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## SYNTHESIS, CHARACTERIZATION AND DFT CALCULATIONS OF SCHIFF-BASE VANADIUM(V) COMPLEXES DERIVED FROM SALICYLDEHYDE WITH 1,2-DIAMINOPROPANE OR 2-PICOLYLAMINE

Khalid Kabel

*Petroleum Applications Department, Egyptian Petroleum Research Institute, Naser City, P.O. 11727, Cairo, Egypt.*

L. Kamel

*Department of Chemistry, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.*

R. Abou-shahaba

*Department of Chemistry, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.*

Azza El-Shenawy

*Department of Chemistry, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.*

Seham Shahan

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*Department of Chemistry, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.,*

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**SYNTHESIS, CHARACTERIZATION AND DFT CALCULATIONS OF SCHIFF-BASE VANADIUM(V) COMPLEXES DERIVED FROM SALICYLDEHYDE WITH 1,2-DIAMINOPROPANE OR 2-PICOLYLAMINE**Enas S. Dafallah<sup>a</sup>, Hassan I. Nimir<sup>b</sup>, Elmugdad A. Ali<sup>a</sup>, Mohamed R. Shehata<sup>c</sup><sup>a</sup>Department of Chemistry, Faculty of Science, Sudan University of science and technology<sup>b</sup>Department of Chemistry & Earth Sciences, Qatar University,

P.O. Box 2713, Doha, state of Qatar. hnimir@qu.edu.qa

<sup>c</sup>Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt**ABSTRACT**

Two ligands were derived from two Schiff-bases of salicylaldehyde with 1,2-diaminopropane, Sal-DAP (L1) and salicylaldehyde with 2-picolyamine, Sal-PA (L2) and their novel dioxovanadium complexes were synthesized. The complexes C1, [VO<sub>2</sub>(Sal-DAP)] and C2, [VO<sub>2</sub>(Sal-PA)] are characterized by conductivity measurements, magnetic susceptibility, UV-Vis, IR, thermal analysis, <sup>1</sup>H- and <sup>13</sup>C-NMR. The molecular structure of the complexes C1 and C2 were confirmed using the DFT calculation to obtain the optimized geometries using the Gaussian09 program at the B3LYP/LANL2DZ level of theory. The vanadium atoms in the two complexes were coordinated in distorted trigonal bipyramidal geometries with L1 acting as a tridentate ligand through nitrogen atoms and one deprotonated phenol oxygen atom leaving the other phenol group free, and L2 acting as a tridentate ligand through nitrogen atoms and deprotonated phenol oxygen atom.

**Keywords:** Schiffbase, Vanadium(v), DFT Calculations, Salicylaldehyde, 1,2-diaminopropane 2-picolyamine

**1. INTRODUCTION**

Vanadium complexes play an important role in biological as well as in catalytic processes. In both cases chiral properties implemented by the ligand frame work can be relevant for specific properties of the systems. In general, this leads to the presence of diastereomers generated by the additional chiral center at the vanadium site [1]. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, *e.g.*, biological, inorganic and analytical chemistry [2,3] and considered to be a very important class of compounds that are widely used due to their good solubility properties and their remarkable versatility [4]. Schiff bases and their metal complexes are known to exhibit a broad variety of biological activity such as anti-viral, [5] anti-parasitic, [6] anti-bacterial, [7] anti-inflammatory, [8] antitumor, [9,10] anti-HIV, [11] anticancer, [12] etc. A large variety of vanadium complexes with ligands bearing oxygen and nitrogen donors have been reported as structural and

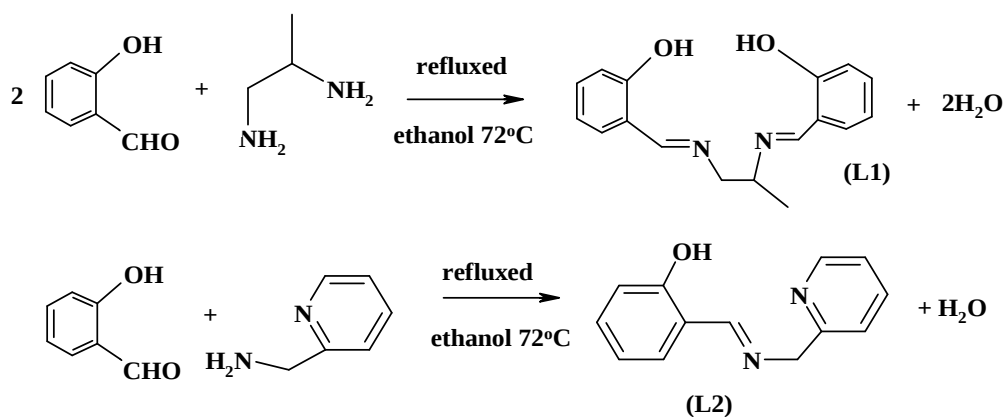
functional mimics of biological systems [13-17].

