

Synthesis and Characterization of a Mononuclear Vanadium(V) complex with Phenol based Ligands

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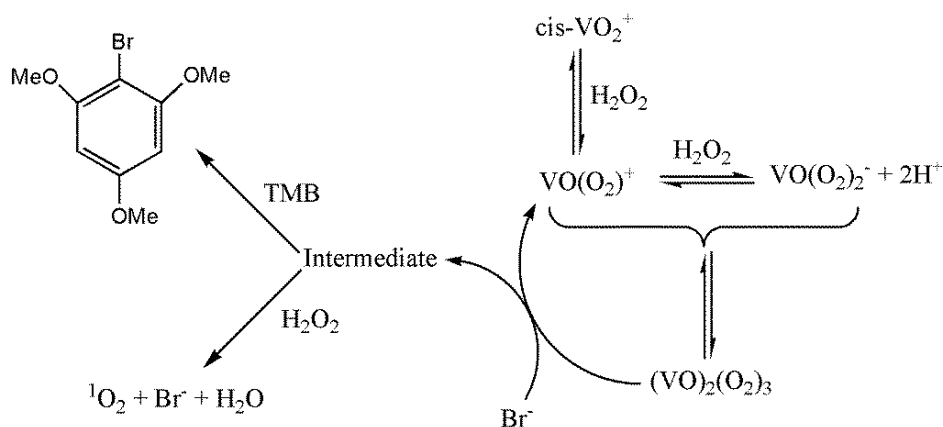
ABSTRACT

The present article demonstrates the synthesis and characterization of a new mononuclear oxido-vanadium(V) complex with two amine-phenol and phenol based ligand fragments. The complex was characterized by spectroscopic techniques like ⁵¹V NMR, UV-Visible and Infrared Spectroscopy. Cyclic Voltametry was also performed to measure the Electrochemical properties that reveal a quasi reversible nature of the synthesized complex.

Keywords: *trans*-1,2-diaminocyclohexane-*bis*(phenolate), oxidovanadium, ⁵¹V NMR, ESI-MS⁺

INTRODUCTION

The study on the coordination chemistry of vanadium has enhanced from the discovery of vanadium(V) in the active site of vanadate dependent haloperoxidases (V-HalPO) [1] and its importance in catalytic reactions [2-9]. A variety of vanadium compounds have been found to act as functional models for V-haloperoxidases [10]. The first reported functional mimic of V-BrPO is *cis*-dioxidovanadium(V) (VO₂⁺) in acidic aqueous solution [11,12]. *Cis*-dioxidovanadium(V) is found to catalyze the bromination of 1,3,5-trimethoxybenzene (TMB) as well as the bromide-mediated disproportionation of H₂O₂ (Scheme 1) [11].



Scheme 1. Bromination activity of the V-BrPO mimic *cis*-dioxidovanadium(V) [11]

Different chemical and electrochemical studies on the reactivity of oxidovanadium(V) complexes, and dioxygen activation along with the ability to form oxido-peroxido vanadium(V) species, which are considered to be important reactive intermediates in the *in-vivo* enzymatic processes [13-16] have been explored and reported in literature. Moreover Oxidoperoxido-vanadium(V) complexes are also well known to exist in some catalytic cycles in the oxidation of various organic substrates [17-19]. On the other hand, due to their high charge/radius ratio, vanadium(V) centres are usually strong Lewis acids, which lead them to activate the peroxidic reagents like H₂O₂, molecular O₂, peroxyacetic acid etc. [20] and thus make them to act as catalyst precursors in various oxidation reactions like bromination, epoxidations of alkenes and allylic alcohols, hydroxylations of alkanes and arenes, oxidations of primary and secondary alcohols to the corresponding aldehydes and ketones [21,22].

All the above findings prompted us to design and synthesize a new mononuclear oxido-vanadium(V) complex with two amine-phenol and phenol based ligand fragments. The complex was characterized by spectroscopic analysis such as, ^{51}V NMR, UV-Vis, ESI- Ms^+ and IR spectroscopy. The cyclic voltametry study reveals the quasi reversible nature of the complex.

EXPERIMENTAL SECTION

A. Physical Measurement

Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyser. Infrared spectra ($400\text{--}4000\text{ cm}^{-1}$) were recorded from KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer. Electronic spectra were recorded from Microprocessor UV-VIS Spectrophotometer, Labard (Single Beam) (Model No.: LIM-330). Mass spectra were recorded on a JEOL GCMATE II GC-MS instrument. ^1H and ^{51}V NMR spectra were recorded by Bruker AVANCE III 500 MHz (AV 500) multi nuclei solution NMR Spectrometer. Electrochemical measurements were carried out using a computer controlled AUTOLAB (Model: 302) cyclic voltammeter with platinum working electrode, platinum-wire counter electrode and saturated calomel (SCE) reference electrode in MeCN using tetrabutyl ammonium perchlorate as supporting electrolyte.

