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## Synthesis of two unprecedented Ni(II) & Oxovanadium Azide bridged complexes derived from compartmental Azo-Linked two different Schiff base H<sub>4</sub>L & H<sub>2</sub>L-Characterization by spectroscopic studies (IR, UV-Vis, <sup>1</sup>H NMR) and magneto structural co-relationship

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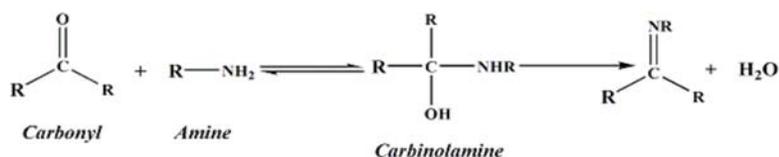
### Abstract

Two sets of new compartmental azo-linked Schiff base ligands set-1 and set-2 have been derived from N, N'-Bis-(2-amino-ethyl)-ethane-1,2-diamine and 1-(5-Chloro-2-hydroxy-phenyl)-ethanone (H<sub>4</sub>L), propane 1,3-diamine and 1-(5-Chloro-2-hydroxy-phenyl)-ethanone (H<sub>2</sub>L) by 1:2 molar ratio in dry methanol solvent medium respectively and the synthesized compartmental ligands are employed for the preparation of complex (1) [Ni(H<sub>2</sub>L)], complex (2) [VO(L<sub>2</sub>)(N<sub>3</sub>)] using Ni(NO)<sub>3</sub>.6H<sub>2</sub>O only & VO(acac)<sub>2</sub> in presence of NaN<sub>3</sub>. In complex (1) compartmental Schiff base (H<sub>4</sub>L) function as hexadentate character through N,O chelating donor but for complex (2) (H<sub>2</sub>L) totally display tetradentate nature via imine nitrogen only. Both Schiff bases and complexes were characterized by elemental (C, H & N), mass (m/e), molar conductivity, IR, UV-Vis, <sup>1</sup>H NMR spectroscopic study. Molar conductivity study strongly support that both complexes are non electrolyte in nature. Additional magnetic moment data will be provided to guess the expected probable structure of complex (1) & complex (2). Electronic spectra and magnetic moment study have been established that the expected geometrical environment of Ni(II), VO(V) complexes (1) & (2) are octahedral, square pyramidal respectively. The complex (1) showed magnetic moment value within the range of μ=2.7-2.9 BM. Complex (2) magnetic moment data strongly support the environment of vanadium is square pyramidal.

**Keywords:** Schiff base H<sub>4</sub>L, H<sub>2</sub>L, N<sub>3</sub><sup>-1</sup> bridging, UV-Vis, <sup>1</sup>H NMR spectra, mass spectra and Magnetic moment.

### 1. Introduction

Novel Schiff base ligands have been in the chemistry catalogue for over 150 years<sup>[1]</sup> when Prof. Sir Hugo Schiff during 19<sup>th</sup> century<sup>[2]</sup> opened the beautiful research gate in the field of coordination chemistry. Schiff bases also known as anils, imine or azomethine and one of the most common way it can be synthesized by condensation reaction between an aldehyde or ketone and a primary amine. The formation of Schiff base was characterized by the presence of azomethine (C=N) linkage<sup>[3]</sup>. The classical method for all Schiff base synthesis to be carried out is the given type of reaction (Scheme 1).



The above synthetic scheme reflects that novel Schiff base formation proceed through beautiful carbinolamine intermediate formation followed by dehydration<sup>[4]</sup>. Today the instant and enduring popularity of Schiff base is due their easily tunable synthesis, their puzzling versatility and wide range of complexing ability once the complex is formed. After a thorough literature survey of this diverse ligand system, several inquisitive inorganic chemists observed that such Schiff base is linked with many important advances field of inorganic chemistry<sup>[5-12]</sup>. Not only such kind of ligands have played a seminal role in the development of coordination chemistry<sup>[5]</sup>, but they are also developed the inorganic biochemistry<sup>[6]</sup>, catalysis<sup>[7-8]</sup>, medical

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imaging [9], optical substances [10], thin films [11-12], enzymatic reactions, magnetism and molecular architectures [13-29]. In the present scenario, Schiff base complexes applications are in the chemical analysis [30], absorption and transport of oxygen [31-32], and polymerization of organic compounds [33-34]. The design and synthesis of transition metal complexes in presence of diverse Schiff base bridged by small conjugated ligands, such as cyano, azido, thiocyanato, dicyanamide are currently under investigation in view of their structural diversity and in the context of molecule based magnets. The most common bridging ligands like  $\text{SCN}^-$ ,  $\text{N}_3^-$  exhibits versatile bridging modes during complex formation in presence of novel Schiff base (Scheme 2). Today plenty of research work have been devoted with Schiff base and transition metal ions like Ni(II),  $\text{V}^{5+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  etc. after making a proper synthetic route in presence of versatile azide/thiocyanate bridging and thus possessing diverse structures from 1-D, 2-D to 3-D supramolecular polymers with different magnetic properties [35-41]. Keeping in mind, in the present research scenario we have synthesized in our laboratory two new compartmental novel Schiff base ( $\text{H}_4\text{L}$ ), ( $\text{H}_2\text{L}$ ), two new Ni(II) &  $\text{V}^{5+}$  complexes using the reference Schiff base ligands. Schiff base and the respective two metal complexes were very carefully characterized by various spectroscopic techniques (IR, UV-Vis,  $^1\text{H}$  NMR, mass) and magnetic studies were also conducted.

