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Synthesis and Characterization of Co(II) and Ni(II) complexes of Schiff base derived from Ninhydrin and Valine

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Abstract : In this study, Complexes of Co (II) and Ni (II) ions with Ruhmann's purple (ligand) were successfully synthesized and characterized. The complexes of $NiL_2$and CoL_2were synthesized by using template condensation synthesis method and characterized by melting point, solubility, elemental analysis, and molar conductance, and magnetic susceptibility, infrared and electronic spectral studies. The complexes, $NiL_2$and CoL_2 are soluble in ethanol, partially soluble in Diethyl ether and chloroform and insoluble in hexane and petroleum ether. The complexes, $NiL_2$and CoL_2 neither melt nor decompose up to 420^0C. The molar conductance of $NiL_2$and CoL_2 was 42 Scm^2/mol and $46Scm^2/mol$ in respectively. The molar magnetic susceptibility of two complexes was 1.74 BM for NiL_2 and 2.76 BM for CoL_2. The metal to ligand ratio of both metal complexes was 1:2; both metal complexes are non-electrolytes in ethanol and are paramagnetic at 21^0C. Based on the spectral data and other analytical data, monobasic ONO donor behavior of the ligand (Ruhmann's purple) generates octahedral geometry for the pink-green colored Ni (II) complex and green colored Co (II) complex.

Keywords : Co(II) & Ni(II) Complex, Ninhydrin, Ruhmann's purple Schiff base.

Introduction

Coordination compounds are formed by the reaction between Lewis acids and Lewis bases. As applied to the transition metals, coordination compounds are among the most extensively investigated areas in the field of inorganic chemistry. These compounds exhibit extensive and interesting spectral and magnetic properties in addition to widely varying structures and stoichiometries [1]. Amino acids are the basic structural building

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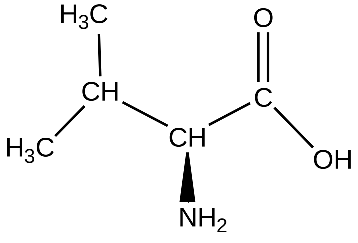
units of proteins. They are organic molecules, which contain at least one carboxyl (COOH) and one amino (-NH_2) group. The variations, between the different amino acids, lie in the nature of their R groups (side chains). An important group of reaction of an amino acid is the condensation of the amino group with many carbonyl Schiff bases depending on the type of the carbonyl compound [2].

Transition metal ions readily form stable complexes with molecules containing nitrogen, oxygen, sulfur, phosphorous or halogen as donor atoms. The metal ions are soft acids in which the electron density is easily polarized. As such they can be bonded readily with soft and highly basic reagents to form stable metal complexes. Certainly d^{10} metal ions form uniformly diamagnetic complexes far more readily, which are significantly covalent [3]. Transition metals behave as Lewis acids due to a partially filled d-orbital and therefore are capable of accepting electron pairs. Cobalt (II) and nickel (II) with a $d^7$and d^8configurations are known in four coordinate (tetrahedral) and six coordinate (octahedral) stereochemistry [2]. L-Valine is essential amino acid widely distributed but rarely occurs in amount exceeding 10%. It is branched chain amino acid and can be derived from alanine by the introduction of two methyl group present on α-carbon atom as shown in Figure-1[4].

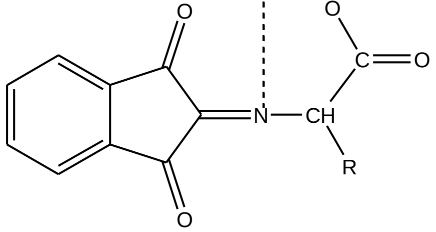


L-Valine

Figure 1: The structure of L- valine

Cobalt is an essential trace element in animal nutrition in the form of vitamin $B_{12}$and is essential for human health as it stimulates the production of red blood cells. Nickel is associated with several enzymes and it plays a role in physiological processes as a co-factor in the absorption of iron from the intestine. Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards transition metals, and azomethine linkage is responsible for the biological activities [5]. Schiff bases of the general formula RR′C=NR″ that are obtained typically by condensation of an aldehyde or ketone (ninhydrin) with a primary amine with elimination of water forming ketimine. Metal complexes of Schiff bases containing nitrogen donor ligands have wide applications in dye and food industry as catalysts and also in biological activities as anti- microbal agents [6].