B. Materials

Starting materials for the synthesis of the ligand and complex (**1**) namely, 2,4-di-*tert*-butylphenol (Aldrich), trans-1,2-diaminocyclohexane (Aldrich), formaldehyde (Merck India), $[\text{VO}(\text{acac})_2]$ (Loba India), trimethylamine (TEA) (Merck India) were of reagent grade and used as received. Solvents like methanol, ethanol, acetonitrile (Merck India) were of reagent grade and dried by standard methods before use.

C. Synthesis

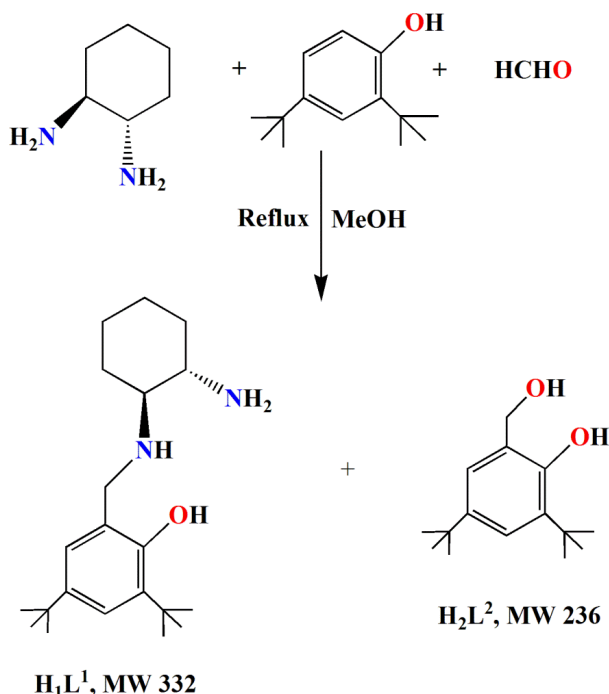
Synthesis of the ligand (H_1L^1): 0.114 gm (1 mmol) of *trans*-1,2-diaminocyclohexane was refluxed with 0.206 gm (1mmol) of 2,4-di-*tert*-butylphenol along with .06 gm (2 mmol) formaldehyde in MeOH (30 ml) for 8 hrs. Colourless solid deposited were collected by filtration and washed with EtOH. Yield ~ 85%. Probable molecular formula of the ligand (H_1L^1) is $\text{C}_{21}\text{H}_{36}\text{N}_2\text{O}$ (MW 332, ESI- Ms^+ appears at $\text{MW}+\text{Na}^+$ i.e. 355.61, **Figure 1**). Another split fragment of the ligand (H_2L^2) appears in the ESI- Ms^+ study at 236.80 (**Figure 1**) with probable molecular formula $\text{C}_{15}\text{H}_{24}\text{O}_2$ (MW 236). ^1H NMR (in CDCl_3 , 500 MHz, ppm): δ (ppm) 1.25-1.40 (36 H, m, $-\text{CH}_3$); 1.48-1.57 (4H, m, $-\text{CH}_2$); 1.76-1.83 (4H, m, $-\text{CH}_2$); 1.93 (1H, t, $-\text{OHCH}_2$); 2.01 (2H, d, $-\text{NH}_2$); 2.11-2.29 (1H, m, $-\text{NH}$); 3.46-3.53 (2H, m, $-\text{CH}$); 3.63 (2H, d, $-\text{CH}_2$); 4.145 (2H, d, $-\text{CH}_2$); 6.79 (2H, t, $-\text{ArH}$); 7.18 (2H, t, $-\text{ArH}$); 10.73-11.04 (2H, b, $-\text{ArOH}$) (**Figure 2, 2a** and **2b**).

Synthesis of the complex: 0.5 mmol (0.166gm) of the ligand was refluxed with 1 mmol (0.1 gm) TEA in MeOH for 10 minutes. It was then cooled to room temperature. A solution of $\text{VO}(\text{acac})_2$ (0.5 mmol, 0.132gm) in MeOH was added to the previous ligand solution and the resulting mixture was refluxed for 3 hours. The intense brown solution was cooled to room temperature and the initial slurry was filtered off and kept in rack for slow evaporation. Dark brown colored rod shaped crystals were isolated with 3 days. Single crystal X-ray diffraction was unsuccessful as the crystals were very thin in nature. However ^{51}V NMR, IR, UV-Vis and HRMS studies of the complex were performed for characterization and prediction about the probable structure. Yield ~ 78%. Molecular formula of the complex is $\text{C}_{36}\text{H}_{57}\text{N}_2\text{O}_4\text{V}$ (MW 632, ESI- Ms^+ appears at 632.2501, **Figure 3**). FTIR (KBr disc; cm^{-1}) for $\text{V}=\text{O}$ appears at $\nu=975$ (**Figure 4**); ^{51}V NMR (in CDCl_3 , 500 MHz) δ (ppm) -546.12 (**Figure 5**).