## 2. Experimental

### 2.1 Materials

All chemicals were of reagent grade, purchased from commercial sources and used as received without further purification.

5-chloro-2-hydroxyacetophenone, triethylenetetramine, 1,3-propanediamine,  $\text{VO}(\text{acac})_2$  all chemicals were purchased from Sigma Aldrich Company, USA. Sodium azide, Ammonium thiocyanate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , were purchased from SDFCL, India. The total synthetic reactions and work-up were done in open atmospheric condition.

**Caution!** The azide complexes are highly explosive particularly in the presence of Schiff base ligand. Even though

no such accident occurred during my research work, since only small amount of materials should be prepared and must be handled with utmost care.

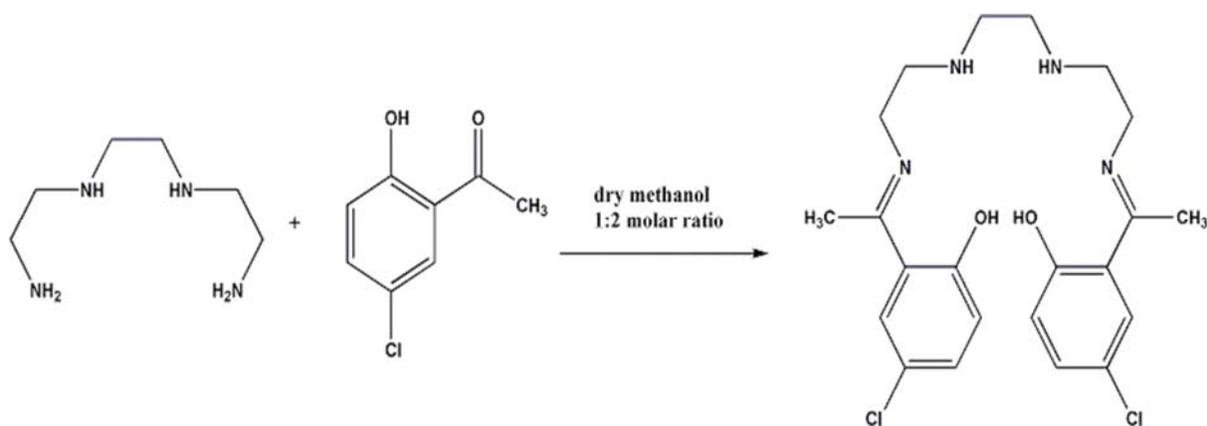
### 2.2 Physical measurement

Elemental analyses (carbon, hydrogen and nitrogen) of two compartmental Schiff base ( $\text{H}_4\text{L}$ ), ( $\text{H}_2\text{L}$ ) and their respective metal complexes (1) & (2) were determined with a Perkin-Elmer CHN analyzer 2400. Mass spectra were done with a JEOLJMS-AX 500 mass spectrometer. IR spectra (KBr pellet,  $400\text{--}4000\text{ cm}^{-1}$ ) were recorded on a Perkin-Elmer model 883 infrared spectrophotometer. The electronic spectra of two complexes (1) & (2) in organic  $\text{CH}_3\text{OH}$  solvent were recorded on a Hitachi model U-3501 spectrophotometer. The  $^1\text{H}$  NMR spectra of novel Schiff base ( $\text{H}_4\text{L}$ ) were recorded on Bruker 300MHz FT-NMR spectrophotometer using trimethylsilane as internal standard in  $\text{CDCl}_3$  solvent. The magnetic susceptibility values of two metal complexes (1) & (2) were determined by Gouy method. Correction for diamagnetism of the constituent atoms was calculated using common Pascal's constant. The effective magnetic moments values ( $\mu_{\text{eff}}$ ) of two respective complexes were calculated using the given equation:  $\mu_{\text{eff}} = 2.83(\chi_M T)^{-1}$

### 3. Synthesis of two compartmental Schiff base ( $\text{H}_4\text{L}$ ) & ( $\text{H}_2\text{L}$ )

#### 3.1 Synthesis of novel Schiff base ( $\text{H}_4\text{L}$ )

To a purified dry methanol solution (50 mL) of 5-chloro-2-hydroxyacetophenone (1.024 g, 6 mmol) was added with triethylenetetramine (0.439 g, 3 mmol) in the same methanol solvent (5mL) with constant stirring for 1 hr. The colour of the overall solution turned to yellow and it was then additionally reflux for 7 hours. The solution was then heated on a steam bath to reduce the volume 15mL and overall solution was cooled on a ice bath. At this moment a deep yellow product was separated out, collected by filtration under suction, washed with cold methanol. Then the yellow solid was dried in vacuum over fused  $\text{CaCl}_2$  desiccator (Scheme 2).

