# Synthesis and Characterization of Some Schiff Bases Complexes With Co(II) and Ni(II)

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## Abstract:

Complexes of Co(II) and Ni (II) with a Schiff bases , N-[5-(propyl) 2- amino-1 , 3,4- thiadiazolebenzylidene] ($L_1$) and N- [5-(propyl) 2- amino-1,3,4- thiadiazole -4 - chlorobenzylidene] ($L_2$) (molar ratio 1 : 2) have been prepared and characterized by their physical , spectral and analytical data .The synthesized Schiff bases act as

**Key words:** 1,3,4-Thiadiazole,Schiff bases, complexes.

## Introduction:

Numerous Schiff bases [1-3] and their transition metal complexes [4-6] , have been investigated by various techniques [7] . Thiadiazole and its derivatives has been found to be of biological significance [8].

Metal complexes of sulphur – nitrogen chelating ligands have attracted considerable attention because of their interesting physicochemical properties , pronounced biological activities [9-11] and as models of the metalloenzyme active sites . It is well known that nitrogen and sulphur atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules [12] . Thiadiazoles are known to possess interesting antibacterial [13,14] , antifungal [15] , nematocidal [16] , cardiovascular [17] , and anti-inflammatory [18] activities . Therefore , it has been found interesting to study of complexes containing Schiff bases derived from thiadiazole and benzaldehyde or p-chlorobenzaldehyde. In our best knowledge , transition metal complexes of the N-[5-(propyl)2-amino-1,3,4-thiadiazole benzylidene]($L_1$) and N- [5-(propyl) 2- amino-1,3,4 – thiadiazole -4- chlorobenzylidene] ($L_2$) have not been synthesized . Therefore , we synthesized the complexes of Co(II) and Ni (II) of the ($L_1$) and ($L_2$) (Figure 1) .
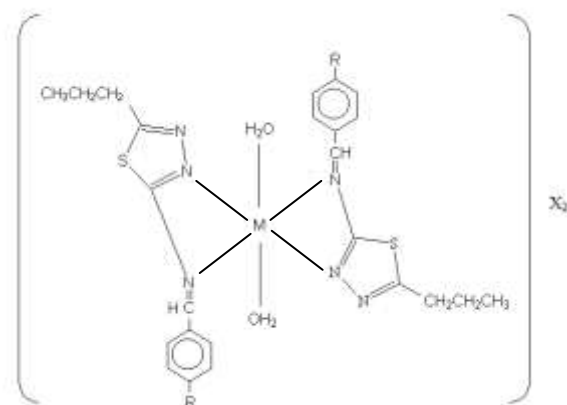


M = Co(II) or Ni(II)
R = H or Cl
X = Cl$^-$ or NO$_3^-$
**Figure (1):** The proposed structure of the complexes

## Experimental:

**Materials** : Chemicals employed were of analytical grade used without further purification.
**Analytical and physical measurements :**

bidentate ligands during the complexation reaction with Co(II) and Ni(II) metal ions. They have the formula [M(L)$_2$ (H$_2$O)$_2$] X$_2$ (where M = Co (II) or Ni (II) , L = $L_1$ or $L_2$ and X = Cl$^-$ or NO$_3^-$) and show an octahedral geometry .

Cobalt and nickel contents have been determind by applying precipitation methods [19] after the decomposition of the complexes with concentrated nitric acid .

Melting points were determind by using Richerk Jung Heizbank melting point apparatus . Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 0.001M of the complexes in dimethylformamide (DMF) solutions at room temperature. IR spectra were recorded on a Bruker tensor 27 spectrophotometer in the 400-4000 cm$^{-1}$ range using KBr disc . Electronic spectra were recorded on a Shimadzu 1601 spectrophotometer in dimethylformamide at 25 C$^o$ for 0.001M solution of the compounds using a 1cm quartz cell. Magnetic susceptibilities of the complexes have been measured by Bruker B.M.6 .

## Preparation of the compounds :

1-Preparation of 2-amino-5-propyl-1,3,4 thiadiazole This compound is prepared by the method reported earlier [20].

2- Preparation of the ligands :

Both ligands ($L_1$)and ($L_2$) are prepared by a similar way :

A mixture of benzaldehyde (0.01 mole),or p-chlorobenzaldehyde (0.01 mole) , absolute ethanol (40 ml) and 2-amino-5-propyl–1,3,4 , thiadiazole (0.01 mole) with (2-3) drops of glacial acetic acid was refluxed for 2 hours with continuous stirring . After cooling to room temperature , the precipitate was filtered , dried and recrystallized from ethanol [21] .

