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Synthesis and characterization of vanadium (IV) and (V) complexes with 2,2'-bipyridine ligand

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Abstract

Four vanadyl VO(II) and vanadate V(V) with 2,2'-bipyridine complexes were synthesized. Different techniques have been used to characterize the complexes such as FT-IR, UV-Vis., mass, ¹H-NMR spectroscopy and magnetic susceptibility. The acquired data show that 2,2'-bipyridine is bound through the nitrogen atoms of the two rings.

Mass spectroscopic data showed that the complexes (1-3) were dinuclear while the complex (4) was mononuclear. The FT-IR, UV-Vis and ¹H-NMR data confirmed the proposed structures of the complexes square pyramidal geometry structures for 1-2 complexes and octahedral geometry structures for 3-4 complexes. All complexes are stable, non-hygroscopic and ionic except the complex (1).

Keywords: VO(II) complexes, V(V) complexes, 2, 2'-bipyridine, spectroscopy, nitrogen donor ligands.

Introduction

Vanadium is a prevalent element in the environment and is present in biological systems with low levels¹. Vanadium can be found in different oxidation states (II), (III), (IV) and (V). The existed oxidation states of abundant vanadium forms under environmental conditions are (III), (IV) and (V)². Vanadium (III) and (IV) are not stable under physiological conditions and in the presence of oxygen, but vanadium (IV) can be easily oxidized into V(V) and its species are found as vanadate anions³. The available forms of vanadium in the oxidation state (V) are derived from vanadate (VO₃⁻) while in the oxidation state (IV) is derived from the vanadyl ion (VO²⁺)⁴.

The solubility of vanadium varies in different complexes where vanadates (V) are soluble easily while vanadyl hydroxide is insoluble thereby it precipitates in the form VO(OH)₂⁵. Vanadium resembles phosphate structurally besides the flexible coordination chemistry of vanadate (V), so it can participate in the reactions of phosphate. Vanadium inhibits and activates some proteins and enzymes and similar actions have been suggested for [VO(OH)₃]⁻ similar to vanadate⁶. Vanadium complexes paid attention towards the exploitation of diversity of the oxidation states and flexibility of change in the coordination sphere around the metal center⁷.

In addition the less sensitivity of vanadium against moisture than other metals, its available complexes are cheap, interconvertible is easy for vanadium oxidation states where the oxidations occur by green oxidants like air, H₂O₂ and O₂ and nature of vanadium center as lewis acid⁸ encourages the researchers to synthesize novel complexes which can be used in different fields. The moieties of vanadium such as [VO]⁺, [VO]²⁺, [V₂O₄]²⁺, [VO]³⁺ and [V₂O₃]ⁿ⁺ where n= 2-4 show strong affinity with N and O donor ligands and the electronic field of metal center in the produced complexes can be controlled by ligands with different electron-withdrawing or donating groups⁹.

Organic chelation had been used to promote the pharmacological actions of vanadium species due to the poor absorption in gastrointestinal tract so chelation would enhance the absorption and lipophilicity and decrease the required dose of vanadium to demonstrate its effects. Ligands with multiple donor atoms such as N, O or S attracted the scientific interest due to their therapeutic applications¹⁰. V^{VO}₂-complexes produce binuclear system under aerobic conditions not only with tridentates ligands but also with less steric interference ligands which may be crystallized in monomeric and binuclear forms¹¹. Dinuclear vanadyl VO(II) complexes had been synthesized and employed in catalytic processes¹².

Vanadium complexes with organic ligands have N, O and S as functional groups have been promised *in vitro* and *in vivo* trials of treatment many cases such as diabetes, tumors, cardiovascular dysfunction and other cases¹³. As soon as the entrance of VO(II) in the bloodstream it oxidizes into (H₂VO₄⁻) and coordinates with serum proteins albumin preferably transferrin, thus it could be allowed for the cellular uptake¹³. In this study, four complexes of vanadyl VO(II) and vanadate V(V) with 2,2'-bipyridine ligand (L) were synthesized in two molar ratio 1:1 and 1:2 (M:L) to obtain binary and ternary complexes characterized by different techniques. The main aim from preparation of these complexes is using chemotherapeutic agents and/or insulin mimic compounds in future studies. The structure of 2,2'-bipyridine ligand (L) is illustrated in fig.1.

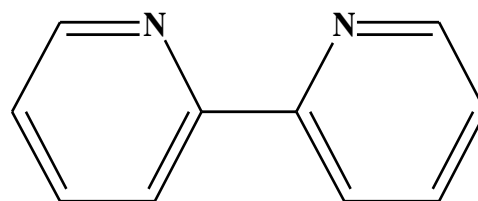


Fig. 1: Structure of 2,2'-bipyridine ligand (L).

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Material and Methods

Materials: Chemicals used in this work were of the highest purity: 2,2'-bipyridine (L) (95%) used without any more purification and was purchased from Sigma Aldrich. Vanadyl VO(II) sulfate pentahydrate (VOSO₄.5H₂O) and vanadium (V) pentoxide (V₂O₅) were purchased from Fluka. All solvents were of analytical grade.