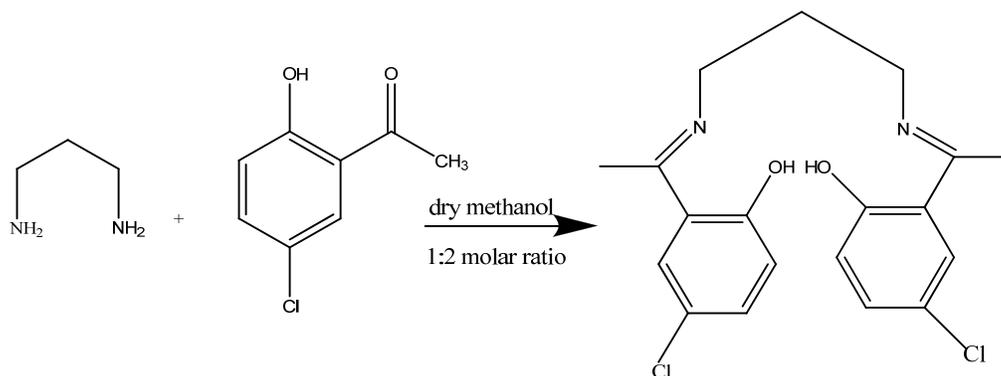


#### Scheme 2: Synthetic procedure for compartmental Schiff base ( $\text{H}_4\text{L}$ )

For novel Schiff base  $\text{H}_4\text{L}$  (Yield: 85%), M.Wt.(451.39), Exact Mass: 450.16, m/e: 451, Anal. Calc. for  $\text{C}_{22}\text{H}_{28}\text{N}_4\text{O}_2\text{Cl}_2$ : C, 58.54; H, 6.25; Cl, 15.71; N, 12.41; O, 7.09 Found: C, 58.6; H, 6.22; Cl, 15.7; N, 12.4; O, 7.00 IR(KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{O-H}) = 2800\text{--}2920$ ;  $\nu(\text{C=N})$  1616.07;  $\nu(\text{C=O})$  1700-1800, UV-Vis spectrum,  $\lambda_{\text{max}}(\text{CH}_3\text{OH})$ : 272 nm, 333 nm, & 400 nm.

#### 3.2 Synthesis of novel Schiff base ( $\text{H}_2\text{L}$ )

To a methanolic solution (30mL) of 5-chloro-2-hydroxyacetophenone(0.171g, 1mmol), propylene diamine(0.0371g, 0.5 mmol) in methanol(5ml) was added with constant stirring. At this moment colour of the solution turned deep yellow and it was refluxed continuously for 3 hours. A yellow solid was immediately separated and collected by filtration after cooling the solution up to room temperature. Then the yellow solid was dried and preserved in a dessicator (Scheme2).



### Scheme 2: Synthetic procedure for compartmental Schiff base ( $H_2L$ )

For novel Schiff base  $H_2L$  (Yield: 75%), M.Wt.(379.28), Exact Mass: 378.09, m/e: 379.00, Anal. Calc. for  $C_{19}H_{20}N_2O_2Cl_2$ : C, 60.17; H, 5.32; Cl, 18.69; N, 7.39; O, 8.44 Found: C, 60.1; H, 5.31; Cl, 18.62; N, 7.35; O, 8.42 IR (KBr:  $v\text{ cm}^{-1}$ ): 1611 ( $v\text{ C=N s}$ ), 1491.03(s), 1290.02(m), 1228.78(m) UV-Vis spectrum,  $\lambda_{\text{max}}(\text{CH}_3\text{OH})$ : 272.89 nm, 334.10 nm, & 400.08 nm.

### 4. Synthesis of complex(1)[Ni( $H_2L$ )], & complex(2) [VO( $L_2$ )( $N_3$ )]

#### 4.1 For complex 1

To the methanolic solution (25mL) of  $\text{Ni}(\text{NO})_3 \cdot 6\text{H}_2\text{O}$  (0.29g, 1 mmol), a solution of the ligand  $H_4L$  (0.451 g, 1 mmol) in same solvent (20 ml) was added dropwise. The whole assembly was stirred for 2.5 hrs. The deep red coloured complex was immediately precipitated out and this was filtered under suction, washed with methanol, dried and preserved in a dessicator properly.

For  $[\text{Ni}(\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_2\text{Cl}_2)]$ : (Yield: 80%), M.Wt.(508.07), Exact Mass: 506.08, m/e: 506.00, Anal. Calc. for complex(1): C, 52.01; H, 5.16; Cl, 13.96; N, 11.03; O, 6.30, Ni, 11.55 Found: C, 52.00; H, 5.14; Cl, 13.94; N, 11.00; O, 6.30, IR (KBr,  $v_{\text{max}}/\text{cm}^{-1}$ ): 1570.93(m), 1451.78(s), 1323.67(s), 1406.25(s), 2347.77(s), 2341.35(s), 670.40(s), 823.20(s), 1236.41(m). UV-Vis spectrum,  $\lambda_{\text{max}}(\text{CH}_3\text{OH})$ : 339 nm, 401 nm.