3- Preparation of the complexes :

(2 mmol) of the ligand was dissolved in 40 ml of absolute ethanol , a solution of (1 mmol) of the metal salt hydrate in 20 ml of ethanol was added drop wise to the ligand solution with continuous stirring and the mixture left to refluxed overnight . The volumes of the solutions were reduced to about 10 ml and complexes were precipitated in diethylether . The precipitate was filtered , washed with water and ethanol and then dried at room temperature .

## Results and discussion:

The analytical data along with some physical properties of the complexes are summarised in (Table 1). The ligands ($L_1$) and ($L_2$) , on interaction with Co(II) and Ni (II) salts , yield complexes corresponding to the general formula [M(L)$_2$(H$_2$O)$_2$]X$_2$ .The analytical data show that the metal to ligand ratio is 1:2 . They are insoluble in

common organic solvents such as ethanol and methanol , but soluble in DMF. The molar conductances of 0.001 M aqueous solutions of the complexes are given in (Table 1). All the complexes show conductance values , indicating their 1 : 2 electrolytic nature [22].

**Table (1) :** Physical and analytical properties of the ligands and their complexes

| Compound | Color | m.p $^0$C | Yield % | % Metal Calc. (Found) | $\Lambda_M$(DMF) $Cm^2 ohm^{-1} mol^{-1}$ |
|---|---|---|---|---|---|
| L1 | Yellow | 223 | 72 | -------- | -------- |
| L2 | Yellow | 209 | 77 | -------- | -------- |
| $[Co(L_1)_2(H_2O)_2]Cl_2$ | Dark yellow | 261 d | 65 | 9.37(8.92) | 145 |
| $[Co(L_1)_2(H_2O)_2](NO_3)_2$ | Pale yellow | 266 d | 57 | 8.64(8.93) | 163 |
| $[Co(L_2)_2(H_2O)_2]Cl_2$ | Dark yellow | 259 | 64 | 8.45(8.11) | 132 |
| $[Co(L_2)_2(H_2O)_2](NO_3)_2$ | Pale yellow | 248 | 51 | 7.85(7.38) | 134 |
| $[Ni(L_1)_2(H_2O)_2]Cl_2$ | Orange | 244 | 69 | 9.34(9.06) | 159 |
| $[Ni(L_1)_2(H_2O)_2](NO_3)_2$ | Orange | 233 d | 66 | 8.61(8.66) | 148 |
| $[Ni(L_2)_2(H_2O)_2]Cl_2$ | Pale yellow | 236 | 58 | 8.42(8.09) | 130 |
| $[Ni(L_2)_2(H_2O)_2](NO_3)_2$ | Dark orange | 262 d | 72 | 7.82(7.22) | 139 |

d = decomposition

**Infrared spectra :**

The infrared spectral data of all the complexes are summarized in (Table 2). All the complexes exhibit broad bands in the range 3450-3425 cm$^{-1}$ due to O-H stretching , confirming the presence of water molecule in the complexes . The bands in the region 1634-1625 cm$^{-1}$ correspond to the $\nu$ (C = N) vibration of thiadiazole ring . The increase in the value of this ring vibration (about 20 cm$^{-1}$) from the free ligands show the coordination of ring nitrogen to the metal [23]. Practically unchanged $\nu$ (C-S-C) 753-751 cm$^{-1}$ of the thiadiazole ring indicate that the thiadiazole group itself does not coordinate to metal atom by sulphur atom [24] . The azomethine vibration of the ligands in the range 1619-1601 cm$^{-1}$ was shifted to lower frequency after complexation , which are 1599-1576 cm$^{-1}$ for Co (II) and Ni (II) complexes. A weak band around 550 cm$^{-1}$ in the complexes spectra assigned to $\nu$ (M - N) vibration [25].

**Table (2) :** Characteristic IR bands of the ligands and their complexes as KBr disc (cm$^{-1}$)

| Compound | $\nu$ (C = N) azomethine | $\nu$ (O-H) | C-S-C | $\nu$ (C = N) thiadiazole ring | M-N |
|---|---|---|---|---|---|
| L1 | 1619 | ----- | 753 | 1634 | -------- |
| L2 | 1601 | ----- | 751 | 1625 | -------- |
| $[Co(L_1)_2(H_2O)_2]Cl_2$ | 1599 | 3446 | 757 | 1653 | 550 |
| $[Co(L_1)_2(H_2O)_2](NO_3)_2$ | 1593 | 3450 | 751 | 1654 | 551 |
| $[Co(L_2)_2(H_2O)_2]Cl_2$ | 1578 | 3447 | 751 | 1648 | 550 |
| $[Co(L_2)_2(H_2O)_2](NO_3)_2$ | 1577 | 3447 | 757 | 1647 | 553 |
| $[Ni(L_1)_2(H_2O)_2]Cl_2$ | 1592 | 3440 | 751 | 1653 | 550 |
| $[Ni(L_1)_2(H_2O)_2](NO_3)_2$ | 1593 | 3441 | 752 | 1657 | 552 |
| $[Ni(L_2)_2(H_2O)_2]Cl_2$ | 1583 | 3425 | 752 | 1650 | 552 |
| $[Ni(L_2)_2(H_2O)_2](NO_3)_2$ | 1576 | 3441 | 753 | 1644 | 551 |