The Ketimine or Schiff base is a potential ligand, that can act as a tridentate forming two stable five membered rings on complexation as shown below in Figure 2.



Where, R is the side chain of amino acid that don’t containing donor atoms.

Figure 2: Possible metal binding centers of a Schiff base derived from Ninhydrin and α-amino acid

Schiff bases and their metal complexes have attracted a great deal of attention as anticancer, catalytic nature, antibacterial, antifungal, antibiotic and anti- inflammability agents [7].

Materials and Methods

Chemicals and Reagents

The chemicals used in the present study were: ninhydrin, nickel chloride hexahydrate, cobalt chloride hexahydrate, silver nitrate ($AgNO_3$ (0.1M), valine , ethanol, conc.HNO_3. Solvents like Distilled water, ethanol, Diethyl ether, chloroform, hexane and petroleum ether were used and were analytical grade. Instruments used were TLC used to check the purity of the complexes and the ligand), Digital Melting point apparatus, conductivity and pH meter, MSB Magnetic balance, Perkin-Elmer-Visible spectrometer, Thermo Fischer FT-IR spectrometer, EA 1112 Flash CHNS/O- analyzer were used.

Synthesis of the ligand

0.001 mole of L- valine (0.586 gm) and 0.002 moles (0.356gm) ofninhydrin were separately dissolved in minimum amount of absolute ethanol. The solutions were mixed and left overnight, the resulting colored precipitate was then filtered off and finally the product was then left in open air for drying and stored in desiccators until dry powder was generated.

Template Synthesis of Ni (II) and Co (II) complexes

A 0.005 mole of ninhydrin (0.89gram) was dissolved in minimum possible amount of absolute ethanol (12 ml) similarly, 0.005 mole (1.19 gm) of the metal salts were dissolved in the minimum possible amount of absolute ethanol separately, and the two solutions were mixed. The pH and the formation of any precipitate were noted and the mixture was refluxed for 45 minutes.

A 0.005 mole of valine (0.586gm) was dissolved in a 50:50 mixture of absolute ethanol and distilled water (10 ml of each) and added to the above solution while refluxing. The pH and the presence of any precipitate were noted and the mixture was refluxed for another two hours. The resulting colored precipitate was then filtered off while hot and washed first with distilled water and then with absolute ethanol. The product was then left in open air for drying and stored in desiccators until dry powder was generated.

Results and discussion

General

The metal complexes isolated from both metals namely Co(II) and Ni(II) are both distinctly colored, stable to atmospheric condition and are partially soluble in solvents like chloroform and diethyl ether, insoluble in petroleum ether, distilled water and hexane and soluble in ethanol. Ni(II) and Co(II) complexes of Schiff bases derived from ninhydrin and L- valine, neither melt nor decompose up to 420^{0}C.

Table 1: General physical characteristics of Co(II), Ni(II) complexes and ligand

S. No	Cpds	M.wt gm/mol	Apr.	Color	M.pt (^{0}C)	Actual(gm)	Theoretical (gm)	Yield (%)
1	CoL_2	662.93	powder	green	> 420	0.684	3.313	19.56
2	NiL_2	662.69	powder	pink-green	> 420	0.582	0.314	17.58
3	RP	302	powder	purple	234-237	0.240	0.34	79.47

Where: Cpds stands for compounds, M.wt is for Molecular weight, Apr. stands for Appearance M.pt means Melting point and % is percentage, RP is Ruhumann's purple

Co(II) and Ni(II) favored the formation of Ruhmann's purple complexes; evidence for the formation, is the analytical and spectral data especially the FTIR and elemental analysis data. The compositions of the complexes are indicated in each case by metal and L in which L = Ligand (Ruhmann's purple).The compositions are judged from the analytical and spectral data which will be presented and discussed in the following sections.

Qualitative studies of Ligand, CoL_2 and NiL_2 complexes

Thin layer chromatography and Melting point test

TLC was used exhaustively to check the purity of the compounds and to control the progress of the reaction. When a small amount of Ni (II), Co (II) and the ligand was subjected to TLC test, a drop of single spot was observed, which confirms the purity of complexes and ligand and also the completion of the reaction. It is important physical property for indicating the purity of compounds, if the range of melting point temperature is in high interval, the compound is impure. As observed from table1, the two complexes neither melt nor decompose up to 420^0C, which indicates the purity of complexes and also the melting point of the ligand is 234-237 ^{0}C which confirms the purity of the ligand.