#### 4.2 For complex 2

To a solution of the ligand (0.379g, 1mmol) in methanol (20 ml),  $\text{VO}(\text{acac})_2$  (0.26516g, 1mmol) taken in same solvent (15mL) was added drop wise with constant stirring. After 10 min  $\text{NaN}_3$  (0.065g, 1mmol) and stirred for 3h. A deep red colored complex was precipitated out and this was filtered under suction, washed with methanol, dried and preserved in a dessicator.

For  $[\text{VO}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{Cl}_2)(\text{N}_3)]$ : (Yield: 85%), M.Wt.(486.23), Exact Mass: 485.23, m/e: 485.00, Anal. Calc. for complex(2): C, 46.93; H, 3.73; Cl, 14.58; N, 14.40; O, 9.87, V, 10.48 Found: C, 46.91; H, 3.72; Cl, 14.56; N, 14.38; O, 9.86, V, 10.46, IR(KBr:  $v\text{ cm}^{-1}$ ): 2340.66  $\text{cm}^{-1}$ (s), 2035.67  $\text{cm}^{-1}$ (s), 1321.07  $\text{cm}^{-1}$ (w), 670.20  $\text{cm}^{-1}$ (w), 648.35  $\text{cm}^{-1}$ , UV-Vis spectrum,  $\lambda_{\text{max}}(\text{CH}_3\text{OH})$ : 365.8729 nm.

## 5. Results and discussion

### 5.1 Synthesis

Compartmental Schiff base ligands ( $H_4L$ ) & ( $H_2L$ ) and two new complexes (1) & (2) have been synthesized very carefully in our laboratory. They are characterized by different physicochemical techniques like elemental analyses, IR, UV-Vis, mass (m/e), and  $^1\text{H}$  NMR spectroscopic studies. Beside, additional magnetic moment data will be provided to establish probable expected geometry of the synthesized Ni(II),  $\text{VO}^{5+}$  complexes (1) & (2) respectively.

### 5.2 Characterization of compartmental Schiff base ligands ( $H_4L$ ) & ( $H_2L$ )

For compartmental Schiff base ( $H_4L$ ), the presence of IR band near  $1616.06\text{ cm}^{-1}$  provides the evidence of for formation of azomethine functional group ( $\text{C}=\text{N}$ ) in the synthesized novel Schiff base. The absence of  $\text{C}=\text{O}$  at around  $1700\text{--}1800\text{ cm}^{-1}$  confirmed the Schiff base formation according to Scheme 1. The very weak band near  $2800\text{--}2920\text{ cm}^{-1}$  indicates the presence of intramolecular hydrogen bond  $-\text{OH}$ . The compartmental Schiff base shows  $^1\text{H}$  NMR following signals:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  2.292 (6H,  $-\text{CH}_3$ ), 2.772 (4H,  $-\text{CH}_2$  alpha to NH), 3.008 (4H,  $-\text{CH}_2$  beta to  $\text{N}=\text{C}$ ), 3.654 (4H,  $-\text{CH}_2$  alpha to  $\text{N}=\text{C}$ ), 6.806- 7.449 (aromatic ring H). The UV-Vis spectrum of novel Schiff base reflects three main peaks at 272nm, 333nm and 400nm. The first two UV-Vis spectrum are assigned due to benzene  $\pi \rightarrow \pi^*$  and imino  $\pi \rightarrow \pi^*$  transitions. Additional peak 400nm is due to  $n \rightarrow \pi^*$  transition [Fig. 1-3]. From IR spectroscopic study, the presence of IR band near at  $1611\text{ cm}^{-1}$  provides the evidence for formation of azomethine group ( $\text{C}=\text{N}$ ) in the azo-linked compartmental Schiff base ( $H_2L$ ). Again the absence of  $\text{C}=\text{O}$  group, IR band around  $1700\text{--}1800\text{ cm}^{-1}$  confirmed the Schiff base formation according to (Scheme 1). The very weak band near  $2800\text{--}2920\text{ cm}^{-1}$  indicates the presence of intramolecular hydrogen bond by  $-\text{OH}$  functional group participation.  $^1\text{H}$  NMR spectroscopic data was further confirmed the formation of novel Schiff base. The UV-Vis spectrum in methanol of novel symmetrical Schiff base ( $H_2L$ ) reflects three main peaks at 272.89nm, 334.10nm and 400.08nm. The first two UV-Vis spectrum are assigned due to benzene  $\pi \rightarrow \pi^*$  and imino  $\pi \rightarrow \pi^*$  transitions. Additional peak 400.08nm is due to  $n \rightarrow \pi^*$  transition [Fig. 4-6].