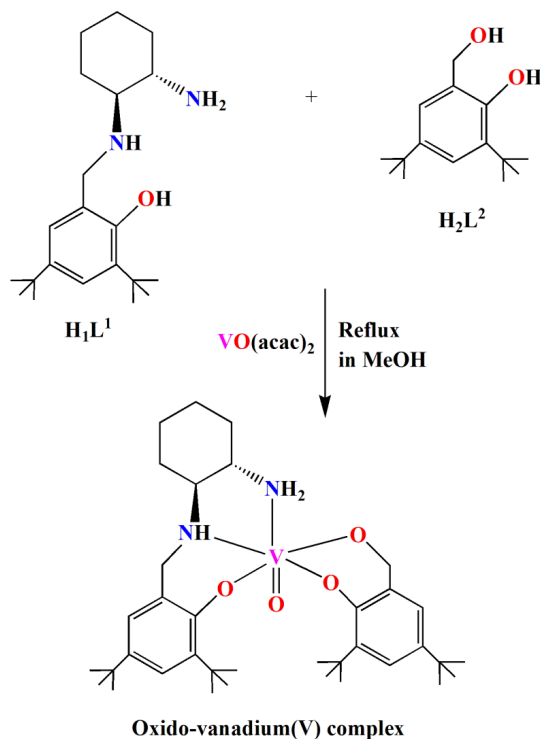
RESULTS AND DISCUSSIONS

Probable structure of the complex

Before discussing about the probable structure of the complex we need to focus on the ligand. From the ESI- Ms^+ and ^1H NMR studies it is clear that the ligand contains mixed fragments, having amine-phenol part (H_1L^1 , MW 332, ESI- Ms^+ appears at 355.61) and phenol based part (H_2L^2 , MW 236, ESI- Ms^+ appears at 236.80) (**Scheme 2**). From the ^1H NMR it is obvious that only one amine ($-\text{NH}_2$) group is involved to form the Mannich base ($-\text{NH}$ appears at δ 2.11-2.29 ppm, **Figure 2** and **2a**) and the other one remains unchanged ($-\text{NH}_2$ appears at δ 2.01 ppm as *doublet*, **Figure 2** and **2a**). Moreover, appearance of $-\text{CH}_2\text{OH}$ (1H) at δ 1.93 ppm as *triplet* (**Figure 2** and **2a**) and $-\text{CH}_2\text{OH}$ (2H) at δ 4.145 ppm as *doublet* (**Figure 2** and **2b**) clearly indicate the existence of the phenol based fragment H_2L^2 . Signals of the thirty six $-\text{CH}_3$ protons appear at different regions (δ 1.25-1.40 ppm), which also confirm the presence of two different ligand fragments H_1L^1 and H_2L^2 .



Straight forwards reaction of the mixed ligand fragments with the metal precursor, $\text{VO}(\text{acac})_2$ produces mononuclear oxido-vanadium(V) complex, $\text{VO}(\text{L}^1)(\text{L}^2)$ having molecular formula $\text{C}_{36}\text{H}_{57}\text{N}_2\text{O}_4\text{V}$ (MW 632) (**Scheme 3**).



Scheme 3: Probable structure of the oxido-vanadium(V) complex prepared from H_1L^1 and H_2L^2

Presence of $\text{V}=\text{O}$ bond is confirmed from IR study ($\nu = 975 \text{ cm}^{-1}$) and the signal from ^{51}V NMR at $\delta -546.12 \text{ ppm}$ confirms the oxidation state of vanadium as +5. Finally ESI- Ms^+ of the complex at 632.25 (**Figure 3**) confirms the hexa-coordination of the metal. Hence the complex probably possesses distorted octahedral geometry.

Electrochemical Study

The electrochemical behaviour of complex is studied by cyclic voltammetry in the range +0.60 to +0.1V at a scan rate 100 mVs^{-1} in acetonitrile at platinum electrode versus SCE using tetrabutyl-ammonium perchlorate (TBAPC) as supporting electrolyte. The cyclic voltammogram for the complex is found (**Figure 6**) to be quasi-reversible in nature with $E_{1/2} = 0.362 \text{ V}$ ($E_{pa} = 0.447 \text{ V}$, $E_{pc} = 0.276 \text{ V}$, $\Delta E = 0.171 \text{ V}$). Controlled coulometric experiment shows that the wave

is one electron transfer process. Since the phenolate ligand could not be reduced in this potential range [23], we assign them as metal centered reduction potentials for the VO^{3+}/VO^{2+} couple.

