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Synthesis And Characterization Of (2,3,10,11-Tetramethyl-1,4,9,12-Tetraazacyclohexadeca-1,9-Diene) Ligand And Its Ni(II) And Co(II),Zn(II) Complexes With Study Spectroscopic

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Abstract : Two complexes of the type $[M(C_{16}H_{32}N_4)][ZnCl_4]$, where M=Ni(II), or Co(II) , which belong to the tetra dentate $[N_4]$ macrocyclic complexes classes, These complexes were synthesized in methanol media using the template method, in which 1,4-diamino butane was condensed with 2,3-butanedione in the presence of metal salts. The complexes were identified using a variety of spectral and physical techniques, including C.H.N, UV-vis spectroscopy, and mass spectroscopy, FTIR spectroscopy, flammable atomic absorption spectroscopy, conductance, and HNMR spectroscopy.

The magnetic susceptibility and molar conductivity for the prepared complexes were measured, from the result data we found the stiocheometrical structure of the complexes has been found to be (1:2:2) (metal: ligand1: ligand2) ratio, and two complexes has ionic behavior, and had no magnetic properties.

The spectral studies proved the cyclic structure of the ligand and the complexes, and proved that the tetra linkage was from the cyclic nitrogen atom, the graphic abstract illustrate the preparation process.

Keyword: macrocyclic complexes; tetraza ; template

1. Introduction:

Macrocyclic ligands are macrocycles that contain at least nine rings (including completely heteroatoms) and at least three donor locations in chemistry. Examples include crown ethers and porphyrins. Macrocyclic ligands are highly reactive with metal ions. [1]

The macrocyclic effects refer to metal cations' greater affinity macrocyclic ligands are more stable than their acyclic analogues. [2, 3]

Macrocyclic ligands are believed to have high affinity as a result of the entropic effect observed in the chelate effect [4]. Additionally contributes energy as a result of the

reorganized nature of the ligating groups (that is, no more straining are introduced to the ligand on coordination) [5].

In the presence of metal ions, template reactions generate macrocyclic ligands. When the metal ion is sufficiently separated from the organic reactants, the same organic reactants generate distinct, primarily polymeric, products. This is a term that is frequently used in coordination chemistry [5], while coordination has an effect on the electronic properties of ligands (acidity, electrophilicity, etc.), template effects highlight the coordination sphere's pre-organization. During the synthesis of templated macrocyclic ligands, it is necessary to remove the ligand's templating metal [6].

The presence of a metal ion as a ‘template' for the cyclization reaction dictates the direction in which the templated cyclization proceeds. Phthalocyanine was the first macrocycle to be synthesized via template reaction, and its structure bears an uncanny resemblance to that of conventional porphyrin systems. [21-38] The metal ion has the ability to either direct condensation toward cyclic rather than polymeric products (the kinetic template effect) or to stabilize the macrocycle once it is formed (the thermodynamic template effect) [7,15].

The size of the template cation has been found to be critical in determining the synthetic path for Schiff base systems.

The compatibility of the template cation's radius with the macrocycle's "hole" contributes to the synthetic pathway's efficacy and the geometry of the resulting complex. [8,19]

Schiff bases play a critical structural role in macrocyclic ligand complexes containing imine or azomethine groups. They are typically formed as a result of the reaction of an active carbonyl compound with a primary amine. [9,20], as shown in fig 1.

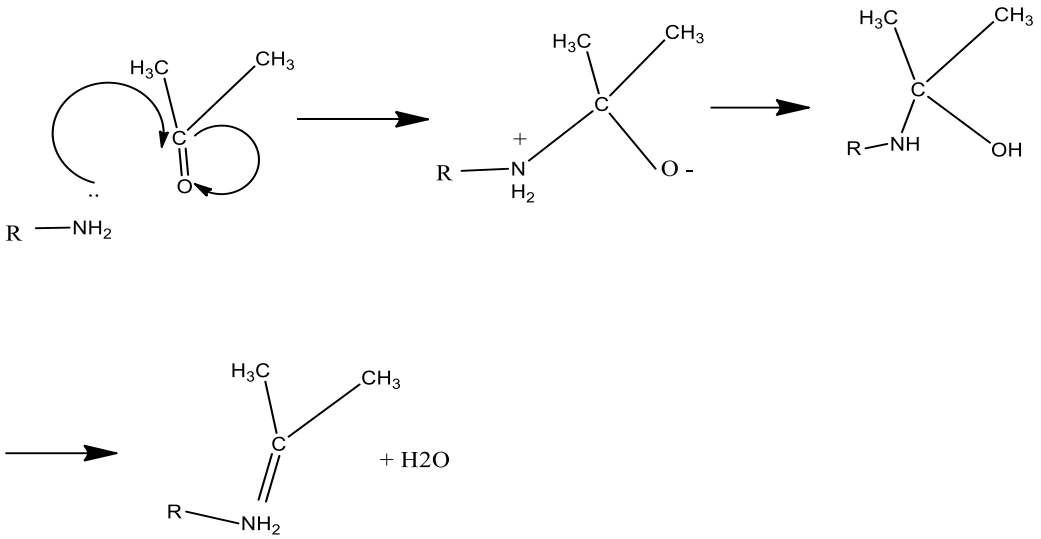


Fig 1 Active carbonyl compound and a primary amine

2. Experimental:

2.1 Materials:

All chemicals and solvents used in this study were of AnalaR grade; 1,4-butanediamine and 2,3-butanedione were obtained and used in their natural state from Acros in New Jersey, USA; and metal salts were obtained and used in their natural state from S.D-fine in Mumbai, India.