Measurements: Infrared measurements of the complexes as KBr pellets were carried out using a Shimadzu (FT-IR)-8400S spectrophotometer in the range 400-4000 cm⁻¹ at Ibn Sina Center, College of Science for Women, Baghdad University. Mass spectrometry measurements were carried out using GCMS-QP1000EX Shimadzu. ¹H-NMR was recorded using ultra shield Bruker 300 MHNMR at Aksaray University for Scientific and Technical Research and Application Center. The magnetic susceptibility measurements of the synthesized complexes were carried out in the solid state using a Balance Magnetic susceptibility Model (MSB-MKI) at Chemistry Department, College of Science, Al-Nahrain University.

UV-Vis spectra were recorded in 1.0 cm path length quartz cell by using a UV-Vis. spectrophotometer type T80 with 10⁻³ M in DMSO at College of Pharmaceutic, Al-Anbar University. Conductivity measurements were carried out in 10⁻³ M solutions in DMSO by using Philips PW digital conductivity meter at College of Science, Baghdad University.

Synthesis of vanadyl VO(II) and vanadate (V) complexes

Synthesis of [VO(H₂O)₂(L)]₂.2H₂O complex (1) and [VO(L)(H₂O)₂(H₂O)]₂.4H₂O complex (2): 0.156 g, 1.0 mmole and 0.312 g, 2.0 mmole of L were dissolved in 20 ml of ethanol and added dropwise to 0.253 g, 1.0 mmole of VOSO₄.5H₂O in 10 ml of distilled water in 1:1 and 1:2 (M:L)

molar ratio respectively. The mixtures of complexes had been refluxed for 4 hours under constant stirring. The products were filtered off, washed with water, ethanol, diethyl ether and dried in dessicator for 24 hours. The obtained light green precipitates for complex (1) have yield: 68%, m.p. > 300 °C and yellow-green precipitates for complex (2) yield: 51%, m.p. > 300 °C.

Synthesis of [VO₂(H₂O)₂L]₂.3/2H₂O complex (3) and [VO₂(L)₂(H₂O)].H₂O complex (4): 0.312 g, 2.0 mmole of L was dissolved in 20 ml of ethanol. The solutions of V₂O₅ prepared by dissolving 0.182 g, 2.0 mmole of V₂O₅ in 50 ml distilled water and then 3 ml of NH₄OH in 1M concentration have been added and 0.09 g, 1.0 mmole of V₂O₅ in 30 ml distilled water and then 3 ml of NH₄OH in 1M concentration have been added. The mixtures have been mixed in 1:1 and 1:2 M:L molar ratio and refluxed for four hours with constant stirring. The products were filtered off, washed with water, ethanol, diethyl ether and dried in dessicator for 24 hours. The obtained light green precipitates for complex (3) have yield: 52%, m.p. > 300 °C and yellow-green precipitates for complex (4) have yield: 50%, m.p. = 210°C.

Results and Discussion

The complexes were obtained upon the reaction between VO(II) and (V) with 2,2'-bipyridine in two molar ratios 1:1 and 1:2 (M:L). The physical properties of the complexes are given in table 1. The molar conductivity indicated that all the complexes are ionic except complex 1. This is in agreement with the fact that the value of conductivity for electrolyte is above 50 Ω⁻¹.cm².mol⁻¹ and for non-electrolyte is below that number¹⁴. The complexes show partial solubility in some solvents like water, ethanol, acetone and the complexes (1-2) are not soluble in chloroform while the complexes (3-4) are partially soluble.

Table 1
The analytical and physical properties for complexes (1-4)

Complex	M.wt g/mol	Color	$\lambda_{m}/\Omega^{-1} \text{ cm}^2.\text{mol}^{-1}$	μ_{eff} B.M.	UV-Vis absorption peaks/nm	Assignment
[VO (H ₂ O) ₂ L] ₂ .2H ₂ O (1)	554.34	Light green	115	1.04	220-280 410-460 800	Intra ligand($\pi \rightarrow \pi^*$) Intra ligand($n \rightarrow \pi^*$) LMCT d-d electronic transition (${}^2B_{2g} \rightarrow E$)
[VO(L)(H ₂ O) ₂ (H ₂ O)] ₂ .4H ₂ O (2)	572.39	Yellow green	27.7	1.78	225-270 445-490 810	Intra ligand($\pi \rightarrow \pi^*$) Intra ligand($n \rightarrow \pi^*$) LMCT d-d electronic transition (${}^2B_{2g} \rightarrow E$)
[VO ₂ (H ₂ O) ₂ L] ₂ .3/2H ₂ O (3)	577.31	Light green	29.8		225-275 440-530	Intra ligand($\pi \rightarrow \pi^*$) Intra ligand($n \rightarrow \pi^*$) LMCT
[VO ₂ (L) ₂ (H ₂ O)].H ₂ O (4)	413.32	Yellow green	22.5		215-260 395-425	Intra ligand($\pi \rightarrow \pi^*$) Intra ligand($n \rightarrow \pi^*$) LMCT