Versatile bridging modes of Azide ( $N_3^{-1}$ ) ion (Scheme 2)

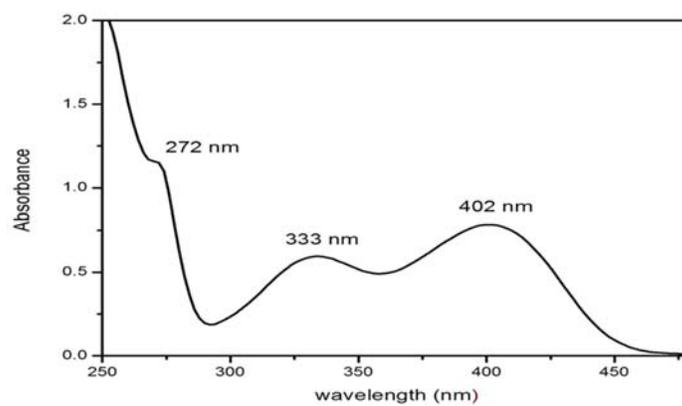
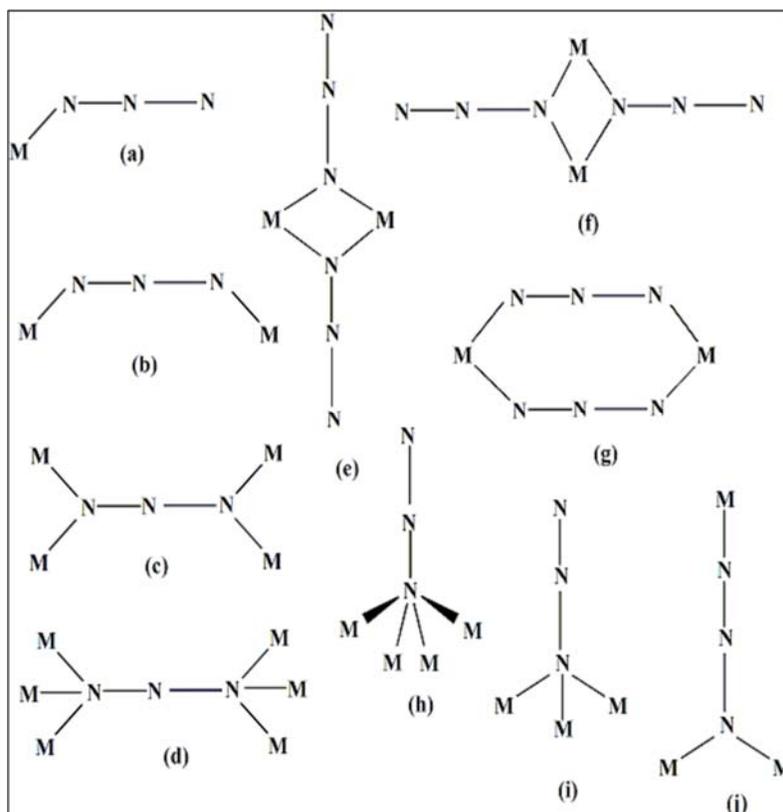


