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SYNTHESIS AND CHARACTERISATION OF Ni (II) COMPLEXES WITH SOME THIAZOLE DERIVATIVES AS LIGANDS

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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 terahedral arrangement of ligands around the central metal ion.

KEYWORDS: Thiazole, Magnetic, Spectra, IR, UV-visible

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 (Prasad *et al.*, 1992) (Srivastava, 1990). 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 H_2 (L_1), H_2 (L_2) H_2 (L_3) H_2 (L_4) H (L_5) & H (L_6).

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

EXPERIMENTALS

The ligands were prepared by the procedure described elsewhere (Srivastava *et al.*, 2019) (Srivastava and Srivastava, 1994) (Srivastava *et al.*, 2014) (Shukla and Srivastava, 2021). The Ni(II) complexes of the ligands were synthesized by by refluxing methanolic solution of Ni (II) acetate hexahyderate 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.

RESULTS AND DISCUSSION

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

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.

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 H_2 (L_1) to H(L_6) in table-2.

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 H_2 (L_1), H_2 (L_2), H_2 (L_3) and H_2 (L_4) found absent

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in two complexes with ligands H(L_5) and H(L_6) indicating the absence of coordinated water molecule in these two complexes. The absorption peak around 1410±5 cm^{-1} from complexes with ligands H_2 (L_1) to H_2 (L_2) indicates that free acetate is also present in the complexes. The absence of peak around 1540 cm^{-1} in the complexes with ligands H_2 (L_1) to H_2 (L_4) clearly indicated that in these complexes the azo group was absent. While it was presented in the complexes with ligands H(L_5) and H(L_6).

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 [Ni (HL_1) (AC) H_2O], [Ni (HL_2) (AC) H_2O], [Ni (L_5)$_2$] and [Ni (L_6)$_2$] and pseudo terahedral geometry for complexes[Ni L_3 H_2O] and [Ni L_4 H_2O].

Table 1: Physical and analytical data of Ni (II) complexes

Name of Ligend, Symbol of Ligand 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-methylthiazolydrazono) 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-thiazolylazo) 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-thiazolylazo)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-thiazolylazo) 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-thiazolylazo) 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)

Table 2: Characteristics I.R spectra of Ni (II) complexes

Complexes	I.R Spectral Bands (cm^{-1})					
	υ_{H_2O}	$\upsilon_{C=O}$	υ_{ac}	$\upsilon_{N=N}$	υ_{CSC}	$\upsilon_{N=C}$
[Ni (HL_1) (AC) H_2O]	3500-3460	1630-1582	1410	____	832	____
[Ni (HL_2) (AC) H_2O]	3410-3470	1625-1580	1440	____	832	____
[Ni L_3 H_2O]	3500-3460	1635-1582	____	____	830	1105
[Ni L_4 H_2O]	3500-3435	1630-1580	____	____	832	1100
[Ni (L_5)$_2$]	____	1582	____	1530	830	____
[Ni (L_6)$_2$]	____	1582	____	1535	832	____

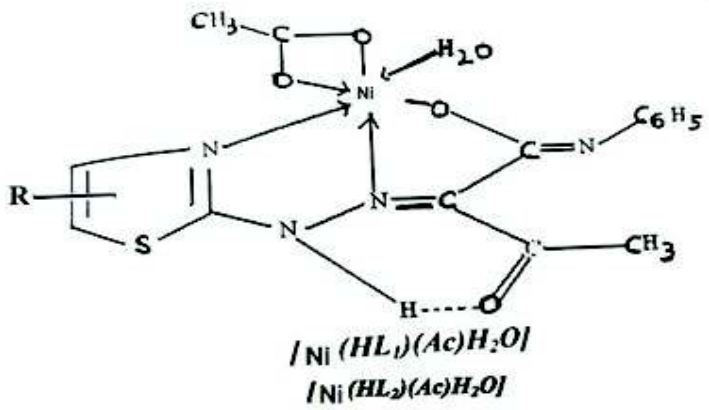
Table 3: Electronic spectral bands of Ni (II) complexes in cm^{-1}