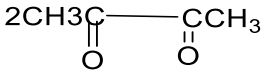
2.2 Preparation of Complexes:

In a 500 mL beaker containing 3 g (0.01 mole) 1,4-butanediamine, 1 g (0.01 mole) concentrated (37 percent) hydrochloric acid is added to 200 mL methanol and cooled to 5 degrees Celsius, followed by the addition of 0.86 g (0.2 mole) 2,3-butanedione (diacetyl) in an effective fume hood. [10,17]

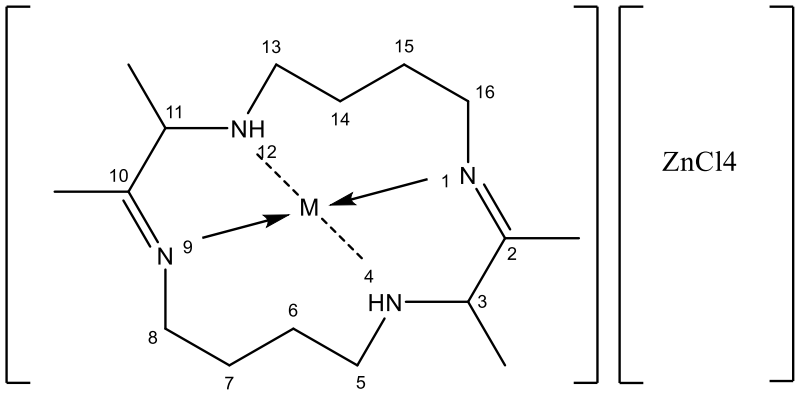
After 30 minutes of stirring and cooling to room temperature, 1.24 g (0.05 mole) nickel(II) acetate tetra hydrate is added to the orange solution. Darkening the solution to a reddish brown hue. After four hours of stirring, 1 g (0.1 mole) concentrated hydrochloric acid and 0.68 g (0.05 mole) zinc chloride are added. [11-14]

[Ni(Me4[16]-1,9-diene-1,4,9,12 N4)][ZnCl4] precipitates and is filtered away immediately.

Additionally, we synthesize [Co(Me4[16]-1,9-diene-1,4,9,12 N4)][ZnCl4] from 1.24 g (0.05 mole) of Cobalt(II) acetate tetra hydrate.:[12,18]

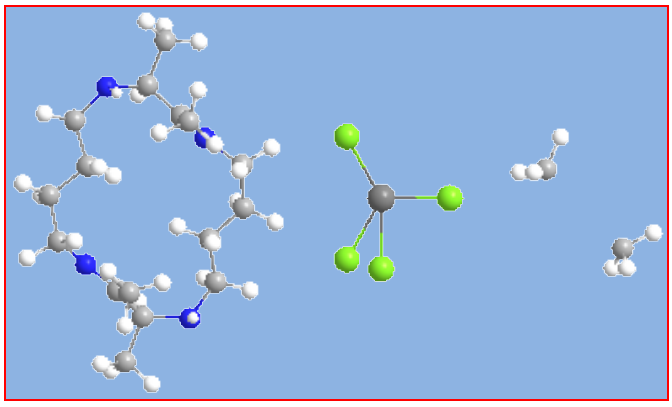
$M(OOCCH_3)_2.4H_2O + 2\ NH_2(CH_2)_4\ NH_2\ .\ HCl +$ 

$\xrightarrow{ZnCl_2,\ HCl}$



(1E,9E)-2,3,10,11-tetramethyl-1,4,9,12-tetraazacyclohexadeca-1,9-diene

Where M= Ni,Co



3D-structure of 2,3,10,11-Tetramethyl-1,4,9,12-Tetraazacyclohexadeca-1,9-diene[$ZnCl_4$]

3. Results and Discussion:

We calculated the analytical data C.H.N for the [Ni(C16H32N4)][ZnCl4] complex in this study; the following table illustrates this data.

Table 1, the spectral and physical properties of the complexes and ligands

Complexes	Milting point	Magnetic Susceptibility	The molar conductivity	**C**%	H %	N %	Molecular weight	Percen t of

	[C°]	[B.M]	[µs/cm]					metal %
[Ni(C16H32N4)][ZnCl4]	281	0.0 Di	203	35.16	5.86	10.25	546.03	10.74
				34.53	5.12	9.42		10.19
[Co(C16H32N4)][ZnCl4]	130	$0.013*10^{-4}$ para	142.3	35.14	5.85	10.25	546.39	10.79
				34.47	5.33	9.71		10.26

The complex's FTIR spectrum was determined using KBr discs in the range (400-4000) [cm^{-1}] with a Shimadzu FTIR-84005 spectroscopy, and the essential vibrational bonds were as follows, as shown in Table 2, The stretching frequency of the N-H group was observed to be (3264-3373) [cm^{-1}] , while the stretching frequency of the C=N group was observed to be (1580-1588) [cm^{-1}].

Table 2, Important FTIR absorption bonds of the complexes and ligands

Assignment [cm^{-1}]	**Ni complex**	**Co complex**	**Dione Ligand**	**Diamine Ligand**
υ(C-N)	1340	1340	------	1323
υ(C=N)	1580	1588	------	1580
υ(N-H)	3264	3373	------	3264
υ(C-C)	2991	2991	2939	2926
υ(C-H)	2965	2943	2989	2965
υ(N-M)	419	440	-----	----