**2. EXPERIMENTAL****2.1 Materials**

1,2-Diaminopropane, 2-Picolyamine, ethanol and Diethyl ether were obtained from Aldrich. Vanadium pentoxide is obtained from Alfa Aesar. Salicylaldehyde is obtained from Loba Chemie, All reactions were performed in argon atmosphere.

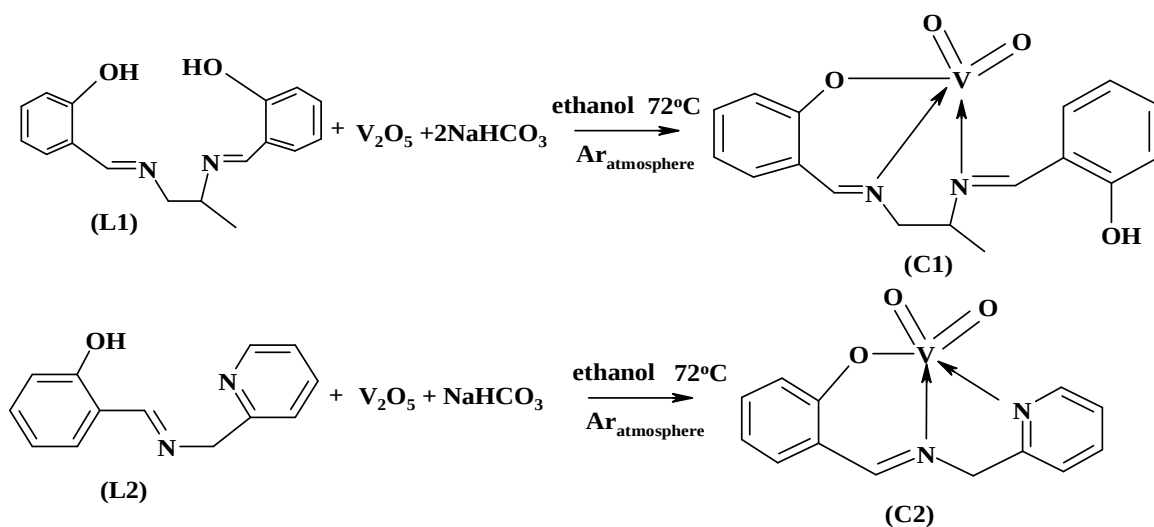
**2.2 Instrumentation**

The melting points of were determined by Fisher-Johns melting point apparatus in °C Fisher Scientific Company - USA model 6200, Molar conductivities of freshly prepared DMF complexes solutions  $c = 1.0 \times 10^{-3} \text{ Mol/dm}^{-3}$  were measured on conductivity meter model-JENCO-3173R-USA, The magnetic susceptibilities were measured on Sherwood scientific-England, UV/Vis spectra in complexes solutions ( $c = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) were recorded on UV.3101PC-Schimadzu Japan, Infrared spectra were recorded on a



washed and dried. Data for  $C_{17}H_{18}N_2O_2$  ( $M_f = 282.34$ ); yield 74%, yellow color; m.p. 140 °C; Anal. Calcd: C, 72.32; H, 6.43; N, 9.92 %. Found: C, 72.4; H, 6.5; N, 9.8%.

**Scheme 1: preparation of ligands L1 and L2**



**Sal-PA**  
[ $C_{13}H_{12}N_2O$ ]  
(L2) Schiff base ligand by mixing (2.42 g, 20 mmol) of

8001-PC FT-IR- Shimadzu spectrophotometer using KBr pellets in the mid-infrared region 4000-400  $Cm^{-1}$ , NMR spectra were recorded on a Varian Mercury VX-300 and VX-500 MHz NMR Spectrometer,  $^1H$  spectra were run at 75.46 MHz and  $^{13}C$  spectra were run at 300 MHz in DMSO- $d_6$  as a solvent and TMS as an internal standard. Chemical shifts ( $\delta$ ) are reported in ppm. TGA was carried on a TGA-Q500 Thermo Gravimetric Analyzer.