Chloride test of complexes and Solubility test

When10mg of each complex was digested in $HNO_3$and is subsequently dissolved in HNO_3, and successively 1% $AgNO_3$solution was added to acidic solution of complexes, a brick- red precipitate was observed, which confirms the absence of counter chloride ion.

Table 2: Solubility tests of the complexes in different solvents

S No	Name of solvent	NiL_2 complex	CoL_2 complex
1	Hexane	In soluble	In soluble
2	Distilled water	In soluble	In soluble
3	Petroleum ether	In soluble	In soluble
4	Chloroform	Partially soluble	Partially soluble
5	Diethyl ether	Partially soluble	Partially soluble
6	Ethanol	Soluble	Soluble

Analytical studies

Molar Conductance Measurement

The molar conductance was determined by taking 15mg of the Ni(II) complex and 15mg of the Co (II) complex in 50ml ethanol and the determination of molar conductance was made using the following relation,

$\Lambda_m = 1000\ L/M$.

The molar conductance (Λ_m) values were calculated from conductivity measurements in ethanol. Specific conductance (L) is a measure of how well solution conducts electricity. Conductibility increases with increasing concentration and mobility of ions. These ions come from the breakdown of a compound and conduct electric current because they are positively and negatively charged when dissolved in the solvent [8]. Specific conductance of 10^{-5}M solution of the complexes at 25^0C is 19 µS/cm, and 21µS/cm, for Ni (II) and Co (II) complexes in respectively(see table 4). Then the molar conductance, Λ_m is 42Scm^2/mol for Ni (II) complex and 46 Scm^2/mol for Co (II) complex.

Table 3: Molar conductance (Λ_m) range for 2 and 3 ion electrolytes in ethanol at 25^0C

Number of ions	Electrolyte nature	Molar conductance (Λ_m) in Scm^2/ mol
None	Non-electrolyte	0-34
2	1:1 electrolyte	35-45
3	2:1 electrolyte	70-90

Table 4: Conductivity of complexes in ethanol at 25 ^{0}C

Name of complex	Solvent	Specific conductance(Scm^2)	Molar conductance (Scm^2/mol)
CoL_2	Ethanol	21	46
NiL_2	Ethanol	19	42

In ethanol at 25^{0}C, substances having the molar conductance of less than 34Scm^{2}mol^{-1} are non-electrolytes ,those having molar conductance of 35-70 Scm^{2}mol^{-1}are 1:1 electrolytes that is one cation and one anion ,total of two number of ions as shown in Table -3 [8]**.** By correlating the molar conductivity of the two complexes that was 42 Scm^2/mol for $NiL_2$and 46 Scm^2/mol for CoL_2 with above table, they have 3 numbers of ions, but their magnitude of conductivity indicates the non- electrolytic nature of these complexes.

Magnetic Susceptibility Measurement

There is a direct relationship between the magnetic properties of matter in the bulk and the number of unpaired electrons. From the magnetic susceptibility data, it can be observed that most of the complexes prefer a low spin configuration, which is exhibited due to the presence of strong field ligands, such as the azomethine and carbonyl groups. Octahedral geometry is possible for d^8 and d^{7}metals with π-acceptor ligands. In the case of Ni(II) complex prepared experimentally, measured gram magnetic susceptibility was 1.95x10^{-6}cgs units at 21^{0}C.The result indicates that the complex is paramagnetic. The molecular weight of the complex is 662.69 g/mol. The magnetic moment of the complex at 21^{0}C is 1.74 BM per metal ion, but theoretically calculated magnetic moment of Ni(II) with two unpaired electrons is 2.45 BM calculated by $\mu_{eff} = (n(n+1))^{1/2}$.