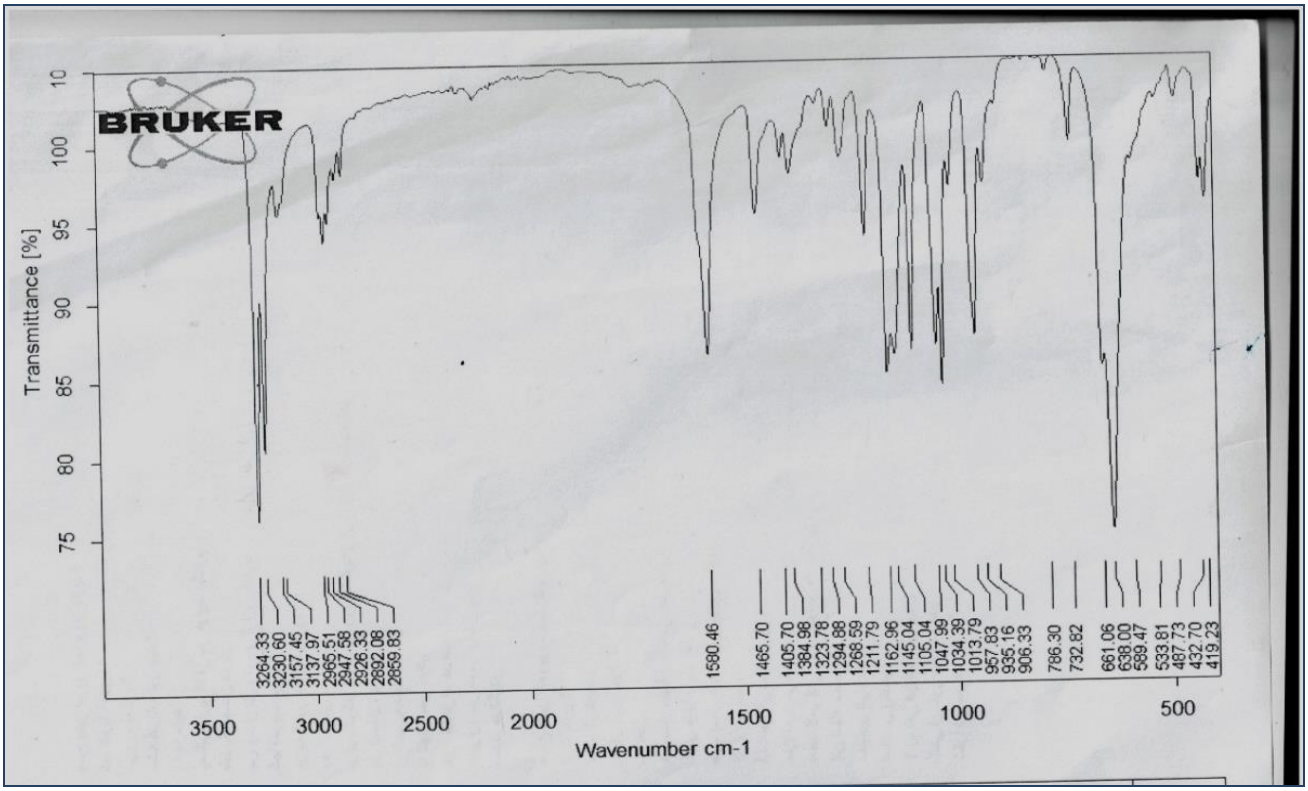


Fig. 1: FTIR spectrum of Ni(II) complex

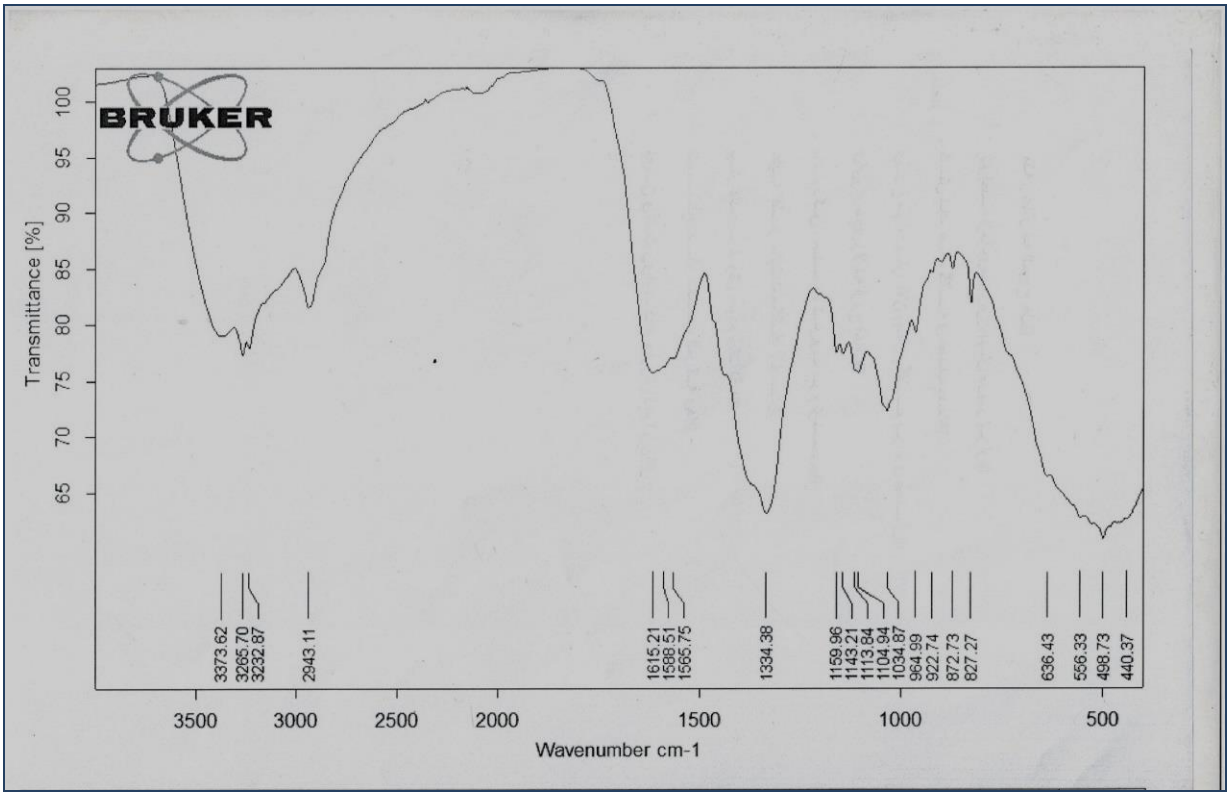


Fig. 2: FTIR spectrum of Co(II) complex

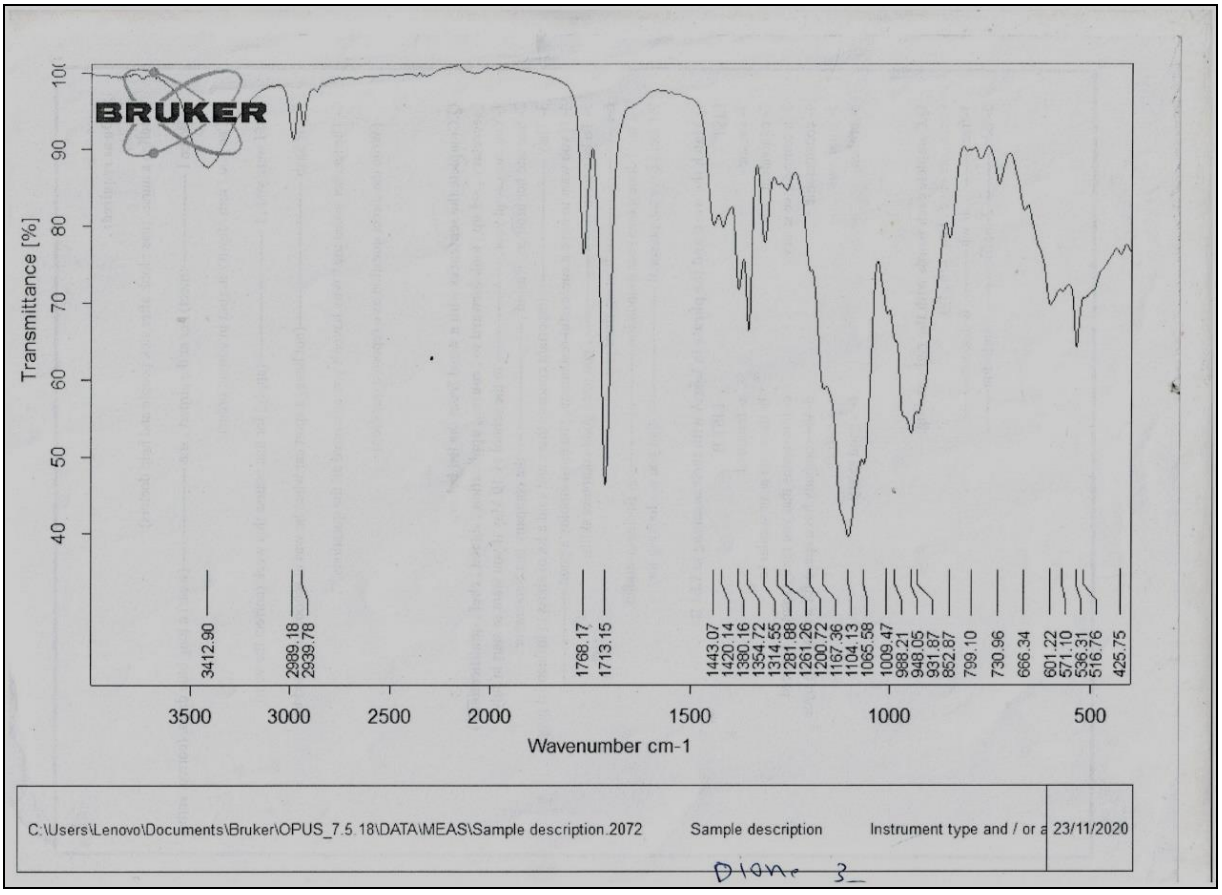


Fig. 3: FTIR spectrum of Dione Ligand

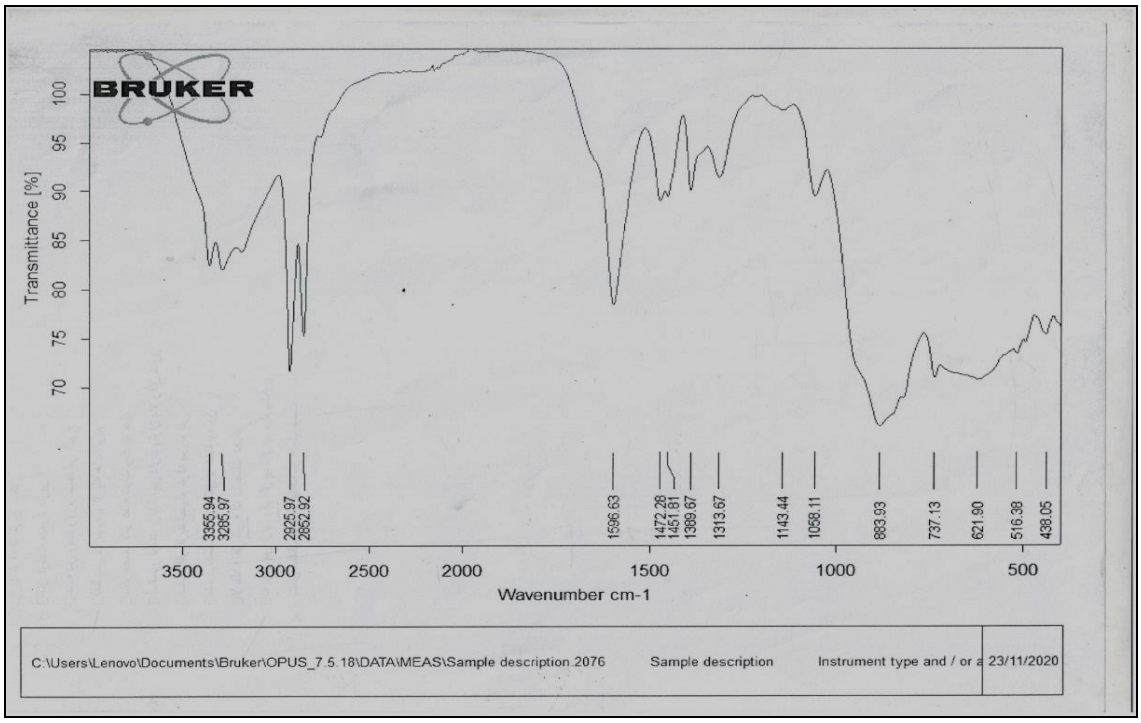


Fig. 4: FTIR spectrum of Diamine Ligand

In figures (5 and 6) we observed Absorption bands at wavelength (281 nm) and (402 nm), because of pair of electrons existence on nitrogen atom in Diamine ligand, and having a double bond between (C and O) in Dione ligand.