## 2.3 Synthesis

### 2.3.1 Synthesis of the Schiff bases L1 & L2

**Sal-DAP** [ $C_{17}H_{18}N_2O_2$ ] (L1) Schiff base ligand was prepared by mixing (2.42 g, 20 mmol) of salicylaldehyde with (0.74 g, 10 mmol) of 1,2-diaminopropane in 20 mL ethanol with continuous stirring and reflux for 3.5 h at 72 °C, **Scheme 1**. Yellow solid was formed and filtered,

salicylaldehyde with (2.16 g, 20 mmol) of 2-picolylamine in 20 mL ethanol with continuous stirring and reflux for 3.5 h at 72 °C, **Scheme 1**. Brown oily solid formed and kept in refrigerator cooling for two weeks, bright yellow solid was formed, filtered, washed and dried. Data for  $C_{13}H_{12}N_2O$  ( $M_f = 212.25$ ); Yellow color; m.p. 130°C; yield (69%); Anal. Calcd: C, 73.57; H, 5.70, N, 13.20%. Found: C, 73.4; H, 5.8; N, 13.3%.

### 2.3.2 Synthesis of the Schiff base complexes

**Scheme 2** illustrates the synthetic routes and final structures of all synthesized complexes (C1) and (C2).

[ $VO_2(\text{Sal-DAP})$ ] (C1) was prepared by (1.81 g, 10 mmol) of vanadium pentoxide was

dissolved in aqueous solution of sodium bicarbonate (1.68 g, 20 mmol) and solutoin was stirred for 15 min, (2.82 g, 10 mmol) of ligand (**L1**) was dissolved in 30 ml ethanol and added to the above solution, the mixture was stirred and refluxed under argon atmosphere for 6 h at 72°C, **Scheme 2**. Yellow ppt was formed, filtered off and washed with ethanol. Data for  $C_{17}H_{17}N_2O_4V$  ( $M_f = 364.27$ ); yield 77%, yellow color; m.p. 280°C; Anal. Calcd: C, 56.05; H, 4.70; N, 7.69 %. Found: C, 55.8; H, 4.6; N, 7.8%.

[VO<sub>2</sub>(Sal-PA)] (**C2**) was prepared by (1.81 g, 10 mmol) of vanadium pentoxide dissolved in aqueous solution of Sodium bicarbonate (1.68 g, 20 mmol) and solutoin was stirred for 15 min, (2.12 g, 10 mmol) of ligand (**L2**) was dissolved in 30 ml ethanol and added to the above solution, the mixture was stirred and refluxed under argon atmosphere for 48 h at 72°C, **Scheme 2**. Greenish yellow ppt was formed, filtered off, washed with ethanol and dried. Data for  $C_{13}H_{11}N_2O_3V$  ( $M_f = 294.18$ ); yield 51%; greenish yellow color; m.p. 255°C; Anal. Calcd: C, 53.08; H, 3.77; N, 9.52; found C, 52.9; H, 3.9; N, 9.6.

### 3. RESULTS AND DISCUSSION

#### 3.1 Physiochemical data

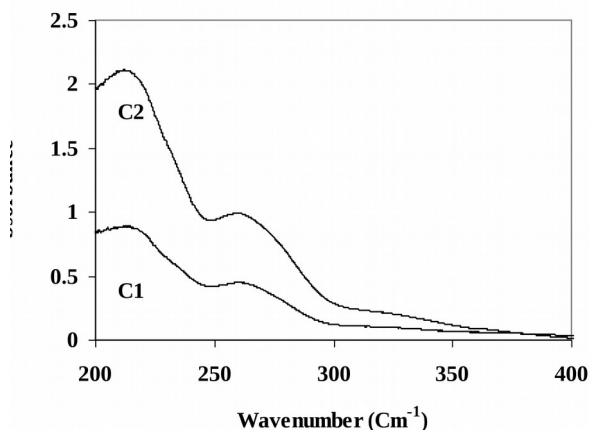
The melting points of complexes C1, C2 were found to be > 250°C (C1 = 280 and C2 = 255°C). The magnetic moment is calculated from the magnetic susceptibility *d*-configuration C1 *d*<sup>0</sup>-C2 *d*<sup>0</sup> and number of unpaired electrons  $\mu_s$  C1 = 0.36  $\mu_s$  C2 = 0.26 for Vanadium V<sup>+5</sup> ions with a trigonal bipyramidal geometry. Molar conductivities of freshly prepared DMF complexes C1 and C2 solutions,  $c = 1.0 \times 10^{-3} \text{ Mol/dm}^{-3}$  were C1 = 23.05 mScm<sup>2</sup>mol<sup>-1</sup> – C2 = 24.3 mScm<sup>2</sup>mol<sup>-1</sup> which indicates its non-electrolytic nature, **Table 1**.

#### 3.2 Spectroscopic studies

##### 3.2.1 UV/Vis Spectra of C1 & C2

The electronic spectra of metal complexes were recorded, Figure 1, and show two high energy absorption bands for **C1** (208, 262 and

very weak at 318 nm) and **C2** (210, 259 and weak at 322 nm).



