

Studies on Ni (II) Complexes of Thiazole Derivatives Containing O,N,S Donors

**Ashok Kumar Srivastava¹, Anjani Kumar Shukla² & Nidhi Srivastava³*

¹*Professor, University Department of Chemistry, B.R.A Bihar University, Muzaffarpur (Bihar) – 842001, India.*

¹*Email:- aksrivastavaa@rediffmail.com*

²*Assistant Professor, P G Dept. of Chemistry, RDS College Muzaffarpur, (Bihar) - 842001, India.*

²*Email:- anjanishukla06@gmail.com*

³*Department of Chemistry, B.R.A Bihar University, Muzaffarpur (Bihar) - 842001, India.*

³*Email :- aksrivastavaa@rediffmail.com*

Abstract: *This paper discusses the preparation and characterisation of Nickel (II) complexes with thiazole derivative having oxygen, Nitrogen and sulphur donor atoms. On the basis of physical characteristics of the complexes, elemental analysis, magnetic moment data and spectral studies it was concluded that the Nickel (II) complexes were possessing octahedral and or tetrahedral arrangement of ligands around the central metal ion.*

Keywords: Thiazole, magnetic, spectra, I R,uv-visible.

1. Introduction:

A number of hetrocyclic compounds containing sulphur and nitrogen atoms have been found their uses as drugs and diagnostic agents in medicinal inorganic chemistry. Medicinal activities of sulphur and nitrogen compounds have been reported earlier by a series of workers [1-2]. The incorporation of transition metal ions have also been reported to enhanced ,such activities in large numbers of with this view, the attempts were made to synthesis and characterisation of Nickel (II) complexes with the ligands derived by the reaction of diazotized solution of 2-aminothiozole and its methyl derivatives with acetoacetanilide, thiouracil and 3-acetylamino-N,N-diethylaniline reported as H₂ (L₁), H₂ (L₂), H₂(L₃),H₂ (L₄), H (L₅) & H (L₆).

The characterisation was done with help of elemental analysis, magnetic moment data, uv-visible spectra and ir spectral studies.

2. Experimentals:

The ligands were prepared by the procedure described elsewhere [3-6] .The Ni(II) complexes of the ligands were synthesized by by refluxing methanolic solution of Ni (II) acetate hexahydrate and the ligands for 3-5 hours and the products were filtered out and crystallized by ethanol. Absence of free ligand was ascertained by TLC.

3. Results and discussion:

The elemental analysis and physical characteristics of the complexes were given in table-1.

Table-1

Physical and analytical data of Ni (II) complexes

Name of Ligands, Symbol of Ligands and Formula Complexes	Colour	Yield %	M.P °c	Magnetic Moment (BM)	Elemental Analysis (%)		
					Ni	N	S
1,2,3-trioxo-1-phenylamine-2-(thiazolyhydrazono) butane $H_2(L_1)$, $[Ni(HL_1)(AC)H_2O]$	Buff	60	255	3.62	15.86 (15.97)	15.29 (15.24)	8.25 (8.81)
1,2,3-trioxo-1-phenylamine-2-(4- methylthiazolyhydrazono) butane $H_2(L_2)$, $[Ni(HL_2)(AC)H_2O]$	Buff	65	231	3.60	18.20 (18.33)	22.10 (22.22)	10.10 (10.15)
5-(2-thiazolyazo) thiouracil $H_2(L_3)$, $[Ni L_3 H_2O]$	Buff	50	210	3.20	19.70 (19.81)	21.75 (21.84)	9.85 (9.98)
5-(4-methy) (2-thiazolyazo)thiouracil, $H_2(L_4)$, $[Ni L_4 H_2O]$	Buff	51	214	3.17	18.97 (19.20)	21.15 (21.50)	9.09 (9.48)
3-(acetylamino)-4-(2-thiazolyazo) N,N-diethylaniline $H(L_5)$, $[Ni(L_5)_2]$	Buff	80	210	3.50	8.28 (8.40)	10.14 (10.14)	4.56 (4.63)
3-(3-acetylamino)-4-(4-methyl-2-thiazolyazo) N,N-diethylaniline $H(L_6)$, $[Ni(L_6)_2]$	Buff	78	213	3.52	8.08 (8.40)	9.84 (10.04)	4.06 (4.51)

All the complexes were insoluble in inorganic and organic solvents. The magnetic value of Ni (II) complexes were in the range 3.50 -3.62 BM for complexes with ligands $H_2(L_1)$, $H_2(L_2)$, $H(L_5)$ and $H(L_6)$ excepted for octahedral geometry with some orbital contribution from excited state. While 3.17'-3.20 BM for complexes with ligands $H_2(L_3)$ and $H_2(L_4)$ having tetrahedral geometry with contribution of spin orbital coupling.