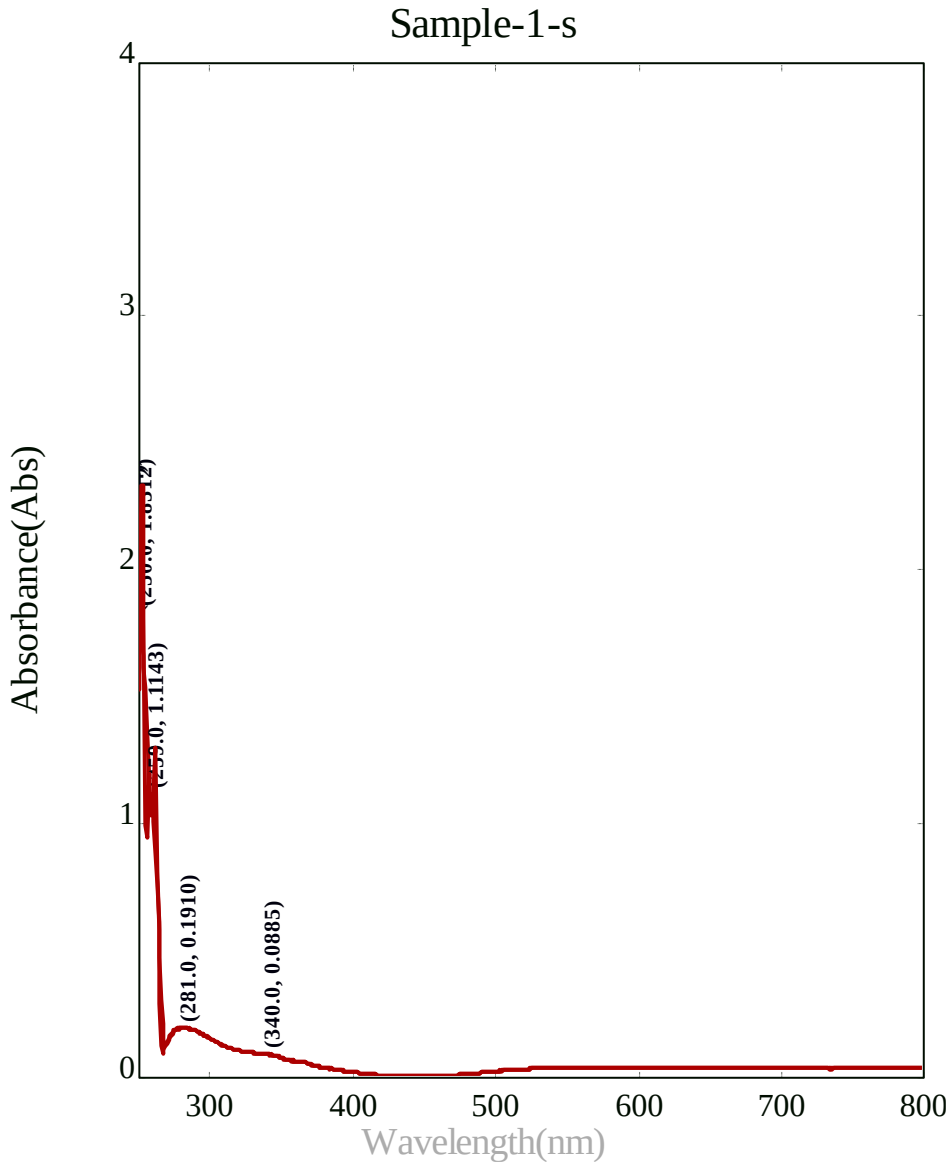


Fig. 5: UV. Visb. of Diamine Ligand

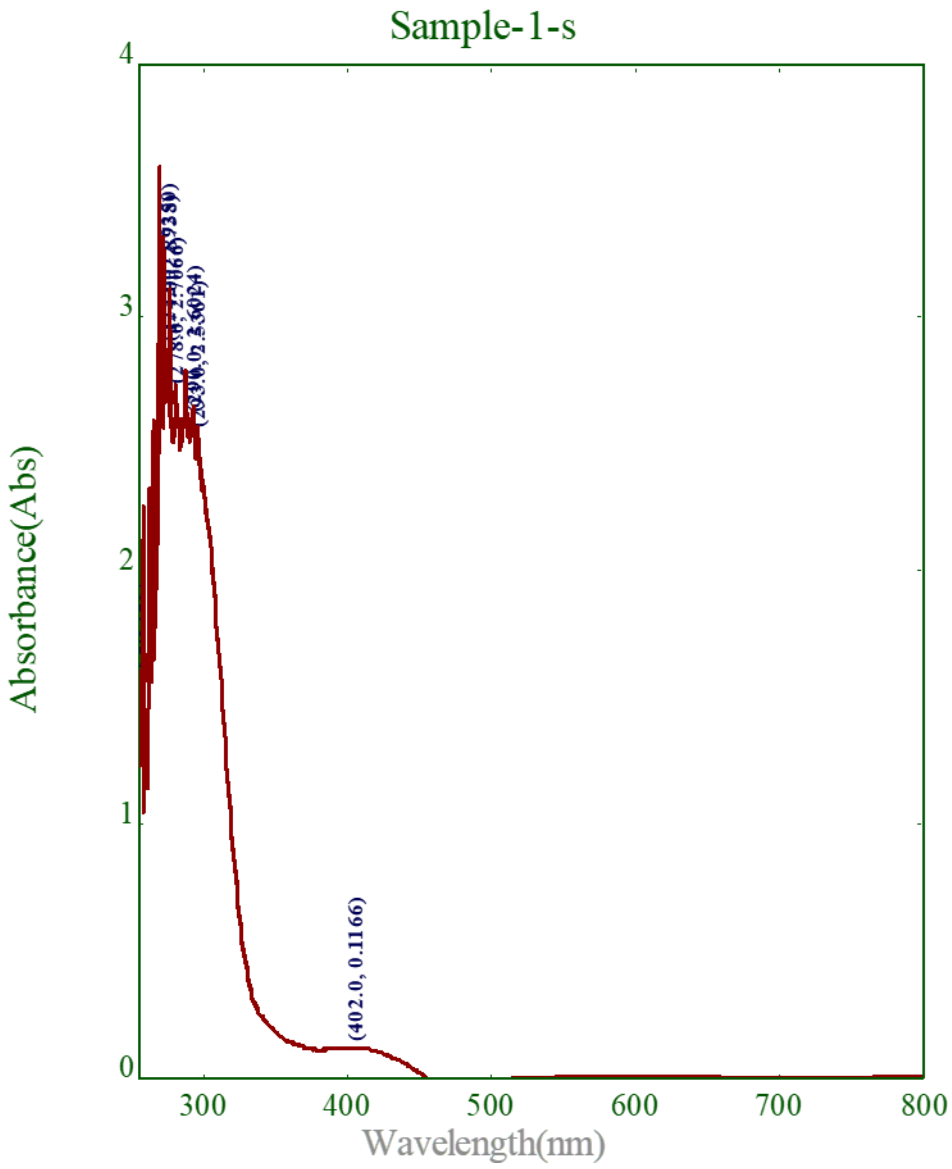


Fig. 6: UV. Visb. of Dione Ligand

In figure (7) we observed Absorption bands at wavelength 293 [nm] , this illustrated electrons transition from metal to ligand (M→L)