FT-IR spectra: The FT-IR data of the complexes are shown in table 2. The obtained data are compared with the spectrum of the free ligand to evaluate the changes in the vibration frequencies in the coordination sites. The spectrum of the ligand (L) showed bands at 1578, 1454 and 1250 cm^{-1} due to $\nu(\text{C}=\text{N})$, ring stretching¹⁵. In the spectra of VO(II) complexes the previous bands were shifted to other frequencies. This indicates the association of N atoms of rings in the coordination of these complexes. This is also observed in the spectra of vanadate (V) complexes. The spectra of complexes (1-2) showed new additional bands at 980-952 cm^{-1} assigned to the $\nu(\text{V}=\text{O})$ stretching mode^{16,17}

while the spectra of (3-4) complexes showed bands at (968-914 cm^{-1}) assigned to the $\nu(\text{O}=\text{V}=\text{O})$ stretching.

It was found that the V=O stretching vibrations in oxocomplexes of vanadyl, when compared to oxocomplexes of vanadate, are placed at higher frequencies¹⁸. The bands in the range 417-463 cm^{-1} suggested to M-N bond¹⁹. The water molecules were responsible for appearance broad bands at the range 3410- 3464 cm^{-1} in the spectra of all complexes¹⁷. The FT-IR spectrum of complex (1) present in figure 2 represented example.

Table 2
FT-IR data cm^{-1} of 2,2'-bipyridine ligand, VO(II) and V(V) complexes.

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{V}=\text{O}),$ $\nu(\text{O}=\text{V}=\text{O})$	$\nu(\text{M}-\text{N})$
2,2' - bipyridine (L)		1578 1454 1250		
$[\text{VO}(\text{H}_2\text{O})_2(\text{L})]_2 \cdot 2\text{H}_2\text{O}$ (1)	3421	1605 1447 1319	980	463
$[\text{VO}(\text{L})(\text{L})]_2$ (2)	3410	1601 1443 1312	952	417
$[\text{VO}_2(\text{H}_2\text{O})_2(\text{L})]_2 \cdot 3/2\text{H}_2\text{O}$ (3)	3441	1601 1443 1312	968	444
$[\text{VO}_2(\text{L})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (4)	3441	1601 1443 1312	914	428

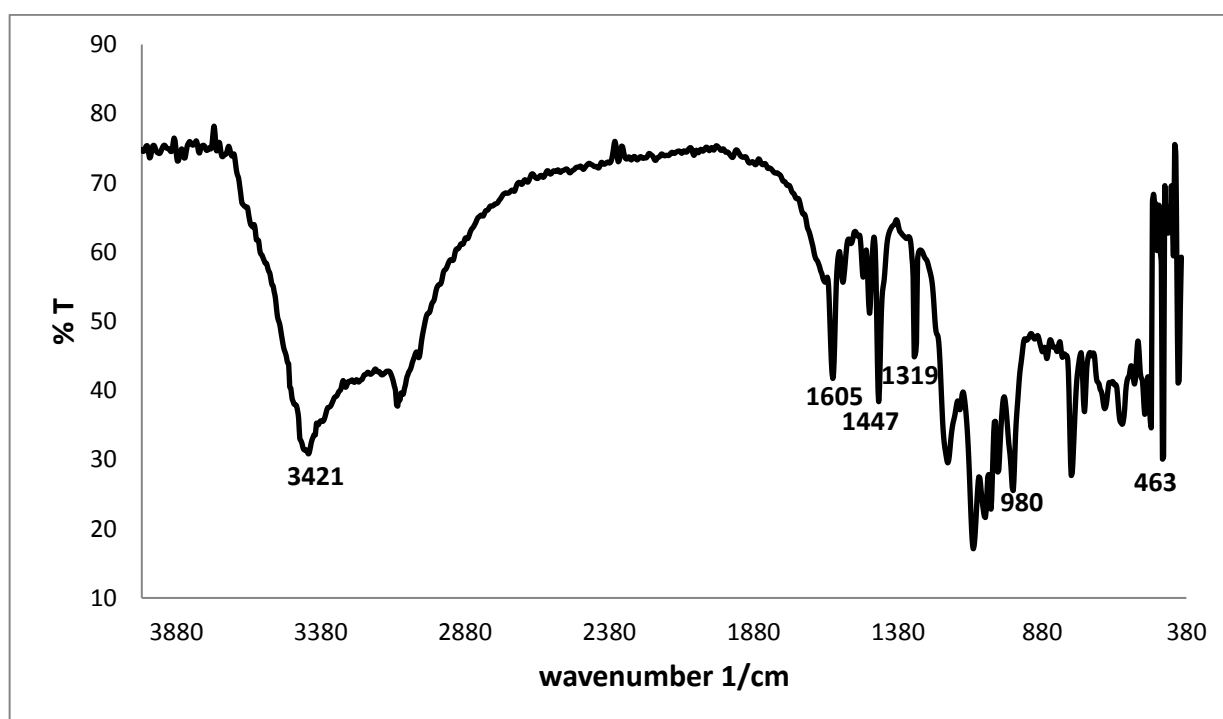


Fig. 2: FT-IR spectrum of the complex (1)