Electronic spectra

The UV-Vis spectrum of the complex shows one peak at 525 nm ($\epsilon/M^{-1}cm^{-1} = 3700$). The spectrum may be attributed to the ligand (Phenoxo) to metal [V(V)] charge transfer (LMCT) bands (Figure 7).

D. Figures and Tables

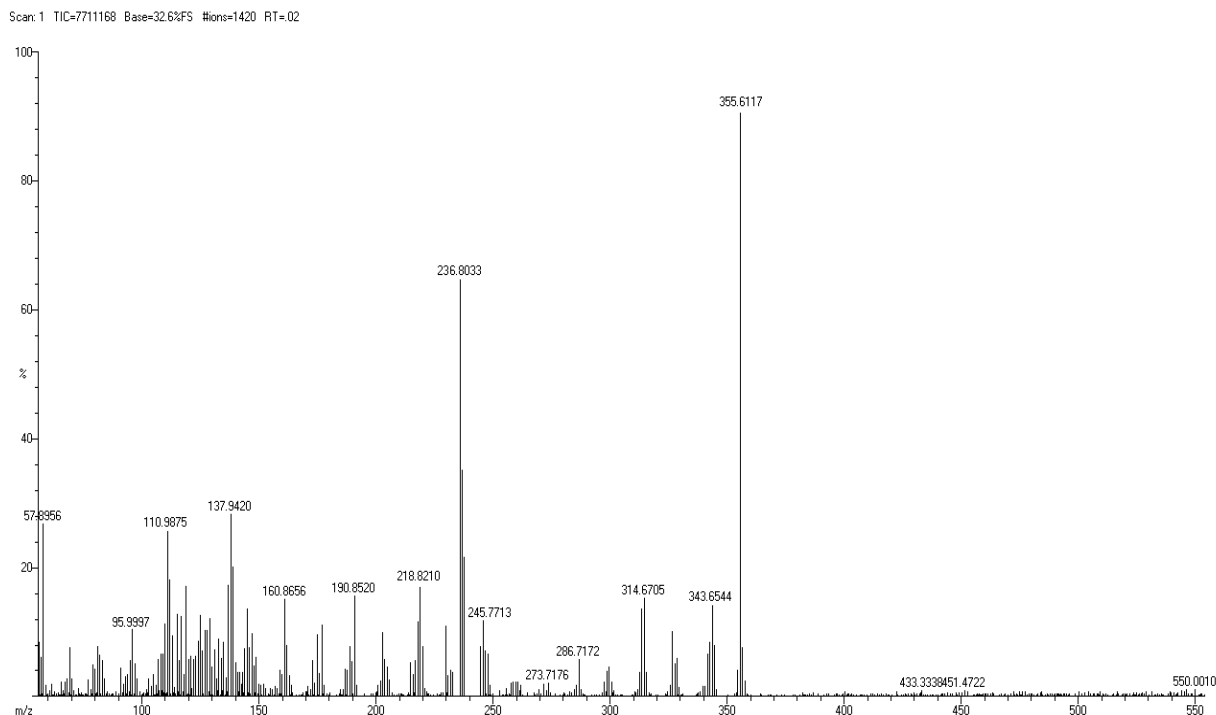


Figure 1: ESI- Ms^+ of the ligand