Table 5:Gram susceptibility and effective magnetic moment of complexes at 21^{0}C

Name of complex	Gram Susceptibility (χ_g)	μ_{eff}in BM
NiL_2	1.950 x 10^{-6}	1.74
CoL_2	4.888 x10^{-6}	2.76

Where: n is number of unpaired electron, $\mu_{eff}$is effective magnetic moment. In the case of Co(II) complex synthesized experimentally, measured gram magnetic susceptibility was 4.888x10^{-6}cgs units at 21^{0}C.The result indicates that the complex is paramagnetic. The molecular weight of the complex is 662.93 g/mol. The magnetic moment of the complex at 21^{0}C is 2.76 BM per metal ion, but theoretically calculated magnetic moment of Co (II) complex with three unpaired electron is 3.46 BM. The value of experimentally calculated magnetic moment for each complex is significantly sub-normal and can be explained only on the basis of substantial anti-ferromagnetic interaction at given temperature. This interaction could be due to super exchange and /or spin neutralization between a pair of metal ions (metal-metal interaction). In view of low magnetic moment of this complex, it may be suggested that both these interactions are operative in these complexes [1, 9]. Even though complexes, NiL_2 and CoL_2 complexes have low magnetic moment with relative to expected magnetic moment at room temperature, both of them are paramagnetic.

Elemental analysis of complexes

Elemental analysis of a compound gives information about the percentage composition of each constitutes in a given compounds. Co (II) and Ni (II) favored the formation of Ruhmann's purple complexes; evidence for the formation, is the analytical and elemental analysis data, as shown below.

Table 6: Elemental analysis data of NiL_2 and CoL_2 complexes

S No	Name of complexes	% C Calculated/ Experimental.	% N Calculated/ experimental	% H Calculated/ experimental
1	NiL_2	65.19/ 66	4.2/3.99	2.41/2.53
2	CoL_2	65.16/ 66.4	4.2/ 3.96	2.41/2.57

Where**,** L is Ruhumann's purple ligand, %= percentage

Table 7: Elemental analysis data of NiS_2 and CoS_2 complexes

S No	Name of complexes	% C Calculated/ Experimental	% N Calculated/ experimental	% H Calculated/ experimental
1	NiS_2 complex	58.46/ 66	4.87/3.99	4.17/2.53
2	CoS_2 complex	58.44/ 66.4	4.87/ 3.96	4.17 /2.57

Where: S is Schiff base ligand, %= percentage

As shown above, the two complexes, NiL_2 and CoL_2 complexes favored the formation by coordination with Ruhumann's purple as a ligand. With this ligand, the theoretical value and experimental value of elemental analysis data of listed constituents of each complex have a very little range of difference with each other. But elemental analysis data of listed constituents of Schiff base ligand complexes (Table 7) of these metals, Ni (II) & Co (II) show a large range of difference between experimental and theoretical value with relative to the Ruhumann's purple ligand.

Spectroscopic studies

Infrared Spectral Studies of Ninhydrin

Ninhydrin shows three bands in the carbonyl stretching region: 1768, 1747.36 and 1710.63cm^{-1}(See appendix 1). The bands at 1747.36 and 1710.63 cm^{-1} are characteristics of its 1,3 – dicarbonyl functional group and 1768 cm^{-1}is the middle carbonyl in the tri-carbonyl species which is in equilibrium with the dihydroxy species. The spectrum of ninhydrin (2, 2-dihydroxy-1,3-indanedione), show some characteristic bands. The main bands are in the regions corresponding to ν_{OH} and $\nu_{C=O}$ functions besides, $\nu_{C=C}$, $\nu_{C\text{-}H}$ and other related bands. A broad band in the region of 3300-3000 cm^{-1} is due to ν_{OH} stretching and two characteristic bands in the region around 1768-1710.61 cm^{-1} are due to $\nu_{C=o}$.

Infrared Spectral Studies of Valine

Valine and all free amino acids show a strong carboxyl anti symmetric stretching peak at 1608.49 cm^{-1} and a weaker symmetric stretching peak at around 1423 cm^{-1},1564.24 cm^{-1},CH/NH stretching at 2935.99 cm^{-1}.

Infrared Spectral Studies of the Ligand and the Co(II) complex

The C=O functional group appears at a region of 1820-1660 cm^{-1},since conjugation of double bonds decrease the wave number. The disappearance of the characteristic band of the free ninhydrin at 1747.36 and 1710.63 cm^{-1} and the appearance of weak sharp band at around 1680 cm^{-1} for C=O group shows the reaction of ninhydrin and valine. Azomethine (N=C) group absorbs in the region 1690-1640, but in aromatic ketimines, absorbs in the lower region 1640- 1600cm^{-1}(Minbale, 2008).since the ligand absorbs at around 1610 cm^{-1}, which assign the N=C stretching. A sharp peak at 1475cm^{-1} and 1589.03 cm^{-1}, indicates the C=C bonds. While, a medium peak at 2944.63 cm^{-1} shows the aromatic C-H stretching. From the data shown the sharp NH stretching band of the free amino acids at 3200-3000 cm^{-1} and the OH stretching frequency of ninhydrin are not observed indicating the derivatization of these groups.