**Fig. 1:** UV/Vis Absorption spectra of C1 and C2

**Table 1:** Molar conductance values, magnetic measurement, and UV/Vis-bands of C1 and C2

Codes Name of the complex	Molar conductance ( $\Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$ )	Magnetic values (298 K)	Bands observed $\lambda_{\text{max}}$
C1	23.05	$\mu_s$ 0.36 diamagnetic	208, 262 and 318 (br)
C2	24.3	$\mu_s$ 0.26 diamagnetic	210, 259 and 322 (br)

##### 3.2.2 Infrared Spectra of C1 and C2 complexes (IR)

The IR spectra of complexes (C1 and C2) and their free ligands (L1 and L2) were determined, Figures 2 and 3.

The free ligands L1 and L2 characteristic stretching vibration bands appear at 1635 and 1629  $\text{cm}^{-1}$  corresponding to the C=N vibration [18-21], which are shifted to 1629 and 1624  $\text{cm}^{-1}$  in their complexes C1 and C2, respectively indicating coordination of the nitrogen to vanadium [18-21]. The broad vibration bands above 3000  $\text{cm}^{-1}$  characteristic of the stretching frequencies of H-bonding OH groups. The (O–H) vibration was present in C1 which confirms the presence of one of the OH group uncoordinated in the optimized complex. The absence of (O–H) vibration in the complex C2 indicates the coordination of the oxygen after deprotonation of OH group. The complexes exhibit the characteristic (V=O) bands at 881 and 921  $\text{cm}^{-1}$  for complex C1 and

at 844 and 1004  $\text{cm}^{-1}$  for complex C2 [18-21]. The (V–O) bands at 618 and 602  $\text{cm}^{-1}$  and (V–N) bands at 541  $\text{cm}^{-1}$ , 544  $\text{cm}^{-1}$  for complex C1 and C2; respectively [18-21], Figures 2 and 3.

### 3.2.3 Nuclear Magnetic Resonance Spectrophotometer (NMR)

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data confirm the complex formation and the coordination mode of the Schiff-base ligand.

$^1\text{H}$ NMR (DMSO- $d_6$ , ppm):  $\delta = 1.18$  and 1.32 ( $\text{CH}_3$ ), 3.05 ( $\text{CH}$ ), 3.36 ( $\text{CH}_2$ ), 6.78–7.55 (8H aromatic), 8.55 and 8.88 (2H,  $\text{H}-\text{C}=\text{N}$ ) and the presence of one uncoordinated phenolic OH was confirmed by chemical shift  $\delta = 13.40$  (1H,  $\text{H}-\text{O}$ ), Figures 4.

$^{13}\text{C}$ NMR (DMSO- $d_6$ , ppm):  $\delta = 20.70$  ( $\text{CH}_3$ ), 65.00 ( $\text{CH}$ ), 65.50 ( $\text{CH}_2$ ), 116.94–163 (12C, aromatic) 165.70 (2C,  $\text{C}=\text{N}$ ), Figures 4.

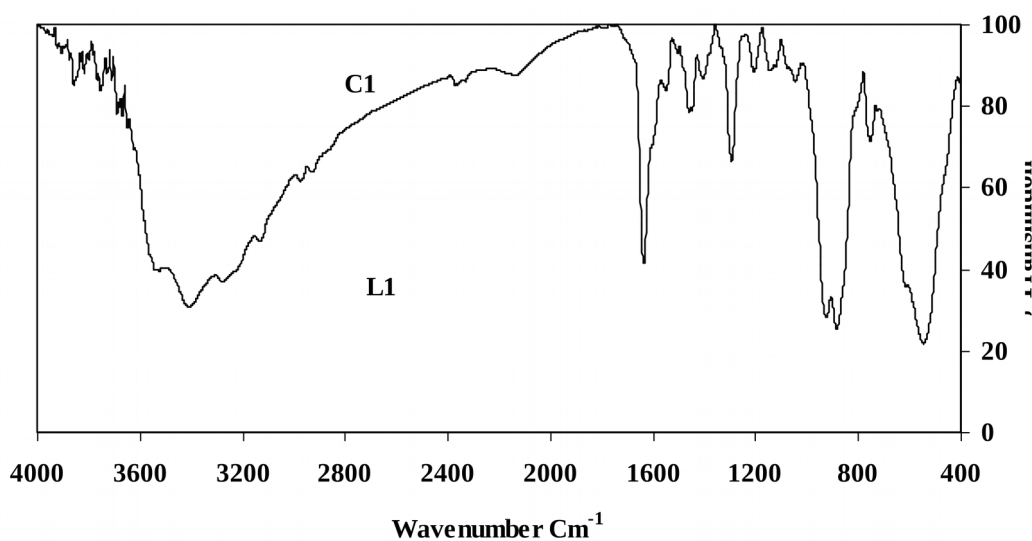


Fig. 2: infra-red spectra of ligand L1 (.....) and complex C1 (—).