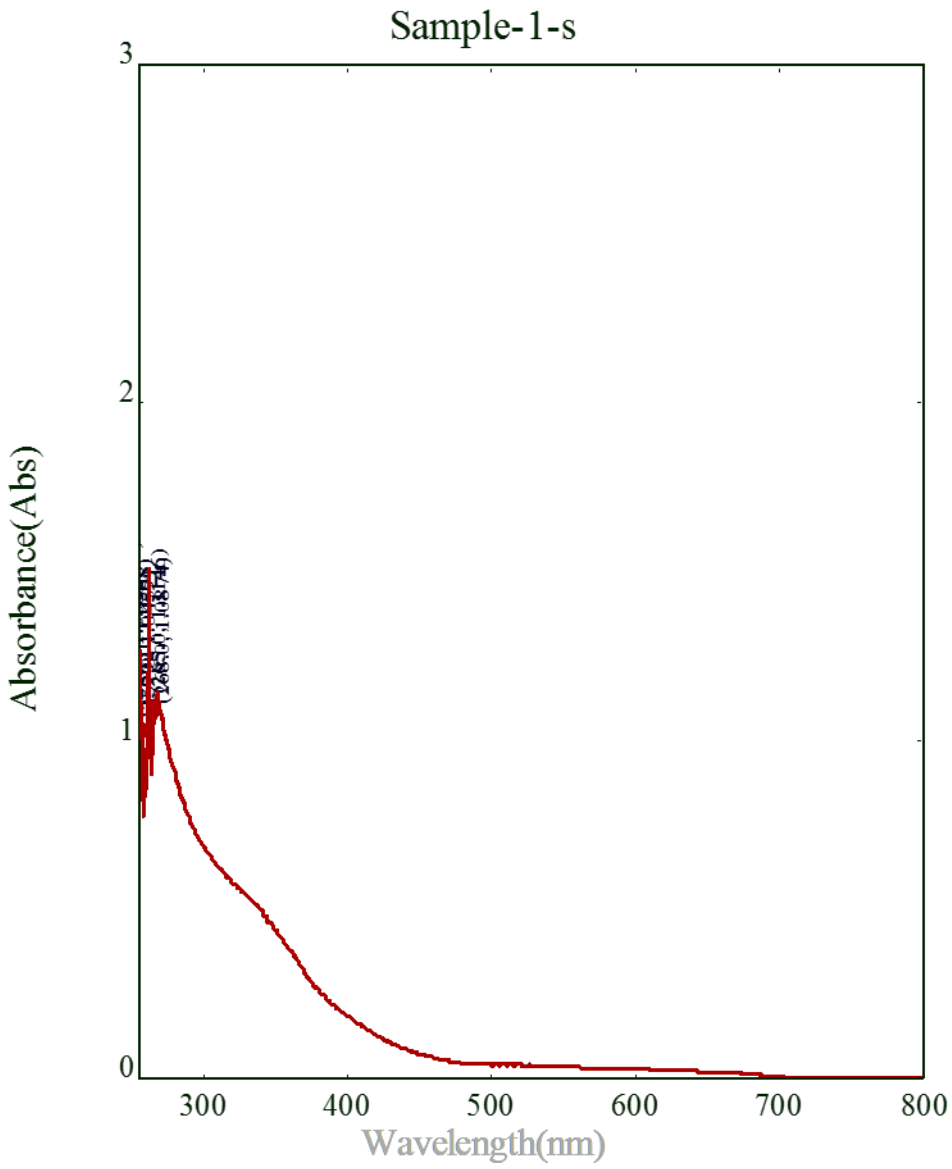


Fig. 7: UV. Visb. of Co(II) complex

And In figure (8) we observed Absorption bands at wavelength 272 [nm], this illustrated electrons transition from metal to ligand (M→L)