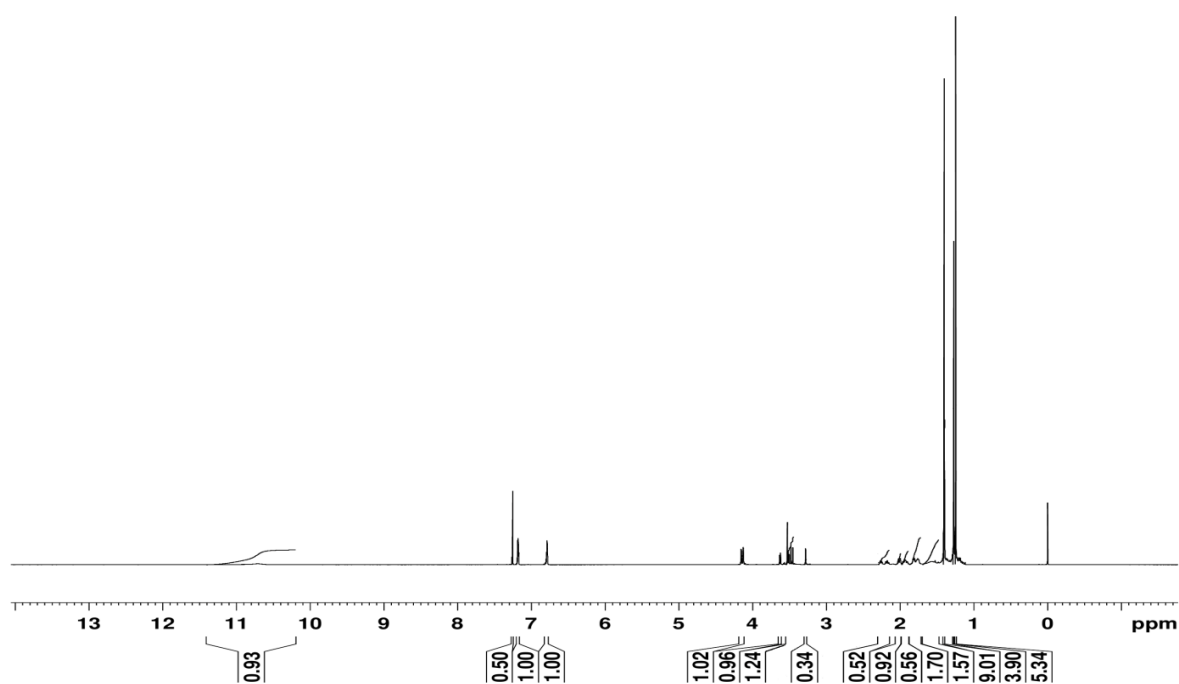


Figure 2: 1H NMR spectrum of the ligand

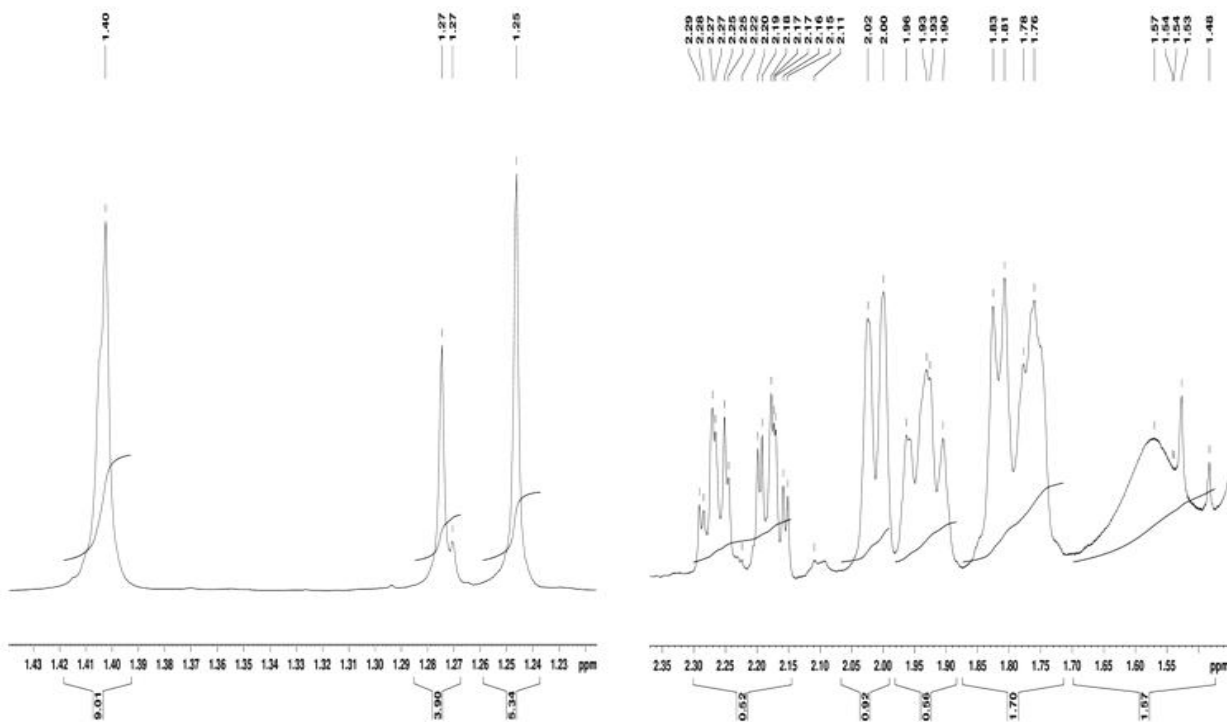


Figure 2a: ^1H NMR spectrum of the ligand

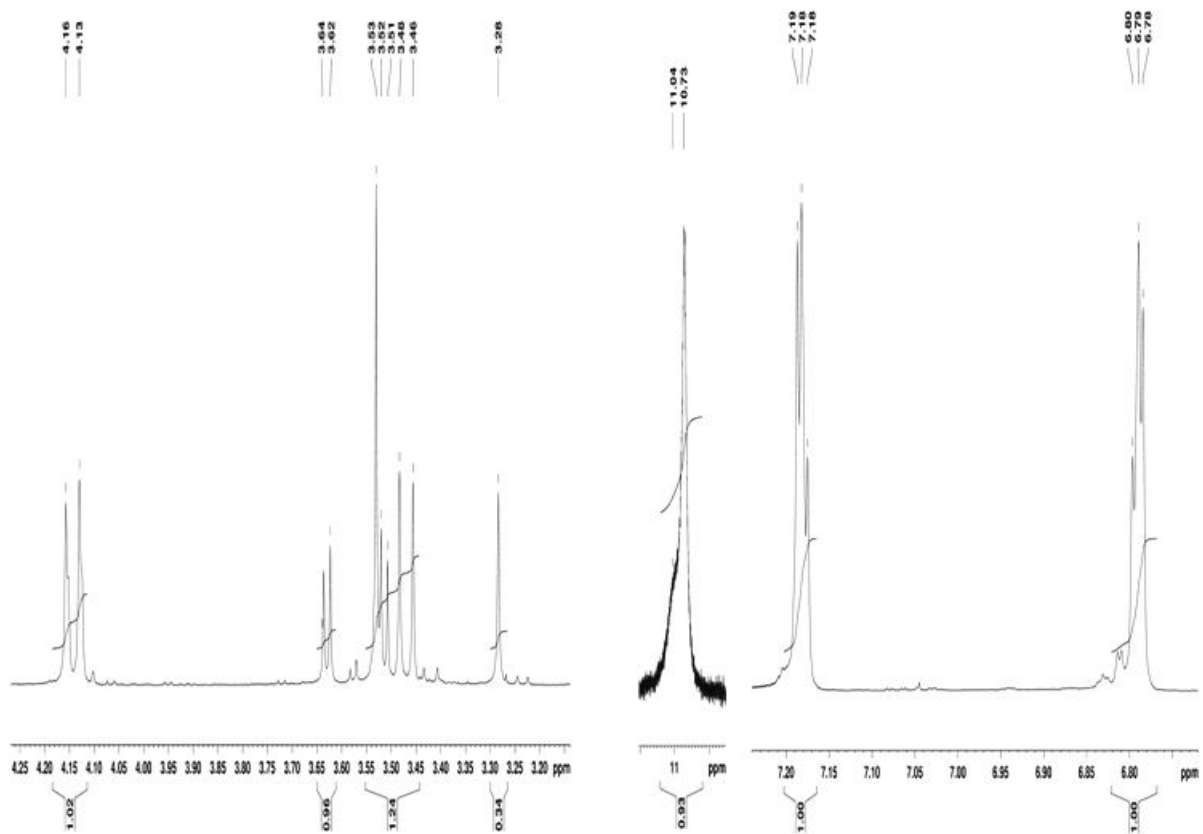


Figure 2b: ^1H NMR spectrum of the ligand

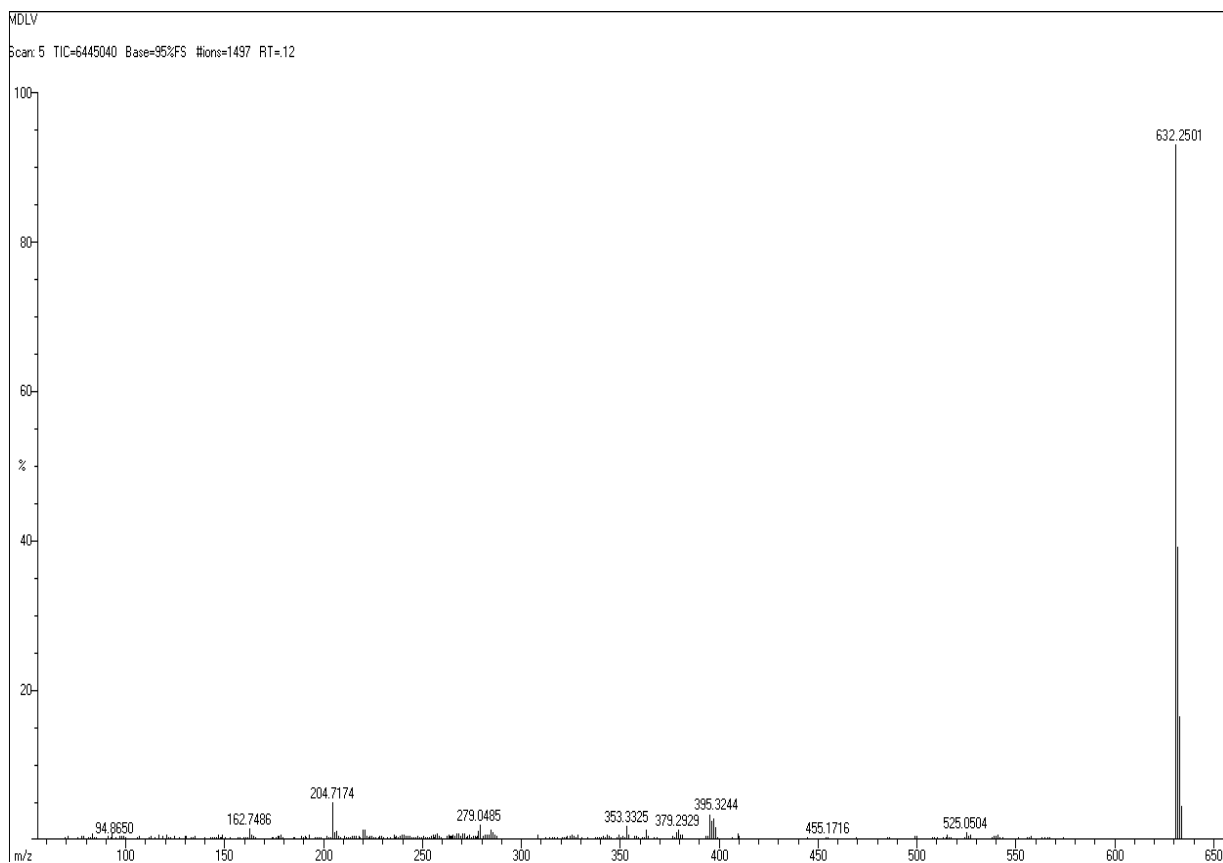


Figure 3: ESI- M_s^+ of the complex