Complexes	$^3A_2g \rightarrow {}^3T_1g$	$^3A_2g \rightarrow {}^3T_1g$ (P)	$^3T_1$ (F) $\rightarrow {}^3T_2$ (F)	$^3T_1$ (F) $\rightarrow {}^3T_2$ (F)	$^3T_1$ (F) $\rightarrow {}^3T_1$ (P)
[Ni (HL_1) (AC) H_2O]	14925	24814	____	____	____
[Ni (HL_2) (AC) H_2O]	14815	25641	____	____	____
[Ni L_3 H_2O]	____	____	7800	14600	14600
[Ni L_4 H_2O]	____	____	7800	14600	14600
[Ni (L_5)$_2$]	15384	25000	____	____	____
[Ni (L_6)$_2$]	15390	25155	____	____	____

CONCLUSION

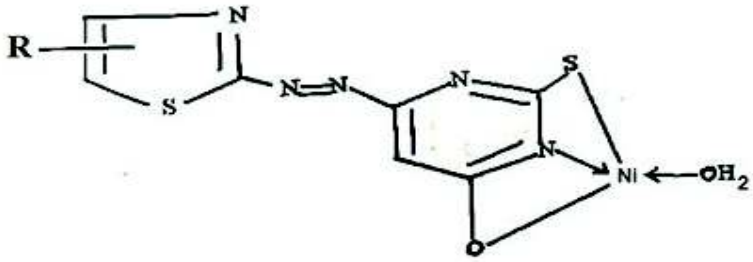
The data of elemental analysis, magnetic moment, ir, uv-visible spectral studies suggested that ligands $H_2(L_1)$ and $H_2(L_2)$ behaves as uninegative N,N,O donor ligand and the synthesized Ni(II) complexes were hydrated with one acetate group in coordination sphere. The octahedral geometry the was proposed. The ligands $H_2(L_3)$,$H_2(L_4)$,$H(L_5)$ and $H(L_6)$ behaved as binegative, O,N,S donor .In complex with $H_2(L_3)$ and $H_2(L_4)$ one water molecule of coordination was also present, therefore a tetrahedral geometry was proposed while in $H(L_5)$ and H (L_6) a six coordinated octahedral geometry was proposed.

The structures are represented as:



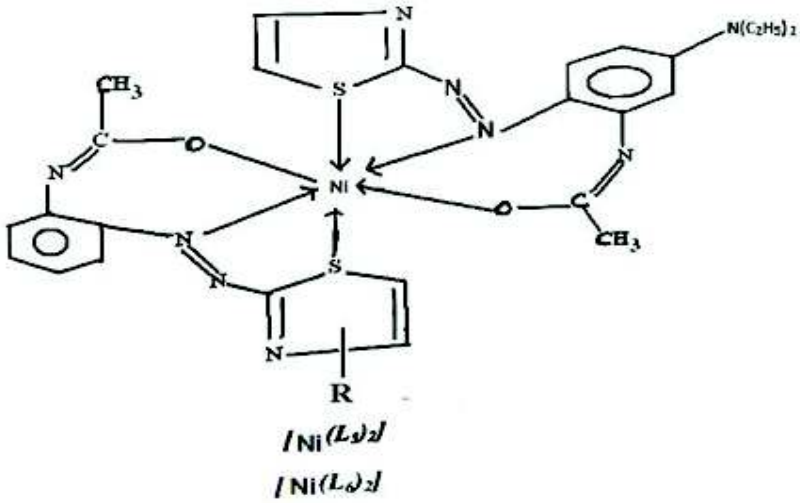
$[Ni(HL_1)(Ac)H_2O]$

$[Ni(HL_2)(Ac)H_2O]$



$[Ni(L_3)H_2O]$

$[Ni(L_4)H_2O]$



$[Ni(L_5)_2]$

$[Ni(L_6)_2]$

Where, R=H, 2-Methyl

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