Table 8:FTIR spectral data of NiL_2 and CoL_2 complexes, ninhydrin, L-valine and ligand.

S No.	Name of Cpd	$V_{OH/NH}$	$V_{freeC=O}$	$V_{cord.C=O}$	$V_{C=C}$	$V_{C=N}$	$V_{sy/as\ COO-1}$	V_{C-O}
1	Ninhydrin	3300-3000 (w)	1747.36,1710.63(s), 1768(w)	__	1585 (s)	__	____	1250 (s)
2	Valine	2935.99 (m)	__	__	__	__	1423.56 (w) /1608.49 (s)	
3	Ligand	__	1680 (w)	__	1475(s)	1610 (m)	__	1250 (s)
4	CoL_2	__	1840-1750(m)	1650(m)	1600(s)	1510 (m)	__	1240 (s)
5	NiL_2	_	1780-1740(m)	1680-1630(m)	1580(s) 1553.07 (s)	1515 (m)	_	1250 (s)

Where: s stands for sharp, m is for medium, w stands for wide and cpd stands for compound

The absence of the free sp^3 CH stretching at a region of 3000- 2900 cm^{-1} indicates the formation of Ruhumann's purple complex. The existence of the broad band at a region of about 1840-1750 cm^{-1} indicates the presence of free carbonyl group. The frequencies for the carbonyl groups in ninhydrin are shifted from: 1768, 1747.36 and1710.63 $cm^{-1}$to at around 1650 cm^{-1}in the complex. This indicates the involvement of one of the two carbonyl groups of ninhydrin in coordination with metal ion

The C=N stretching frequency of the free aromatic azomethine groups occur between 1640-1600 cm^{-1} (1610 cm^{-1} in Ruhemann's purple) but with complexes it occurs at 1550, 1510cm^{-1}. A negative shift of about 60-100cm^{-1} is a strong evidence of the coordination of the azomethine group via nitrogen. This is one indication for the condensation reactions that occurred between the amine group of the amino acid and the carbonyl group of the ninhydrin, and further the absence of peaks due to such groups from the starting material infers that condensation reaction has taken place.

Infrared Spectral Studies of the Ni (II) complex

From the data shown the sharp NH stretching band of the free amino acids at 3200-3000 cm^{-1} and the OH stretching frequency of ninhydrin are not observed indicating the derivatization of these groups. The absence of free sp^3 CH stretching at a region of 3000- 2900 cm^{-1} indicates the formation of Ruhumann's purple complex. The existence of the broad band at a region of about 1780-1740 cm^{-1} indicates the presence of free carbonyl group. The frequencies for the carbonyl groups in ninhydrin are shifted from: 1768, 1747.36 and 1710.63cm^{-1}toat a region around 1680-1650 cm^{-1}in the complex. This indicates the involvement of one of the two carbonyl groups of ninhydrin in coordination with metal ion. The C=N stretching frequency of the free aromatic azomethine groups occur between 1640-1600cm^{-1} (1610cm^{-1} in Ruhemann's purple) but with complexes it occurs at around 1570, 1530cm^{-1}. A negative shift of about 30-70cm^{-1} is a strong evidence of the coordination of the azomethine group via nitrogen. This is one indication for the condensation reaction that occurred between the amine group of the amino acid and the carbonyl group of the ninhydrin, and further the absence of peaks due to such groups from the starting material confirms that condensation reaction has taken place.

UV-Vis spectral studies of the ligand, Co (II) and Ni(II)complexes

The electronic spectrum of the Ruhemann's purple was recorded at room temperature using ethanol as a solvent. The spectrum of the ligand consists of three main bands at 247 nm, 282 nm and 323 nm.