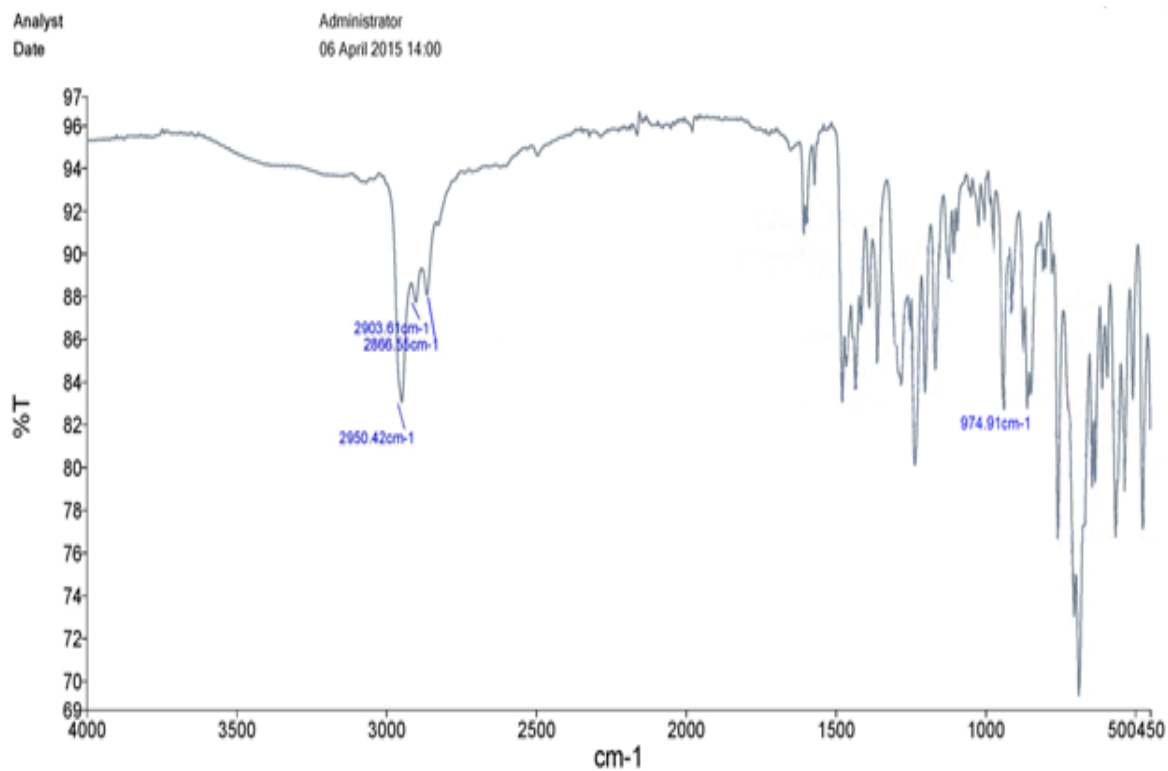


Figure 4: IR study of the complex

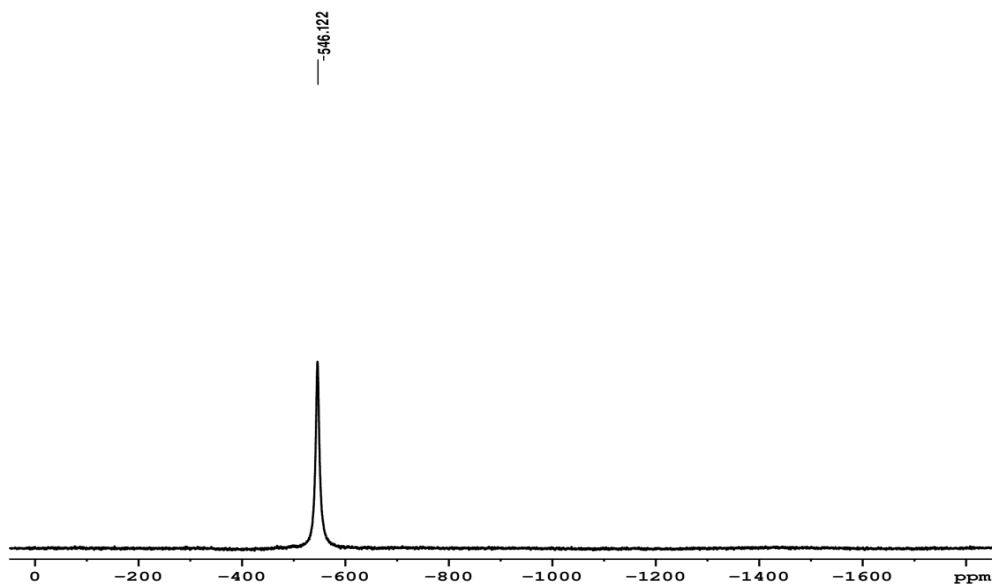


Figure 5: ^{51}V NMR of the complex

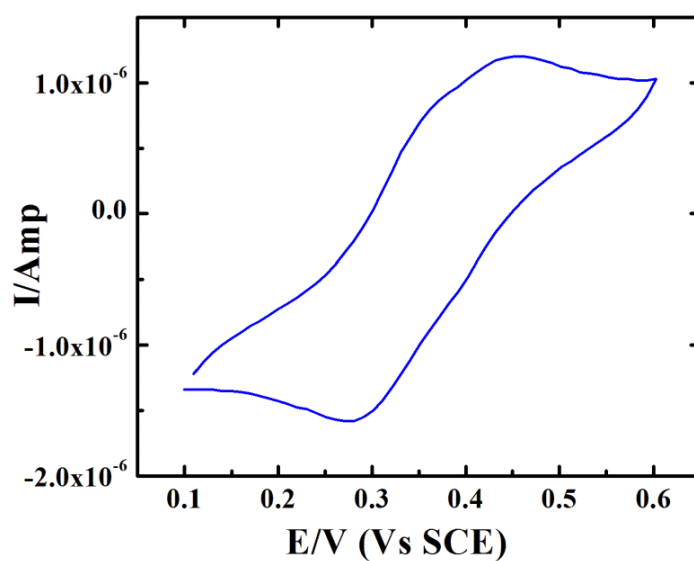


Figure 6: CV of complex in MeCN solvent at 25°C , $[\text{C}] = 1.0 \text{ mM}$; $[\text{TBAPC}] = 0.10 \text{ M}$, scan rate = 100 mV s^{-1}