4. I.R spectra:

The spectra of Ni (II) complexes have been recorded by using parkin Elmer 577 modal. IR absorption bands of Ni (II) complexes with ligands H₂ (L₁) to H(L₆) in table-2.

Table-2

Characteristics I.R spectra of Ni (II) complexes

Complexes	I.R Spectral Bands (cm ⁻¹)					
	$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{C=O}}$	ν_{ac}	$\nu_{\text{N=N}}$	ν_{CSC}	$\nu_{\text{N=C}}$
[Ni (HL ₁) (AC) H ₂ O]	3500-3460	1630-1582	1410	—	832	—
[Ni (HL ₂) (AC) H ₂ O]	3410-3470	1625-1580	1440	—	832	—
[Ni L ₃ H ₂ O]	3500-3460	1635-1582	—	—	830	1105
[Ni L ₄ H ₂ O]	3500-3435	1630-1580	—	—	832	1100
[Ni (L ₅) ₂]	—	1582	—	1530	830	—
[Ni (L ₆) ₂]	—	1582	—	1535	832	—

The close examination of table-2, clearly indicated that no peak around 3200 cm⁻¹ is obtained in all Ni (II) complexes which were found present in all ligands. The absence of this peak clearly indicated about deprotonation of N-H group in all ligands and also involvement of amino benzothiazol nitrogen in coordination. The absorption peak due to C-S-C cyclic group located around 830±5 cm⁻¹ in ligands remain approximately unchanged. This indicated that sulphur atom of the ligands is not involved in coordination in the Ni(II) complexes. A broad and strong peak in region 1630 -1580 cm⁻¹ clearly indicated about the involvement of carbonyl group in coordination or presence of azo group in the ligands itself remained unchange. The occurrence of weak and medium peak around 3550 – 3480 cm⁻¹ are indicative of presence of water molecule in coordination sphere of Ni (II) ion in complexes with ligands H₂ (L₁), H₂ (L₂), H₂ (L₃) and H₂ (L₄) found absent in two complexes with ligands H(L₅) and H(L₆) indicating the absence of coordinated water molecule in these two complexes. The absorption peak around 1410±5 cm⁻¹ from complexes with ligands H₂ (L₁) to H₂ (L₂) indicates that free acetate is also present in the complexes. The absence of peak around 1540 cm⁻¹ in the complexes with ligands H₂ (L₁) to H₂ (L₄) clearly indicated that in these complexes the azo group was absent. While it was presented in the complexes with ligands H(L₅) and H(L₆).

5. Electronic spectra:

The electronic spectra of all Nickel (II) complexes have been recorded in the region 240 -800 cm^{-1} using diffused reflectance methods and are given in table-3 along with their tentative assignment by assuming pseudo octahedral geometry for complex $[\text{Ni}(\text{HL}_1)(\text{AC})\text{H}_2\text{O}]$, $[\text{Ni}(\text{HL}_2)(\text{AC})\text{H}_2\text{O}]$, $[\text{Ni}(\text{L}_5)_2]$ and $[\text{Ni}(\text{L}_6)_2]$ and pseudo tetrahedral geometry for complexes $[\text{Ni}(\text{L}_3)_2\text{H}_2\text{O}]$ and $[\text{Ni}(\text{L}_4)_2\text{H}_2\text{O}]$.