**Electronic spectra and magnetic moments :**

The electronic spectra of the $L_1$ and $L_2$ show strong bands in the range 41666-42553 cm$^{-1}$ and 33444-33222 cm$^{-1}$ which are attributed $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ respectively . The electronic spectra of the cobalt (II) complexes show two bands , in the range 20618-20408 cm$^{-1}$ and 14814 –14705 cm$^{-1}$ , which may be assigned to $^4T_1g$ (F) $\rightarrow$ $^4T_1g$ (P)( $\nu$ ) and $^4T_1g$ (F) $\rightarrow$ $^4A_2g$ (P)( $\nu_2$) transitions , respectively in octahedral complexes . Electronic spectra of the Ni(II) complexes present the two bands in the range 25000-24691 cm$^{-1}$ and the other in the range 21276-21052 cm$^{-1}$ , which might be assigned to the $^3A_2g$ (F)$\rightarrow$ $^3T_1g$ (P) ( $\nu$ ) and $^3A_2g$ (F)$\rightarrow$ $^3T_1g$ (F) ( $\nu_2$) transitions , respectively in octahedral complexes [26,27] (Table 3).

The magnetic moment ($\mu_{eff}$) of the Co(II) and Ni(II) complexes at room temperature falls in the range 4.51-4.62 B.M and 3.1 – 3.23B.M. , respectively (Table 3) , which is characteristic for mononuclear high spin octahedral complexes [28,29] .

**Table (3) :** Electronic spectral data and magnetic moments of the complexes

| Compound | Electronic bands (cm$^{-1}$) | | | $\mu_{eff}$ |
|---|---|---|---|---|
| | $\nu_1$ | $\nu_2$ | $\nu$ | B.M |
| $[Co(L_1)_2(H_2O)_2]Cl_2$ | ----- | 14771 | 20533 | 4.54 |
| $[Co(L_1)_2(H_2O)_2](NO_3)_2$ | ----- | 14749 | 20491 | 4.51 |
| $[Co(L_2)_2(H_2O)_2]Cl_2$ | ----- | 14814 | 20618 | 4.62 |
| $[Co(L_2)_2(H_2O)_2](NO_3)_2$ | ----- | 14705 | 20408 | 4.58 |
| $[Ni(L_1)_2(H_2O)_2]Cl_2$ | ----- | 21276 | 24691 | 3.1 |
| $[Ni(L_1)_2(H_2O)_2](NO_3)_2$ | ----- | 21097 | 24875 | 3.16 |
| $[Ni(L_2)_2(H_2O)_2]Cl_2$ | ----- | 21052 | 25000 | 3.23 |
| $[Ni(L_2)_2(H_2O)_2](NO_3)_2$ | ----- | 21097 | 24752 | 3.11 |

**Conclusions:**

From the above consideration , it could be concluded that the both ligands in these complexes coordinated as bidentate ligands . Further coordination at the metal ion was occurred with two moles of water on the Z axes . Thus hexacoordinated distorted octahedral geometry was suggested for the cobalt and nickel complexes (Figure1).

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# تحضير وتشخيص بعض معقدات قواعد شيف لايونات الكوبلت والنيكل الثنائية

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**الملخص:**

تم تحضير معقدات الكوبلت والنيكل الثنائية مع قواعد شيف ن[ – ٥ – (بروبيل) ٢– امينو – ١،٣،٤ –ثايا دايازول بنزيلدين] ($L_1$) و ن [– ٥ – (بروبيل) ٢– امينو –١،٣،٤ – ثايادايازول–٤– كلورو بنزيلدين ] ($L_2$) بنسب مولية ٢:١ (فلز : ليكالد) . تم تشخيص المعقدات المحضرة بالطرق التحليلية والفيزيائية والطيفية.

لقد اتضح من هذه الدراسات عمل الليكاندين بشكل ثنائي السن لتعطي معقدات لها معقدات لها التناسق السداسي ذي بنية ثماني السطوح حيث تمتلك هذه المعقدات الصيغة العامة $[M(L)_2 (H_2O)_2]X_2$ (حيث M = (II)Co او (II)Ni ، L=L1 او L2 و X = -Cl او -NO3).