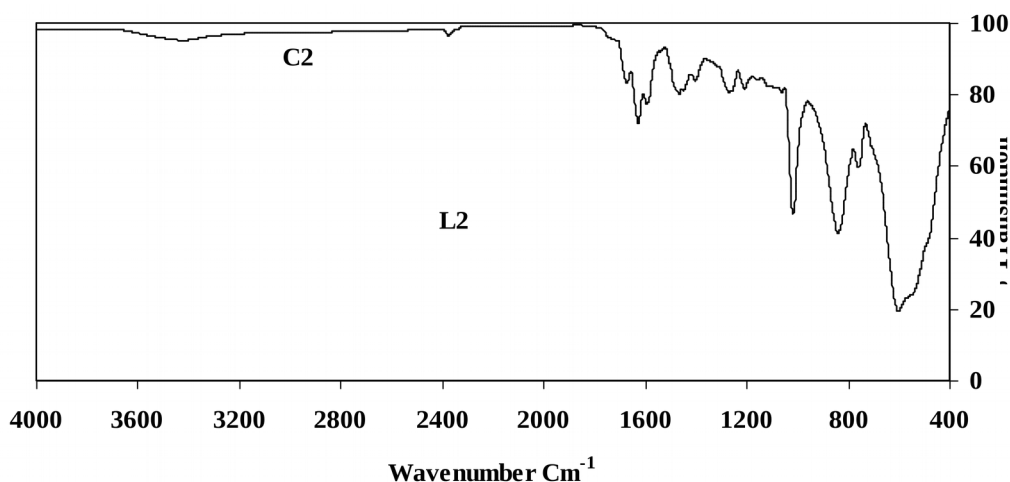


Fig. 3: infra-red spectra of ligand L2 (.....) and complex C2 (—).

For complex C2:

$^1\text{H}$ NMR (DMSO- $d_6$ , ppm):  $\delta = 3.32$  ( $\text{CH}_2$ ), 6.96–8.71 (8H aromatic), 10.25 (aromatic,  $\text{H}-\text{C}=\text{N}$ ) and 10.90 ( $\text{H}-\text{C}=\text{N}$ ) [18,19], Figures 5.

$^{13}\text{C}$ NMR (DMSO- $d_6$ , ppm):  $\delta = 52.96$  (1C,  $\text{CH}_2$ ), 121.54–160.46 (10C, aromatic), 162.75 (1C,  $\text{C}=\text{N}$ ) and 163.00 (1C,  $\text{C}=\text{N}$ ), Figures 5.

### 3.3. Thermo gravimetric

For complex C1:

studies (TGA):

Thermo gravimetric studies TGA for the complexes C1 and C2 were carried out within the temperature range from room temperature up to 1000 °C with a heating rate of 10 degree/min. There is no weight loss before 200 °C indicating absence of water from both complexes. The remaining residue is in both

The steps of weight loss cannot be definitely assigned to certain formulae due to their overlap and the complexity of complexes.

### 3.4 Theoretical DFT calculations

The density functional theory was applied to calculate the optimized geometries using Gaussian09 program [21].  
The