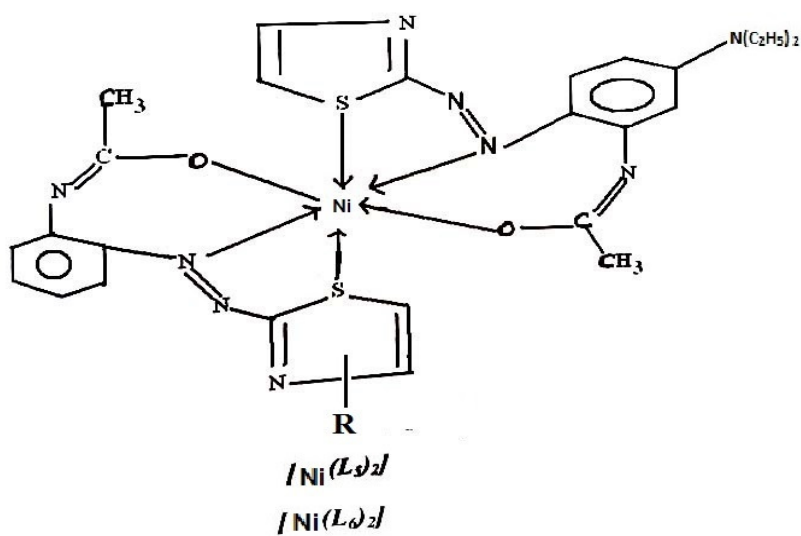
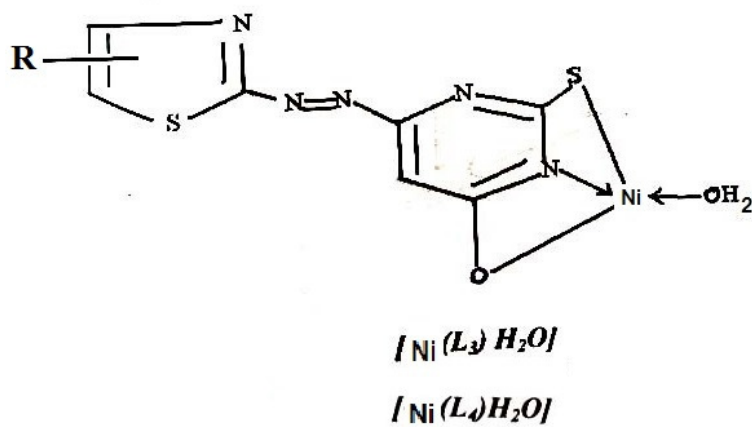
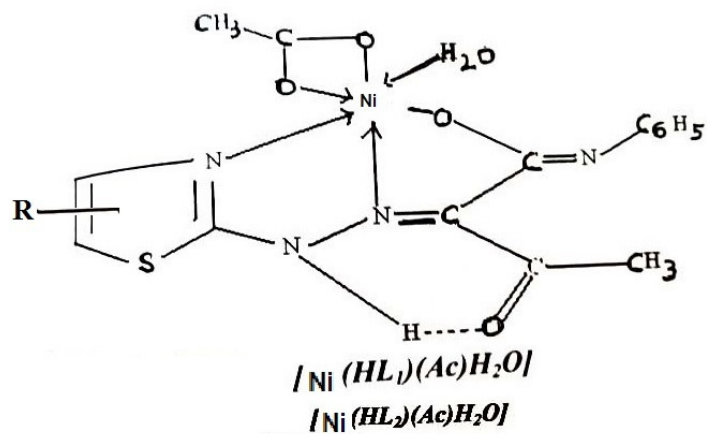
Table-3
Electronic spectral bands of Ni (II) complexes in cm^{-1}

Complexes	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{P})$
$[\text{Ni}(\text{HL}_1)(\text{AC})\text{H}_2\text{O}]$	14925	24814	—	—	—
$[\text{Ni}(\text{HL}_2)(\text{AC})\text{H}_2\text{O}]$	14815	25641	—	—	—
$[\text{Ni}(\text{L}_3)_2\text{H}_2\text{O}]$	—	—	7800	14600	14600
$[\text{Ni}(\text{L}_4)_2\text{H}_2\text{O}]$	—	—	7800	14600	14600
$[\text{Ni}(\text{L}_5)_2]$	15384	25000	—	—	—
$[\text{Ni}(\text{L}_6)_2]$	15390	25155	—	—	—

6. Conclusion:

The data of elemental analysis, magnetic moment, ir ,uv-visible spectral studies suggested that ligands $\text{H}_2(\text{L}_1)$ and $\text{H}_2(\text{L}_2)$ behaves as uninegative N,N,O donor ligand and the synthesized Ni(II) complexes were hydrated with one acetate group in coordination sphere .The octahedral geometry was the proposed. The ligands $\text{H}_2(\text{L}_3), \text{H}_2(\text{L}_4), \text{H}(\text{L}_5)$ and $\text{H}(\text{L}_6)$ behaved as binegative, O,N,S donor .In complex with $\text{H}_2(\text{L}_3)$ and $\text{H}_2(\text{L}_4)$ one water molecule of coordination was also present, therefore a tetrahedral geometry was proposed while in $\text{H}(\text{L}_5)$ and $\text{H}(\text{L}_6)$ a six coordinated octahedral geometry was proposed.

The structures are represented as:



Where,

R=H, 2-Methyl

7. Acknowledgement:

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8. References:

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