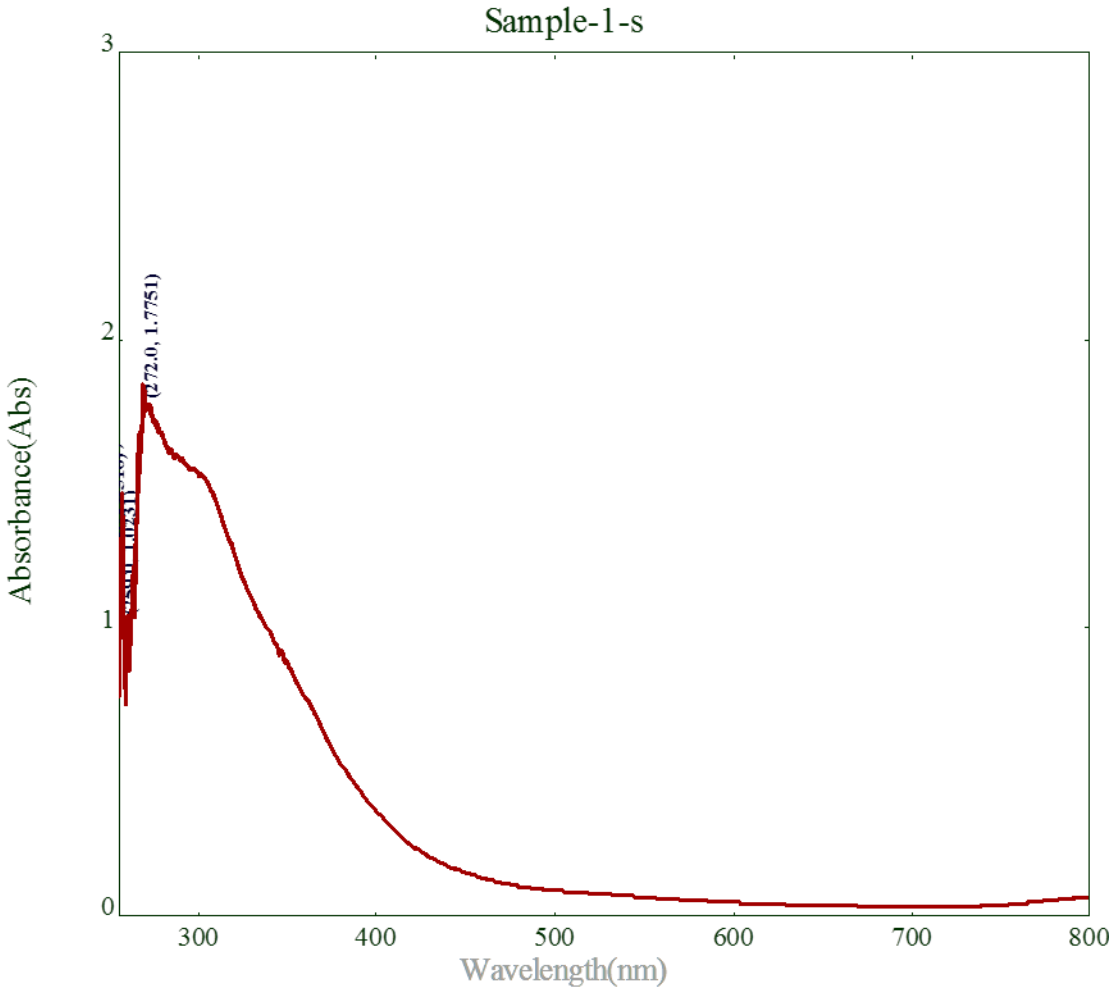


Fig. 8: UV. Visb. of Ni (II) complex

From HNMR spectroscopy to (Co and Ni) complexes in figures (9 and 10) we found many different chemical spaces, which appear in range (1-4) ppm, it appears single signal at range (1-1.6) ppm because of the protons of (CH_3) groups.

And appears signal at range (2-3) ppm because of the protons of (CH_2) and (CH) groups, and at range (3-4) ppm because the protons of (NH) group.