Mass spectral analysis: The mass spectral data of the vanadyl VO(II) and vanadate V(V) complexes exhibited the main mass fragmentation peaks which are tabulated in table 3. Mass spectrum of the complex (1) (molecular weight 554.34) gave molecular ion peaks [M] at $m/z = 551.22$, a peak at $m/z = 444.91$ assigned to (M-6H₂O), a peak at $m/z = 287.79$ assigned for (M-6H₂O, L) and a peak at $m/z = 156.90$ assigned for (M-6H₂O, 2L). The spectrum of complex (2) (molecular weight 572.39) gave molecular ion peaks [M⁺] at $m/z = 576.76$, a peak at $m/z = 522.77$ assigned for (M-3H₂O), a peak at $m/z = 466.67$ assigned for (M-6H₂O), a peak at $m/z = 444.81$ assigned for (M-7H₂O), a peak at $m/z = 286.78$ assigned for (M-7H₂O, L) and a peak at $m/z = 156.89$ assigned for (M-7H₂O, 2L).

The spectrum of complex (3) (molecular weight 577.31) gave molecular ion peaks [M] at $m/z = 576.72$, a peak at $m/z = 551.23$ assigned for (M-3/2H₂O), a peak at $m/z = 494.76$ assigned for (M-9/2H₂O), a peak at $m/z = 316.77$ assigned for (M-11/2 H₂O, L) and a peak at $m/z = 156.90$ assigned for (M-11/2 H₂O, 2L). The spectrum of complex (4) (molecular weight 413.32) gave molecular ion peaks [M] at $m/z = 417.72$, a peak at $m/z = 238.82$ assigned for (M-H₂O, L) and a peak at $m/z = 156.90$ assigned for (M-H₂O, 2L)²⁰. The mass spectrum data of complex (1) is present in figure 3 as a sample.

Table 3
Mass fragments data of VO(II) and V(V) complexes.

Complex	Molar mass	Important mass fragmentations (m/z) values
[VO (H ₂ O) ₂ (L)] ₂ .2H ₂ O (1)	554.34	551.22 [M ⁺³], 444.91(M-6H ₂ O), 287.79 (M-6H ₂ O, L), 156.90(M-6H ₂ O, 2L)
[VO(L) ₂] ₂ (2)	572.39	576.76[M ⁺⁴], 522.77(M-3H ₂ O), 466.67 (M-6H ₂ O), 444.81(M-7H ₂ O), 286.78(M-7H ₂ O, L), 156.89(M-7H ₂ O, 2L)
[VO ₂ (H ₂ O) ₂ L] ₂ .3/2H ₂ O (3)	577.31	576.72[M], 551.23 (M-3/2H ₂ O), 494.76(M-9/2H ₂ O), 316.77(M-11/2H ₂ O, L), 156.90(M-11/2H ₂ O, 2L)
[VO ₂ (L) ₂ (H ₂ O)].H ₂ O (4)	413.32	417.72[M ⁺⁴], 238.82(M-H ₂ O, L), 156.90(M-H ₂ O, 2L)