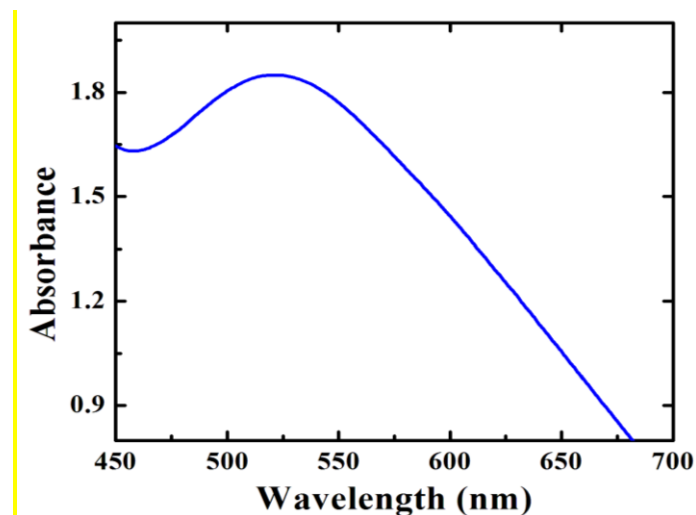


Figure 7: Electronic spectra of the complex in MeCN solvent at 25°C , $[\text{C}] = 5 \times 10^{-4} \text{ M}$

CONCLUSION

We have synthesized a mononuclear oxido-vanadium(V) complex with two ligand fragments (H_1L^1 and H_2L^2) having nitrogen and oxygen donor atoms and characterized spectroscopically. 1H NMR and ESI- Ms^+ confirm the existence of the two separate ligand fragments which bind with the vanadium centre to form the complex $VO(L^1)(L^2)$. FTIR, ^{51}V NMR and ESI- Ms^+ studies suggest the hexa-coordinating binding mode of the vanadium(V) centre.

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