The band at 247 nm can be assigned to the $\pi\rightarrow\pi^*$ transition of the aromatic group of nihydrin, the second band at 282 nm can be assigned to the $n\rightarrow\pi^*$ transition of the carbonyl group of nihydrin and the third band at 323 nm is $n\rightarrow\pi^*$ of azomethine group.

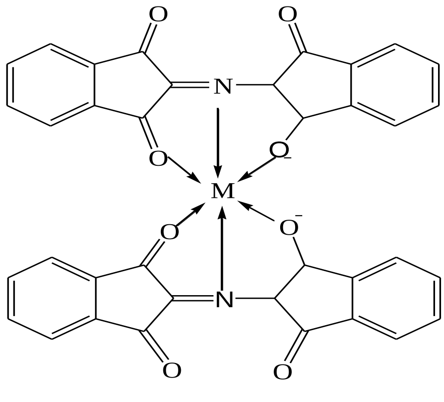
The electronic spectrum of the Co (II) complex was recorded at room temperature using ethanol as a solvent. The spectrum of the Co (II) complex consists of three main bands at (247, 288 and 343) nm. The band at 247 nm can be assigned to the п→π* transition of the aromatic group of nihydrin, the second band at 288 nm can be assigned to the n→π* transition of the carbonyl group of nihydrin and the third band at 343 nm is n→π* of azomethine group, a positive shift of 20 nm of this transition in this complex is the indication of cordination of azomethine group. The band at a region of (400- 600) nm, especially at 501 nm and 560 nm in the UV-Vis spectrum of this complex indicates the presence of d-d transition of the metal ion.

Table 9: Electronic spectra of the ligand and complexes

S No.	Name of Compound	Non ligand electronic spectral bands	Assignment	Ligand Electronics pectral Bands	Assignment
1	Ligand	__	___	247 282, 323	π→π*(C=C) n→ π*(C=O) n→ π*(C=N)
2	CoL_2	501 560	$^4T_{1g}\rightarrow{}^4T_{1g}$(P) $^4T_{1g}\rightarrow{}^4A_{2g}$ (F)	247 288 363	π→π*(C=C) n→ π*(C=O) n→ π*(C=N)
3	NiL_2	472 509	$^3A_{2g} \rightarrow {}^3T_{1g}$(P) $^3A_{2g} \rightarrow {}^3T_{1g}$(F)	251 290 363	π→π*(C=C) n→ π*(C=O) n→ π*(C=N)

The electronic spectrum of the Ni (II) complex was recorded at room temperature using ethanol as a solvent. The spectrum of the Ni (II) complex consists of three main bands at 251 nm, 290 nm and 363 nm. The band at 251 nm can be assigned to the п→π* transition of the aromatic group of nihydrin, the second band at 290 nm can be assigned to the n→π* transition of the carbonyl group of nihydrin and the third band at 363nm is n→π* of azomethine group, a positive shift of 40 nm from free ligand in this complex is the indication of coordination of azomethine group via nitrogen

Ni(II) complexes have the ability of forming both blue colored tetrahedral and green/ greenish octahedral complexes , but in this complex, NiL_2 was pink-green colored complex and directs formation of octahedral complex. Finally, based on the elemental analysis, conductance, magnetic susceptibility, Infrared and electronic spectral data, octahedral geometry is proposed for the template condensation of ninhydrin with valine in the presence of Co (II) and Ni (II) ions (Figure 3).



Where, M is Co and Ni

Figure 3: proposed structure of NiL_2 and CoL_2 complexes, where L is the ligand

Conclusion

Low spin Co (II) and Ni (II) complexes of Schiff base derived from ninhydrin and valine were successfully synthesized and characterized. When Co (II) and Ni (II) ions reacted with valine and ninhydrin in ethanoic media, they form Ruhemann's Purple complexes. This is confirmed specially from FTIR and elemental analysis data. The molar conductivity of NiL_2 and CoL_2 complexes was $42Scm^2mol^{-1}$ and $46Scm^2mol^{-1}$in respectively, they are non-electrolytes. Complexes of NiL_2 and CoL_2possess molar magnetic moment of 1.75BM and 2.7BM in respectively. Therefore they are paramagnetic and generally based on the elemental analysis, conductance, magnetic susceptibility, Infrared and electronic spectral data, octahedral geometry is proposed for the template condensation of ninhydrin with valine in the presence of Co (II) and Ni (II) ions.

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