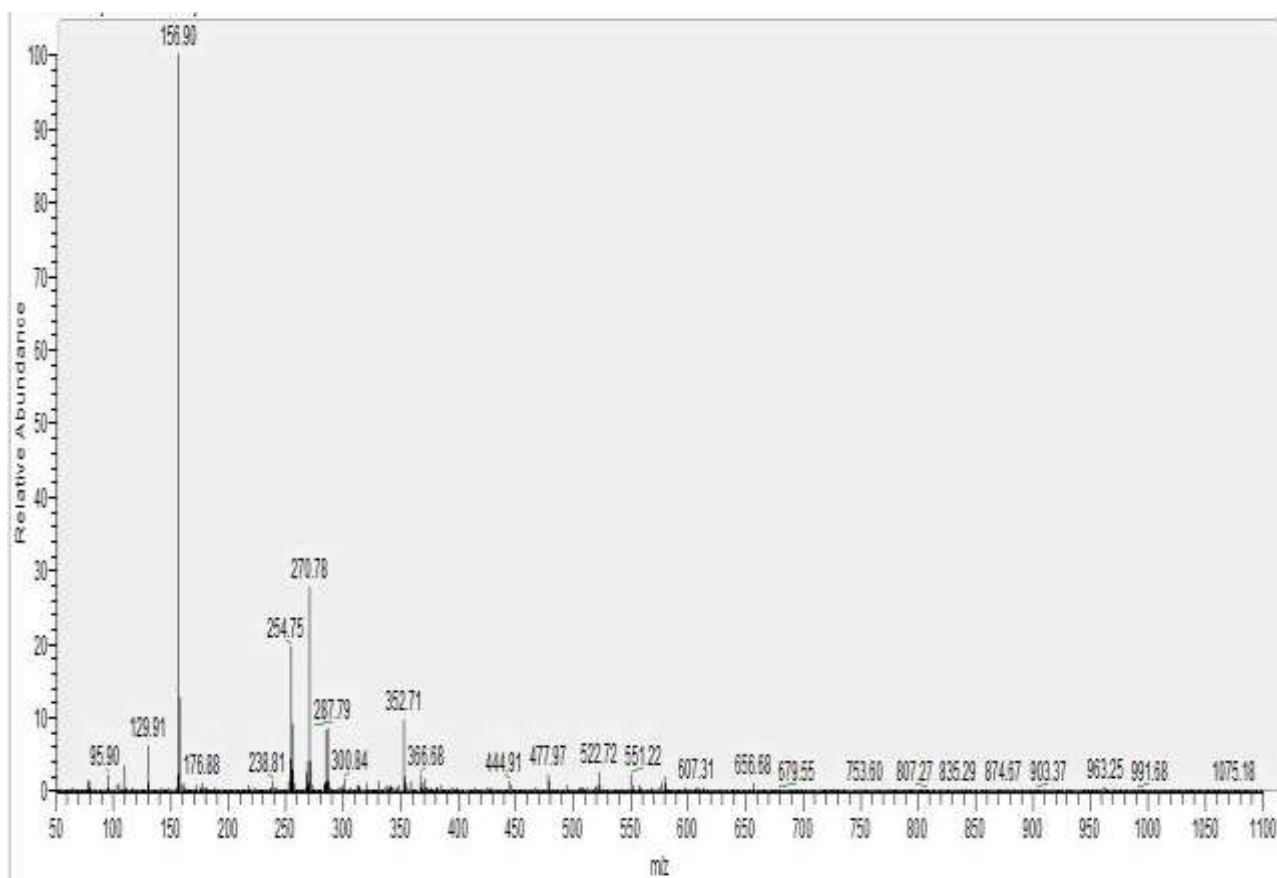


Fig. 3: The mass spectrum data of complex (1).

¹H-NMR spectra: The ¹H-NMR spectral data for the 2,2'-bipyridine ligand and the V(V) complexes in DMSO-d₆ are listed in table 4. The spectrum of the ligand showed multiple peaks at (7.3-8.5) ppm (integrated to 8 protons) which were attributed to the protons of the two rings of the ligand²¹. Signals for aromatic protons of the ligand and (3-4) complexes showed substantial upfield shifted at 7.5-9.2, 8H ppm for complex 3 and at 7.4-8.7, 8H ppm for complex 4 adjacent to the ligand nitrogen's in comparison to the free ligand which indicated the coordination between metal ions and the ligand through N atoms. The spectrum of 3-4 complexes showed new singlet bands at 3.3, 2H ppm assigned to one type of H₂O protons²². It is known that vanadyl VO(II) complexes are paramagnetic, therefore the ¹H-NMR spectra were not useful. The ¹H-NMR spectrum data is presented in figure 4.

Electronic spectra: The electronic spectral data of the DMSO solutions of the vanadyl VO(II) and vanadate V(V)

complexes were recorded in the range 200-1100 nm and shown in table 1. The vanadyl VO(II) complexes (1-2) showed absorption bands at the range (220-280 nm) assigned to the $\pi \rightarrow \pi^*$ transitions of ligand rings²³. The spectra also exhibited shoulders at the range (410-490 nm) assigned to merge between $n \rightarrow \pi^*$ and LMCT (ligand to metal charge transfer)^{24,25}. The peaks at the range (800-810 nm) were assigned to the d-d electronic transitions type ${}^2B_{2g} \rightarrow E (d_{xy} \rightarrow d_{xz})$ of the VO(II) complexes¹⁵. The spectra of vanadate V(V) complexes (3-4) showed bands at the range 215-275 nm which could be assigned to the $\pi \rightarrow \pi^*$ transitions and exhibited absorption bands in the range 395-530 nm assigned to merge between $n \rightarrow \pi^*$ and LMCT. Vanadium (V) complexes were not demonstrating d-d electronic transition which can be elucidated by the empty d orbital of V(V)²⁶. The UV-Vis spectrum of complex (1) is present in figure 5.

Table 4
¹H-NMR data of the 2,2'-bipyridine ligand and vanadate V(V) complexes in DMSO-d₆ solvent.

Compound	Assignment	δ (ppm)
2,2'-bipyridine	benzene ring protons	7.3-8.5
[VO ₂ (H ₂ O) ₂ L] ₂ .3/2H ₂ O (3)	benzene ring protons	7.5-9.2
	H ₂ O	3.3
[VO ₂ (H ₂ O) ₂ L] ₂ .3/2H ₂ O (3)	benzene ring protons	7.4-8.7
	H ₂ O	3.3