Fig 1

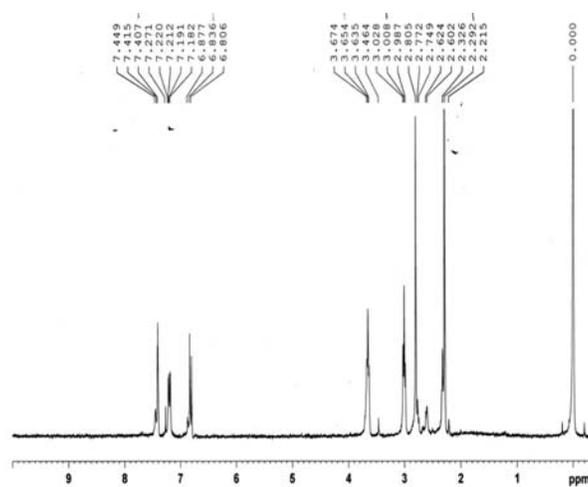


Fig 2



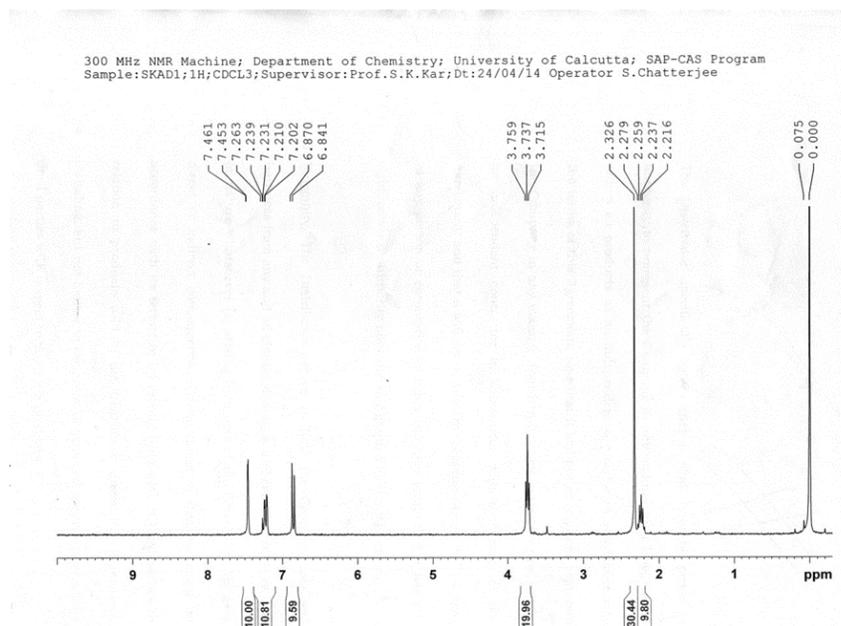


Fig 6

IR,  $^1\text{H}$  NMR and UV-Vis spectra of compartmental Schiff base ( $\text{H}_2\text{L}$ ) (Fig. 4-6).

### 5.3 Characterization of two new complexes (1) & (2)

Schiff base complexes (1) & (2) shows IR frequency band near at  $1570\text{ cm}^{-1}$  and  $2340.66\text{ cm}^{-1}$  strongly support that azomethine nitrogen coordinated to the respective nickel & vanadium metal centers. Moreover IR band near  $2340.66\text{ cm}^{-1}$  for complex (2) is obtained due to asymmetric bridging for azide ligand. For complex (2) the peak being bifurcated, that's why azide ligand being function as bridging moiety. The lowering frequency of  $\text{C}=\text{N}$  group indicates the coordination

of  $\text{C}=\text{N}$  nitrogen to the respective metal. Since  $\text{Ni}(\text{II})\text{ d}^8$  configuration in complex (1), it does not appear d-d transition due to very low intensity. The spectral band  $339\text{ nm}$  &  $401\text{ nm}$  is due to Schiff base coordination with Ni metal centre. The spectral band  $339\text{ nm}$ ,  $401\text{ nm}$  is due to  $\pi\rightarrow\pi^*$  and  $n\rightarrow\pi^*$  transition. The UV-Vis peak of complex 2  $365.8729\text{ nm}$  directly confirmed  $\text{N}_3^-$  bridged complex formation takes place with vanadium metal [Fig. 7-12].