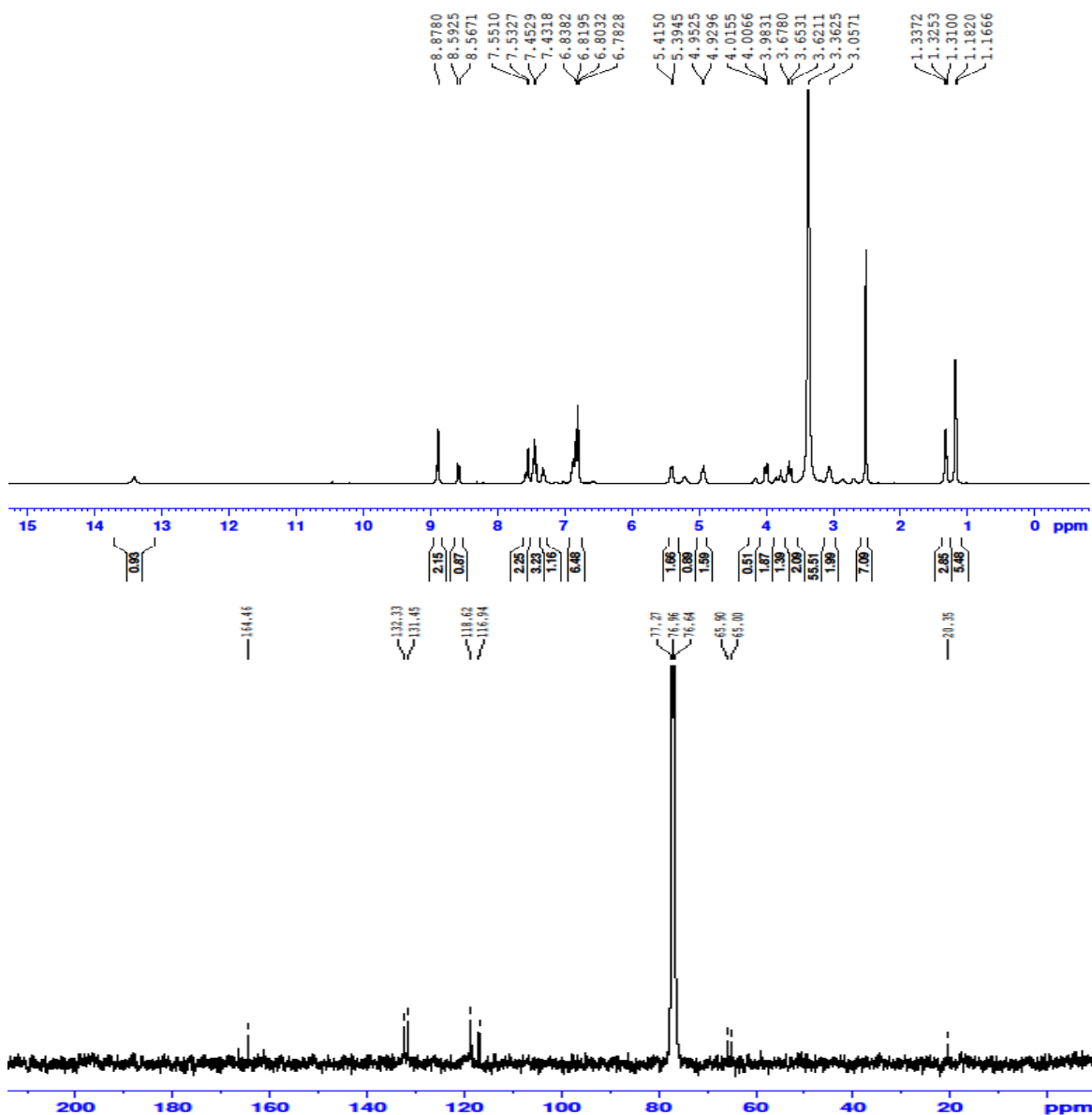


Fig. 4: <sup>1</sup>H-NMR (upper) and <sup>13</sup>C-NMR for complex C1(lower).

complexes is V<sub>2</sub>O<sub>5</sub>. The total weight loss is 74.1 for C1 and 68.9 for C2. The remaining residue of V<sub>2</sub>O<sub>5</sub> is 25.9 (calculated 24.96) for C1 and is 31.1 (calculated 30.91) for C2, Figure 6.



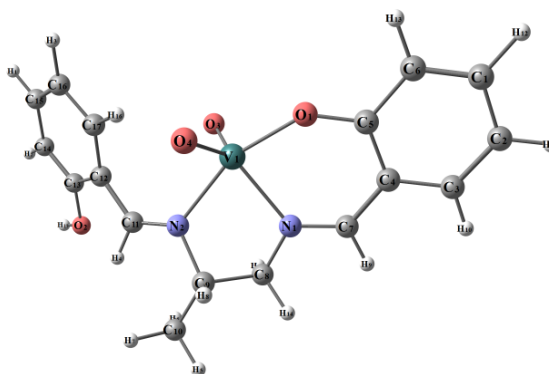
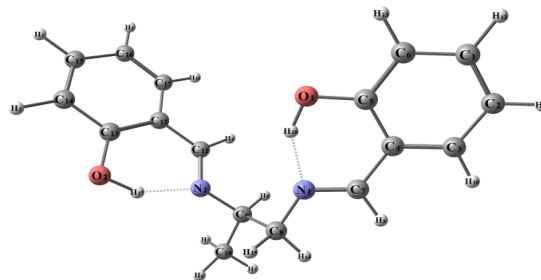
DFT/B3LYP/LANL2DZ level of theory was used for the geometry optimization. Full geometry optimization was performed using B3LYP method with LANL2DZ as a basis set to generate the optimized structure of minimum energy for ligands and complexes.