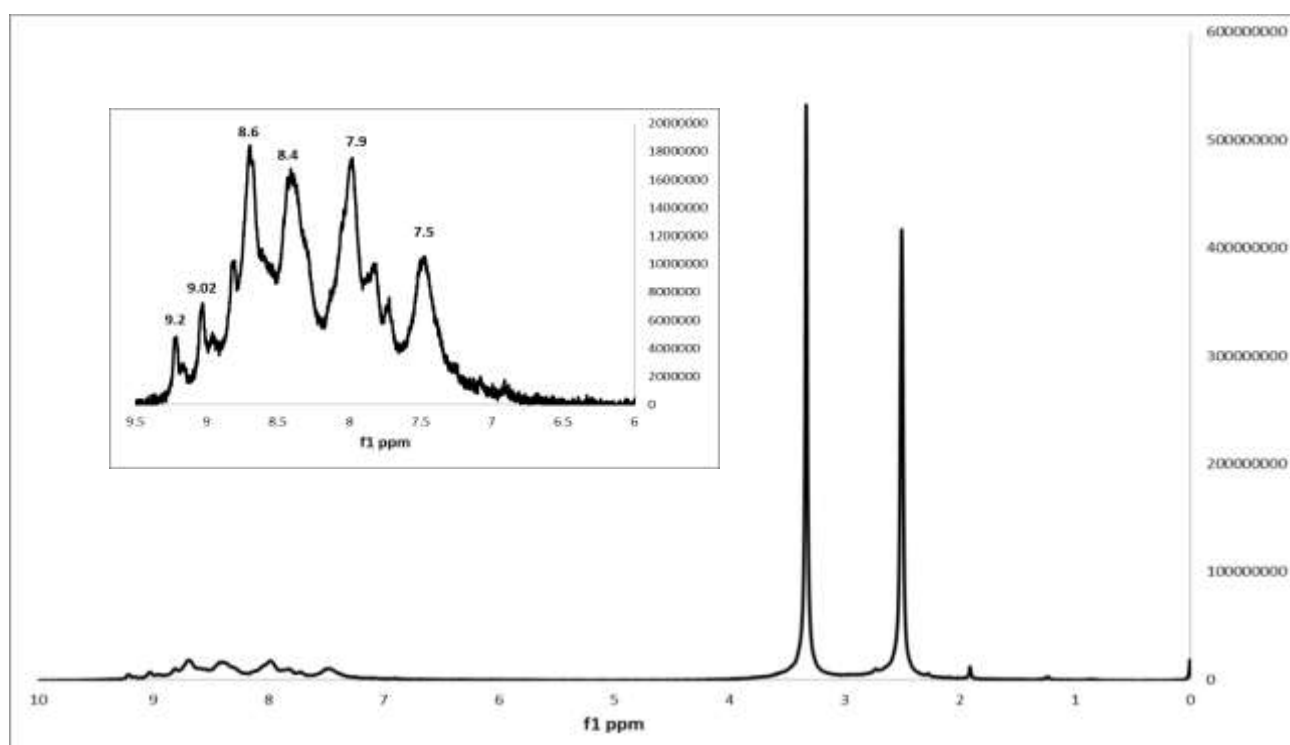


Fig. 4: The ¹H-NMR spectrum of complex (3) recorded in DMSO-d₆.

Magnetic susceptibility measurement: The magnetic moments of the vanadyl VO(II) complexes are listed in table1. The effective magnetic moments μ_{eff} of VO(II) complexes (1,2) had been located in the range 1.04-1.78 B.M. These values are close to the expected values of μ_{eff} of VO(II) paramagnetic complexes with d^1 configuration and considered subnormal that may be due to the strong

antiferromagnetic exchange which suggested the dimeric nature of these complexes²⁷. The vanadate (V) complexes (3,4) are diamagnetic which can be elucidated by the octahedral (d^0) geometry nature of V(V)²⁸. The proposed structures of the vanadyl VO(II) and vanadate V(V) complexes are depicted in figure 6.

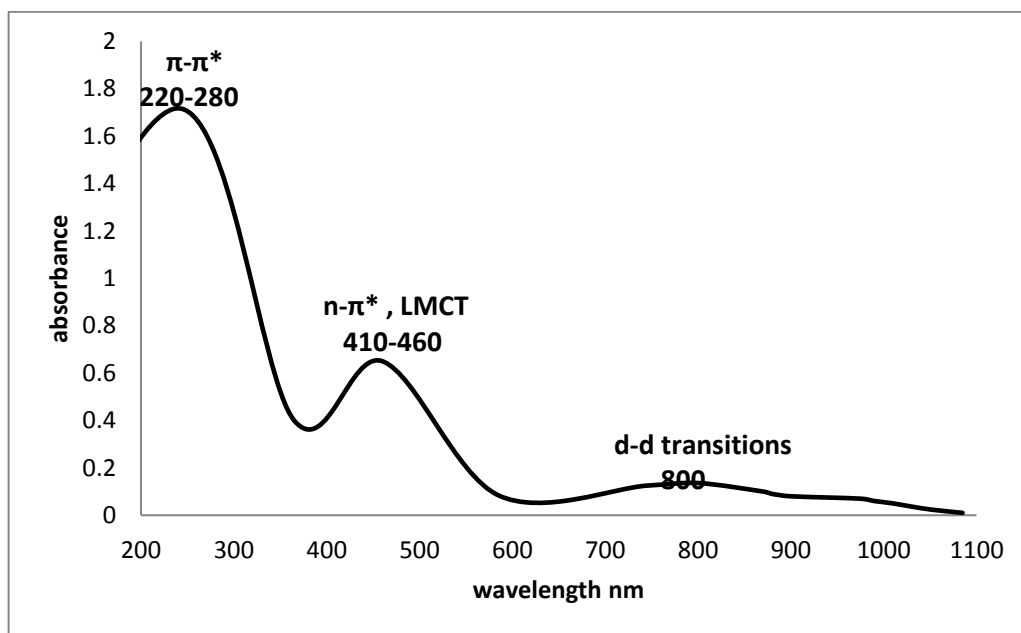


Fig. 5: The UV-Vis. spectrum of the complex (1).