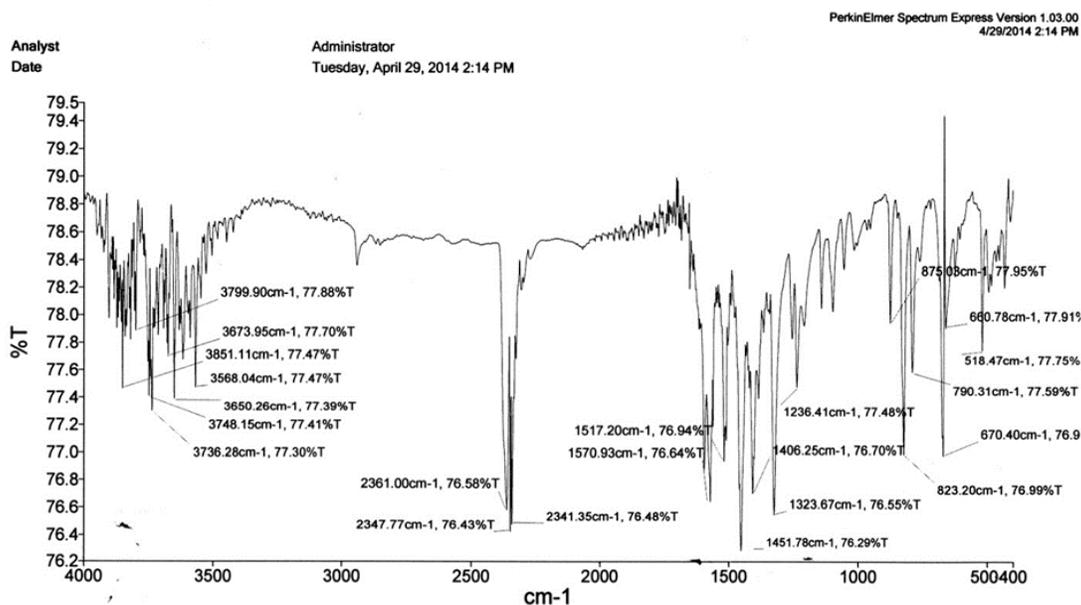


Fig 7

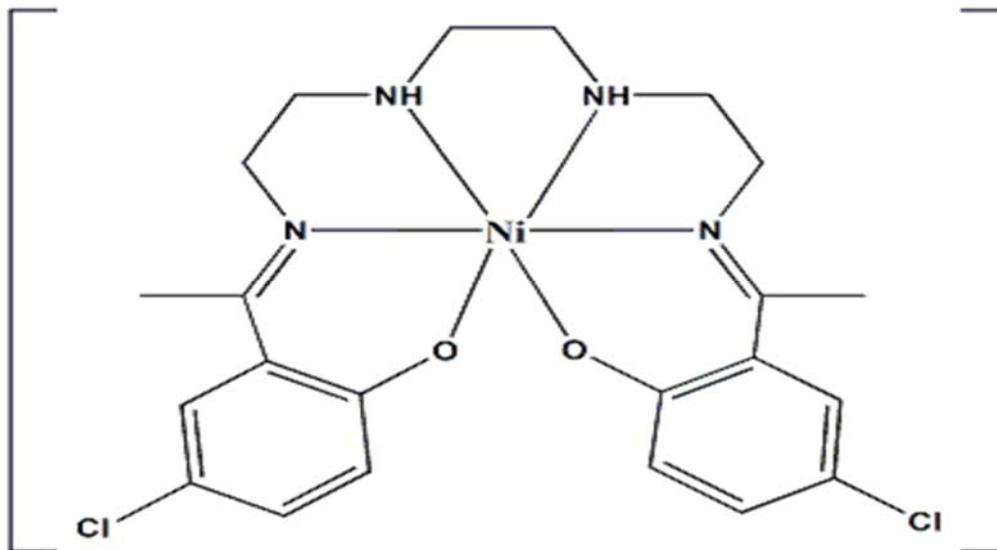


Fig 8

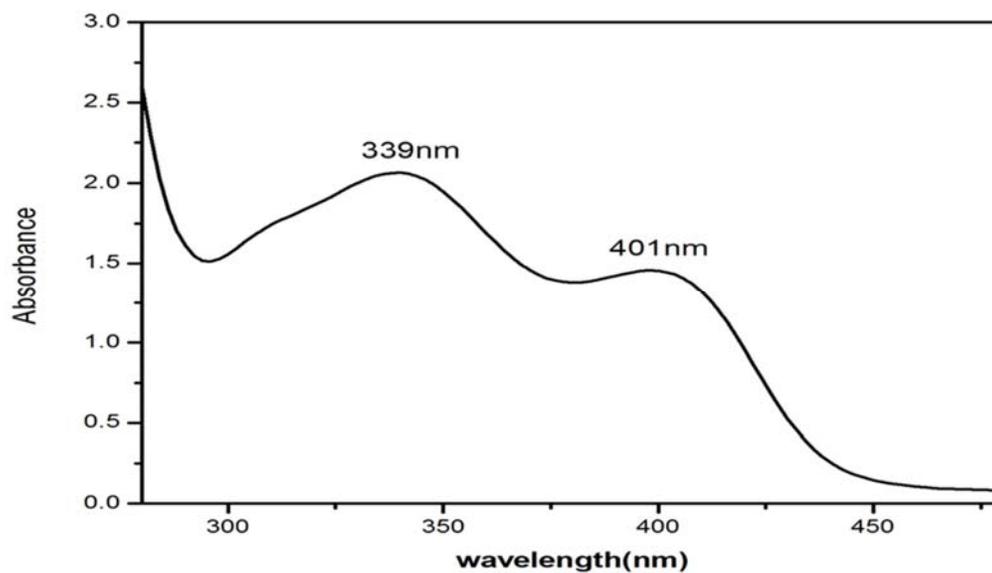


Fig 9

Complex-1 IR, UV-Vis spectra & expected probable geometry (Fig. 7-9).