### The Molecular modeling of ligand L1 and complex C1:

Figure 7, shows the optimized structures of ligand (L1) and its complex (C1) as the minimum energy configurations. The vanadium atom is five-coordinate in a distorted trigonal bipyramidal geometry and the bond angles ranging from 76.93° to 158.9°, Table 2.

The atoms N1, O3, O4 and V are almost in one plane deviated by 9.26°. The axial bond angle of O1-V-N2, 158.9°, is deviated from linearity due to coordination to vanadium. The bite angles N1-V-N2 and O1-V-N1 are 76.94 and 82.60° lower than 90° due to coordination. Moreover, the angles N1-C8-C9 and N2-C9-C8 were decreased upon complex formation, from 111.5 and 109.6 to 108.2 and 105.1, respectively.

The distance between donor atoms involved in coordination N1- - -N2 is decreased upon complex formation from 2.963 Å (in free ligand) to 2.683 Å (in the complex) but the distance between and N1- - -O1 is slightly increased from 2.618 Å (in free ligand) to 2.676 Å (in the complex), which is probably due to the formation of hydrogen bonds between N1 and HO1 in L1, Figure 7. The two hydroxyl atoms in L1 are hydrogen bonded to the nitrogen atoms. The bond length of V-O1 is 1.900 Å longer than those of V=O3 and V=O4, which are 1.616 and 1.627 Å, respectively. The elongation of N1=C7 and N2=C11 bonds from 1.286 and 1.286 Å in L1 to 1.319 and 1.305 Å in C1 was due to coordination of V to both N1 and N2., Table 2.



**Fig.7: Optimized minimum energy structure of L1 (upper) and its complex C1 (lower) calculated by density function B3LYP/LANL2DZ.**

**Table 2: Optimized Bond Lengths and angles of ligand L1 and complex C1**

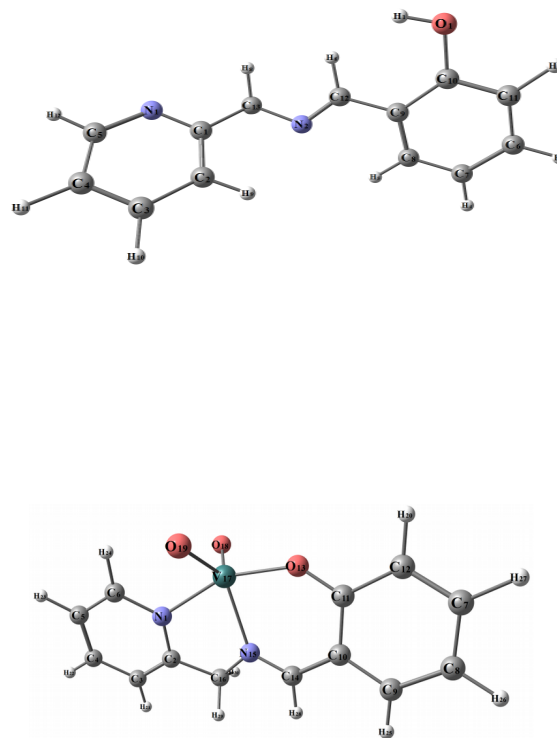
Type of bond	Bond length (Å)		Type of Angle	Angle (°)	
	L1	C1		L1	C1
V-O1	-	1.900	O4-V-N2	-	88.23
V=O3	-	1.616	O4-V-O3	-	110.9
V=O4	-	1.627	N1-V-O3	-	118.5
V-N1	-	2.145	N1-V-N2	-	76.93
V-N2	-	2.168	N2-V-O3	-	91.85
N1----N2	2.963	2.683	O1-V-O3	-	102.4
N1----O1	2.618	2.676	O1-V-O4	-	100.8
N1=C7	1.286	1.319	O1-V-N1	-	82.60
N2=C11	1.286	1.305	O1-V-N2	-	158.9
			O4-V-N1	-	128.5
			N1-C8-C9	111.5	108.2
			N2-C9-C8	109.6	105.1

### The Molecular Modeling of ligand L2 and complex C2:



Figure 8, shows the optimized structures of ligand (L2) and its complex (C2) as the minimum energy configurations. The vanadium atom is five-coordinate in distorted trigonal bipyramidal geometry and the bond angles ranging from 74.58 to 157.3°, Table 4. The atoms N1, O2, O3 and V are almost in one plane deviated by 11.85°. The axial bond angle of O1-V-N1, 157.3°, is deviated from linearity due to coordination to vanadium. The bite angles N1-V1-N2 and O1-V-N2 are 74.58 and 82.84° lower than 90° due to coordination. Moreover, the angles C12-N2-C13 and O1-C10-C9 were decreased upon complex formation, from 118.2 and 124.1 to 116.6 and 121.0, respectively.