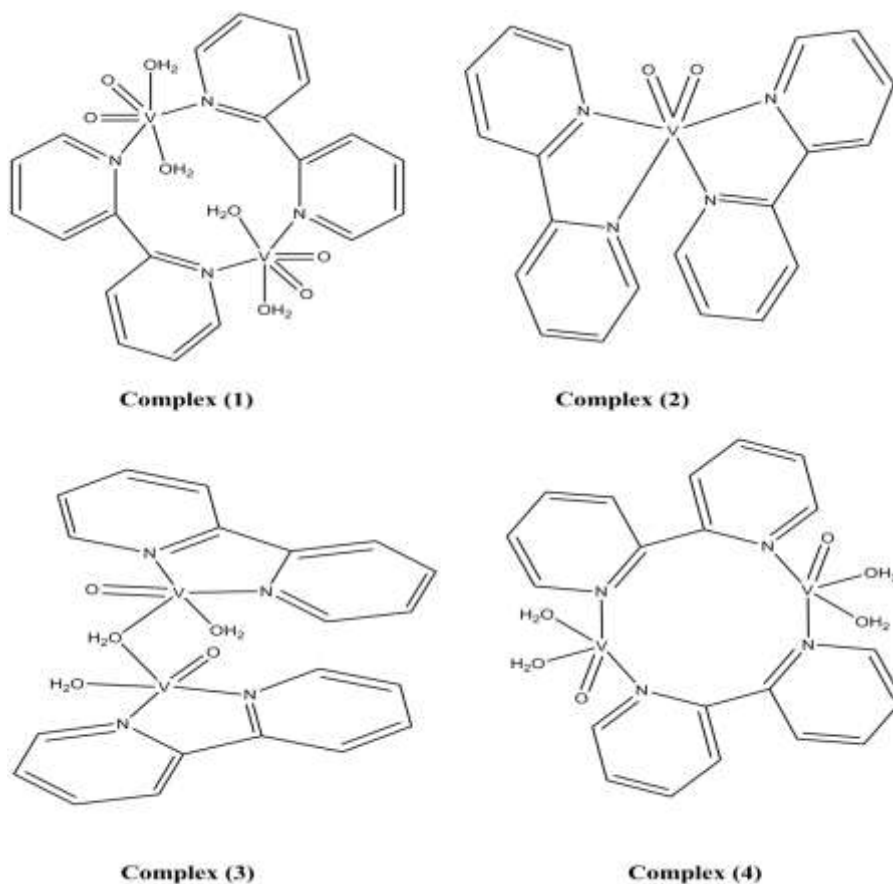
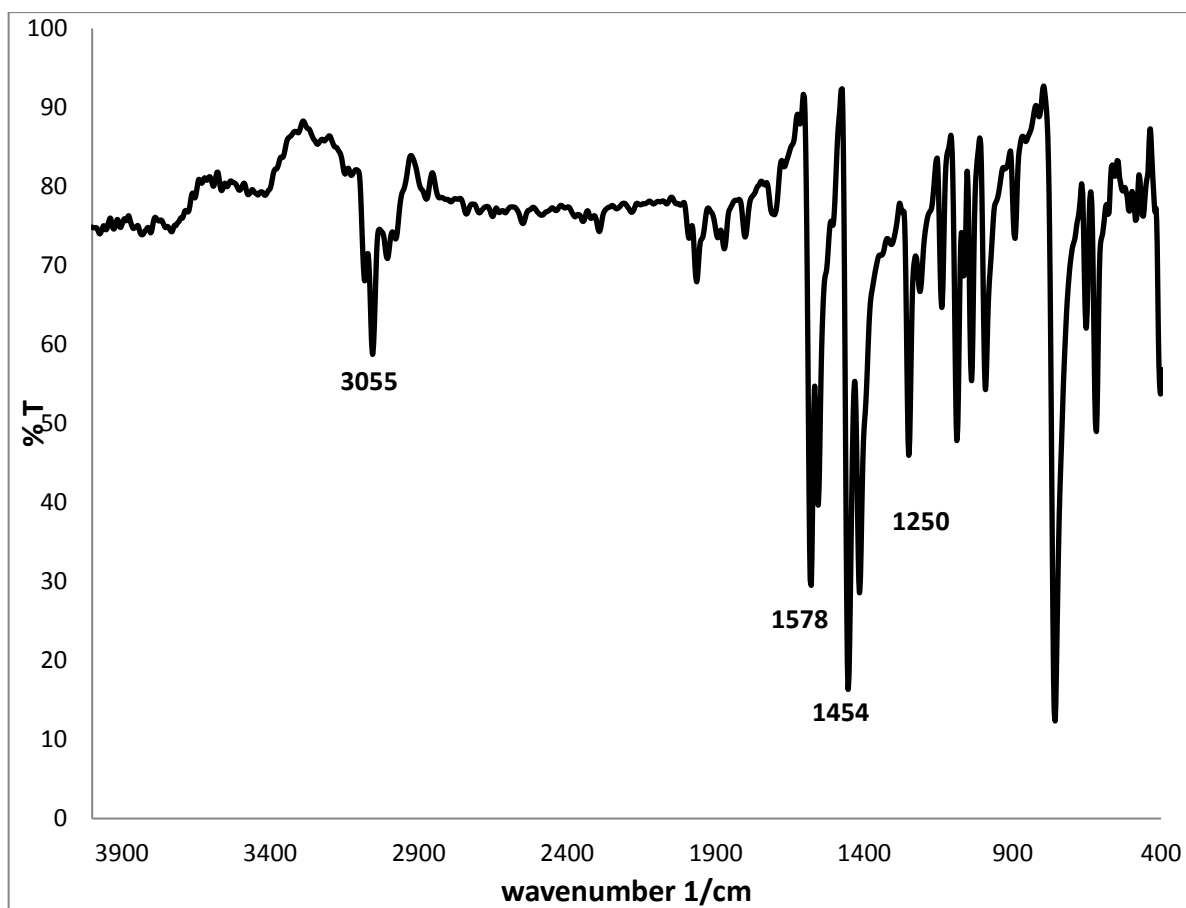