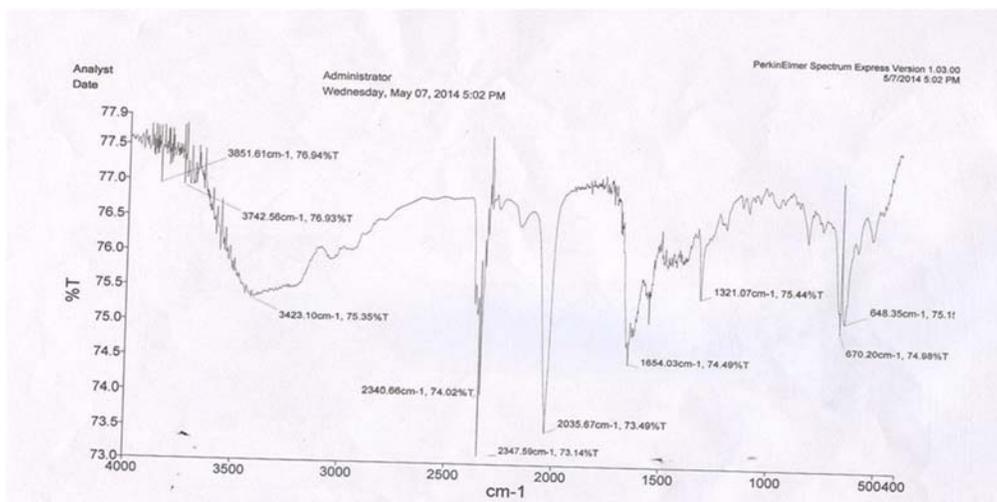


Fig 10

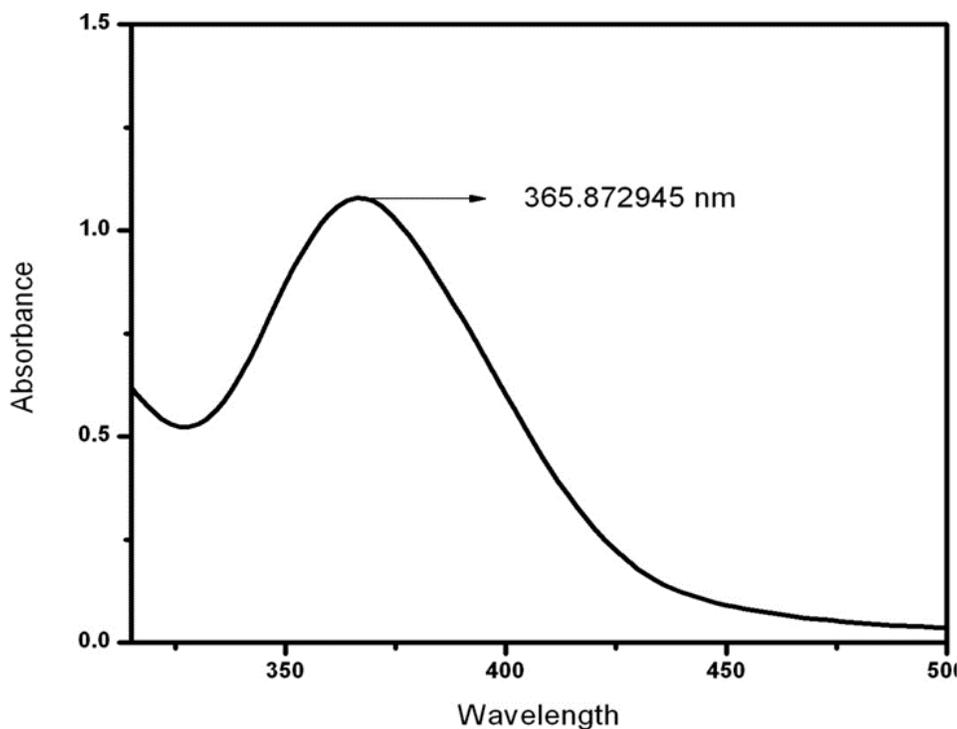


Fig 11

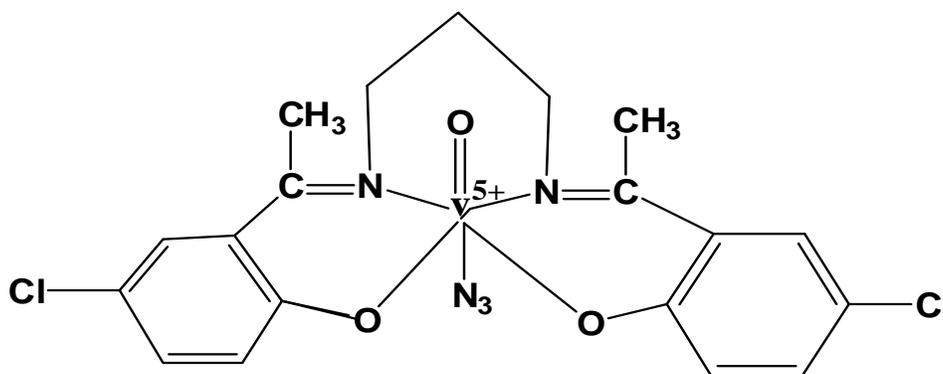


Fig 12

#### 5.4 Magnetic moment study

The nickel(II) metal ion ( $3d^8$ ) have two unpaired electron in the 3d shell, therefore all Ni(II) complexes were considered to have magnetic moments close to the spin-only value,  $2.9\mu_B$  but due to spin orbit coupling and orbital contribution higher values are often expected. The magnetic moment values calculated for complex (1) are in the range of  $2.8-2.9\mu_B$ . Hence the environment around the nickel metal in complex (1) is consistent with octahedral geometry. The geometry around vanadium is square pyramidal supported by complex (2) magnetic moment data.

#### 6. Conclusion

We have successfully synthesized in our laboratory two compartmental azo-linked novel Schiff base ( $H_4L$ ) & ( $H_2L$ ), two new complexes (1) & (2). Schiff base ( $H_4L$ )& ( $H_2L$ ) and two new complexes have been characterized by elemental analyses, FT-IR, UV-Vis, mass, and  $^1H$  NMR spectroscopic study. Additionally magnetic moment data will be provided to confirmed the probable expected geometry of synthesized complexes (1) & (2). Our prime aim for current research work

to investigate primarily the nature of bridging modes of versatile azide around vanadium metal centre. That's why we have to consider microanalytical as well as spectroscopic techniques for characterization of all complexes in the current research work.

#### 7. Acknowledgements

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