <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	3.45	271°C	Brownish black	80%	17.60	17.62	21.25	19.43	19.45	25.51	25.53	
NiC <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	3.46	273°C	Light brown	82%	16.91	16.90	20.38	20.40	13.97	13.99	27.96	27.98

**Table – 2:Ligand field Parameters of Ni(II) complexes**

Name of Complexes	$v_3/v_2$	$1_0 dq$ in (Cm <sup>-1</sup> )	B in (Cm <sup>-1</sup> )	$\beta$	$\beta^\circ$ Percentage	$v_2/v_1$ (Cal.)
Ni(L <sub>1</sub> ) <sub>2</sub> 2H <sub>2</sub> O	1.580	10236	915	0.86	14	1.52
Ni(L <sub>2</sub> ) <sub>2</sub> 2H <sub>2</sub> O	1.573	10325	920	0.87	13	1.50
Ni(L <sub>3</sub> ) <sub>2</sub> 2H <sub>2</sub> O	1.645	9300	804	0.76	24	1.65
Ni(L <sub>4</sub> ) <sub>2</sub> 2H <sub>2</sub> O	1.609	10000	862	0.81	19	1.54

**Table – 3:Characteristic Infrared Spectral bands of Ni(II) complexes (in cm<sup>-1</sup>)**

Name of Complexes	$\nu$ H <sub>2</sub> O	$\nu$ C=O	$\nu$ C=N	$\nu$ C-S-C	thioamide
Ni(L <sub>1</sub> ) <sub>2</sub> 2H <sub>2</sub> O	3430-3440 (b)	1512 (S)	1553(m)	812 (m)	
Ni(L <sub>2</sub> ) <sub>2</sub> 2H <sub>2</sub> O	3442-3450 (b)	1518 (s)	1547(m)	815 (m)	
Ni(L <sub>3</sub> ) <sub>2</sub> 2H <sub>2</sub> O	3428-3433 (b)	1530 (s)	1570 m)	810 (m)	
Ni(L <sub>4</sub> ) <sub>2</sub> 2H <sub>2</sub> O	3431-3436 (b)	1507 (s)	1550(m)	815 (m)	
Ni(L <sub>5</sub> ) <sub>2</sub> 2H <sub>2</sub> O	3429-3434 (b)	1526 (s)≈1600 (s)	1535(m)	820(m),830(m)	1392,1043,784
Ni(L <sub>6</sub> ) <sub>2</sub> 2H <sub>2</sub> O	3432-3437(b)	1529 (s)≈1610 (s)	1532(m)	815 (m), 825(m)	1389,1038,780

#### 4. Conclusion

On the basis of physical characteristics presented in table-1 it was concluded that the complexes were monomeric and non electrolytic in nature. The IR spectral studies led us to believe that all the compounds contain coordinated water molecule in its coordination sphere and the ligand HL1 to HL4 behaved as S-O donor in uninegative form after enolisation and deprotonation, however the ligands HL5 and HL6 behaved as tridentate SNO donor after rearrangement of the structure and deprotonation of OH and SH group.

The electronic spectral studies were interpreted in terms of octahedral geometry for the complexes with ligand HL1 to HL4. The transitions around 15038 - 15625 cm<sup>-1</sup> and 24570 - 25316 cm<sup>-1</sup> were assigned to 3A<sub>2</sub>g-> 3T<sub>1</sub>g(F), ( $v_2$ ) and 3A<sub>2</sub>g->3T<sub>1</sub>g(P),( $v_3$ ) transition. The crystal field parameters i.e 10Dq and B were found to be in the range of 9300 - 10236 cm<sup>-1</sup> and 804 - 920 cm<sup>-1</sup>. It gives the percentage covalent values character in the synthysised complexes as 18+- 6% .The  $v_2/v_1$ , values

further suggest an approximate octahedral geometry. Based upon the general formula of the complexes along with the above observation, a tentative structure for the complexes may be assigned.

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