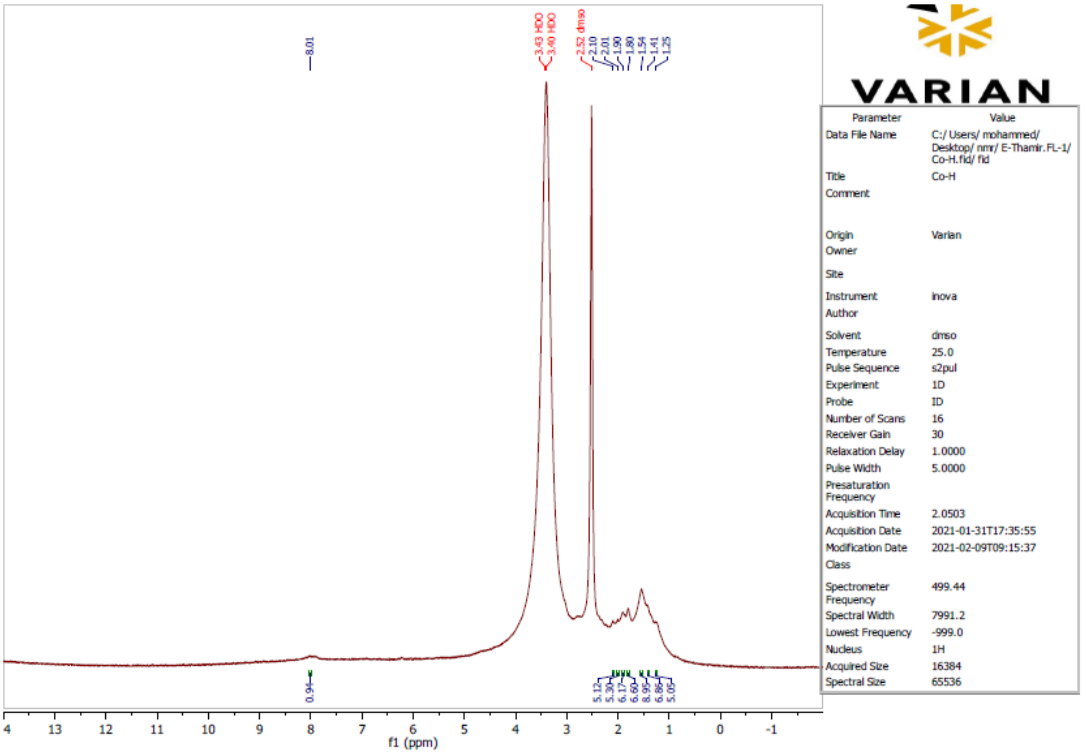


Fig. 9: HNMR spectroscopy of Co complex

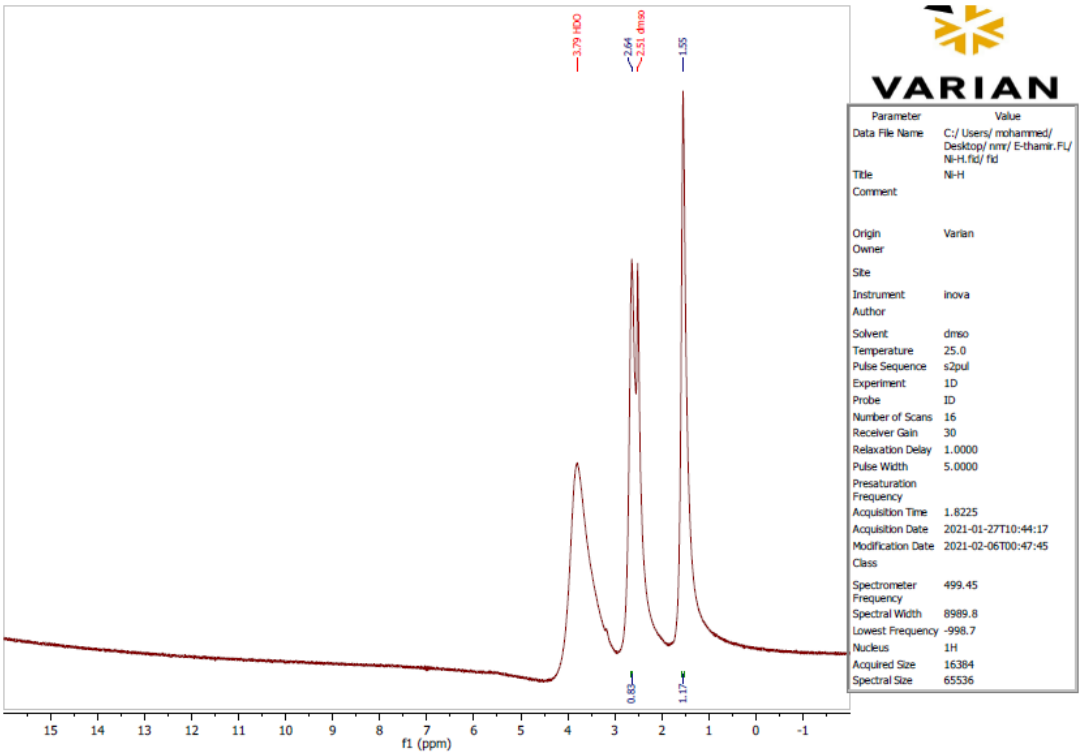
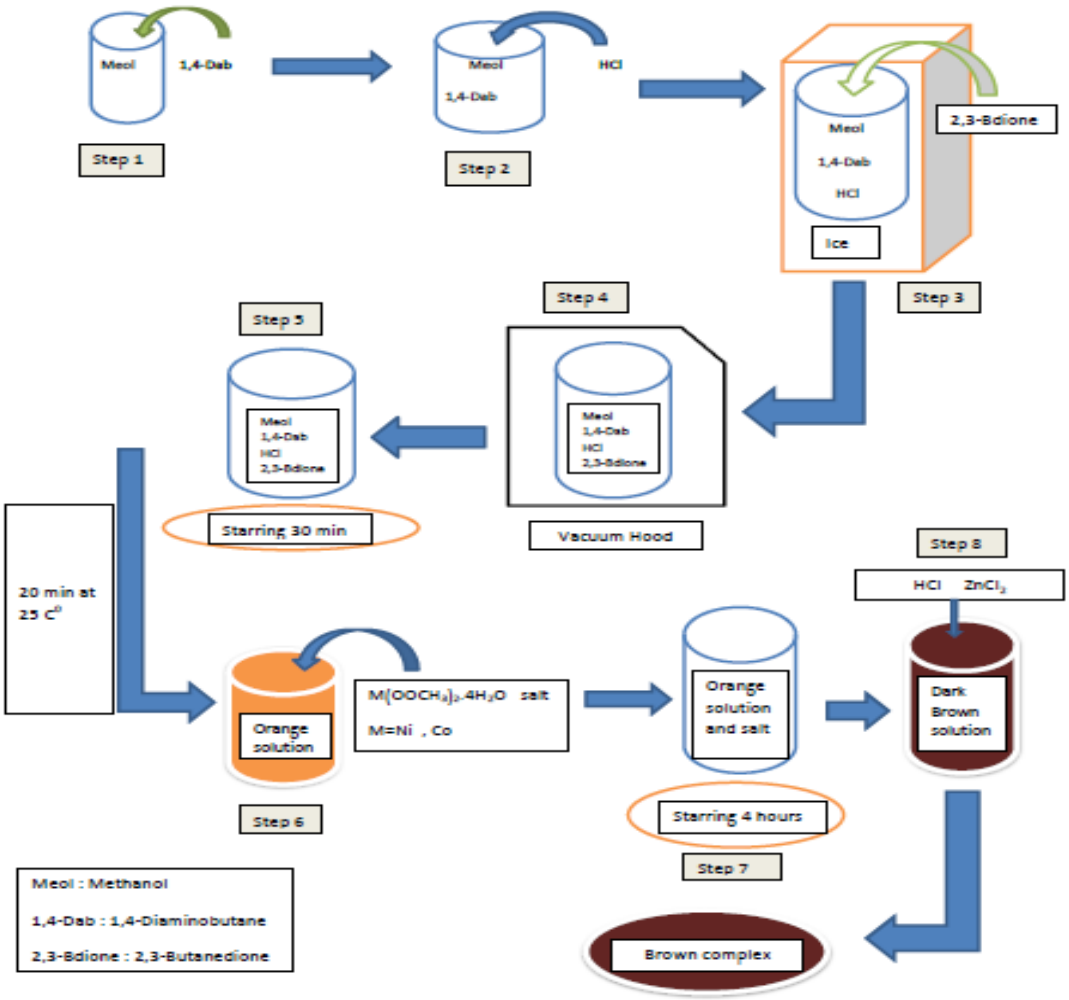


Fig. 10: HNMR spectroscopy of Ni complex

4. Conclusion:

In this study, we studies elemental analysis and FTIR &UV visible spectrums, we found absorption bands for active sites (N-H),(C=N) and (M-N).

UV visible spectrum illustrated types of electrons transition between metal and complex.



Steps of Complex preparation

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