The distance between donor atoms involved in coordination N1- - - -N2 is decreased upon complex formation from 3.677Å (in free ligand) to 2.597 Å (in the complex) and the distance between N1- - - -O1 and N2- - - -O1 are also decreased from 7.099 and 4.219Å (in free ligand) to 3.952 and 2.685 Å (in the complex), respectively, confirming the chelating to V atom. The bond length of V-O1 is 1.895 Å longer than those of V=O2 and V=O3, 1.619 and 1.623 Å, respectively, Table 4. The elongation of N2=C12 and N2=C13 bonds was also observed.



**Fig. 8: Optimized minimum energy structure of L2 (upper) and its complex C2 (lower) calculated by density function B3LYP/LANL2DZ**

**Table 3: Optimized Bond Lengths and angles of ligand L2 and complex C2**

Type of bond	Bond length (Å)		Type of Angle	Angle (°)	
	L2	C2		L2	C2
V-O1	-	1.895	O1-V-O2	-	88.23
V=O2	-	1.619	O1-V-O3	-	110.9
V=O3	-	1.623	O1-V-N1	-	118.5
V-N1	-	2.135	O1-V-N2	-	76.93
V-N2	-	2.151	O2-V-O3	-	91.85
N1- - - N2	3.677	2.597	O2-V-N1	-	89.77
O1- - - N2	4.219	2.685	O2-V-N2	-	121.3
N2=C12	1.275	1.320	N1-V-O3	-	88.60
N2=C13	1.448	1.483	N1-V-N2	-	74.58
			N2-V-O3	-	124.5
			C12-N2-C13	118.2	116.6
			O1-C10-C9	124.1	121.0

The computed total energy, the highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies and the dipole moment for the ligands L1 and L2 and their complexes C1

and C2 were calculated, Table 4. The more negative values of total energy of the complexes than those of free ligands indicate the extra stability of the complexes than the free ligands. The polarities of the complexes are much larger than those of the free ligands, Table 4. The highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies of C1 and C2 are represented in Figures 9 and 10, respectively.

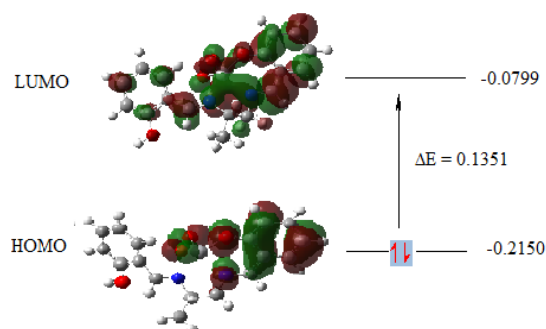
**Table 4:** Calculated energies of Ligands, L1 and L2, and complexes, C1 and C2.

	E <sup>a</sup>	HOMO <sup>b</sup>	LUMO <sup>c</sup>	$\Delta E^d$	Dipole moment <sup>e</sup>
L1	-918.635	-0.2126	-0.0511	0.1615	3.601
C1	-1139.801	-0.2150	-0.0799	0.1351	7.648
L2	-687.335	-0.2264	-0.0504	0.1760	1.228
C2	-908.582	-0.2206	-0.0881	0.1325	9.6808

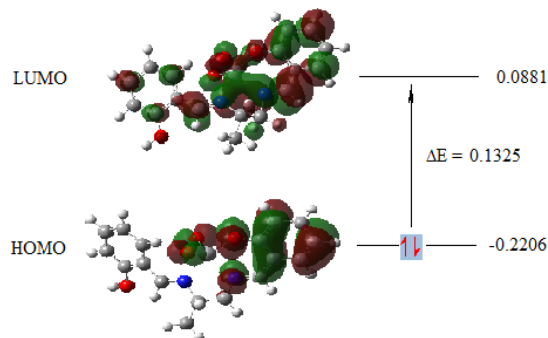
<sup>a</sup>E: the total energy (a.u.). <sup>b</sup>HOMO: highest occupied molecular orbital (eV).

<sup>c</sup>LUMO: lowest unoccupied molecular orbital (eV).

<sup>d</sup> $\Delta E: E_{LUMO} - E_{HOMO}$  (eV). <sup>e</sup> dipole moment (Debye).



**Fig. 9:** The highest occupied molecular orbital (HOMO) energies and the lowest unoccupied molecular orbital (LUMO) energies in eV for C1.



**Fig. 10:** The highest occupied molecular orbital (HOMO) energies and the lowest unoccupied molecular orbital (LUMO) energies in eV for C2.

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