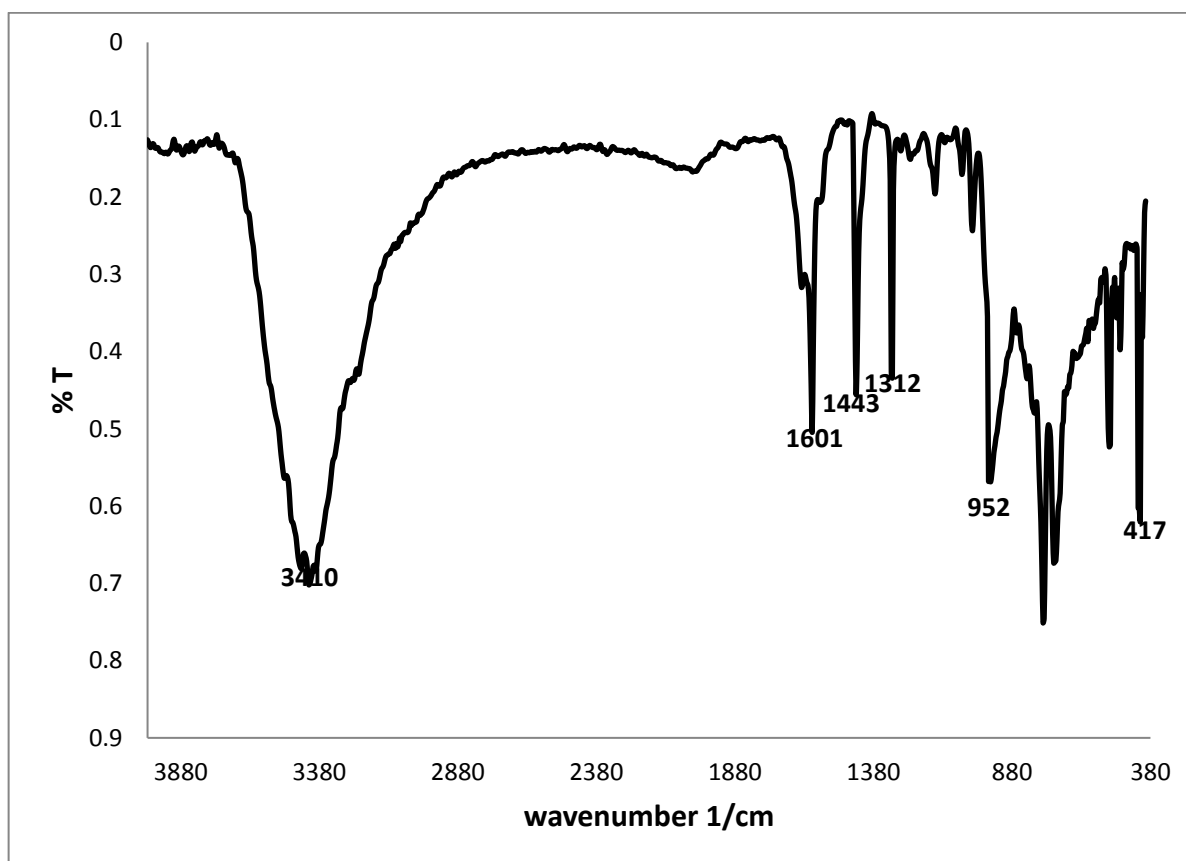


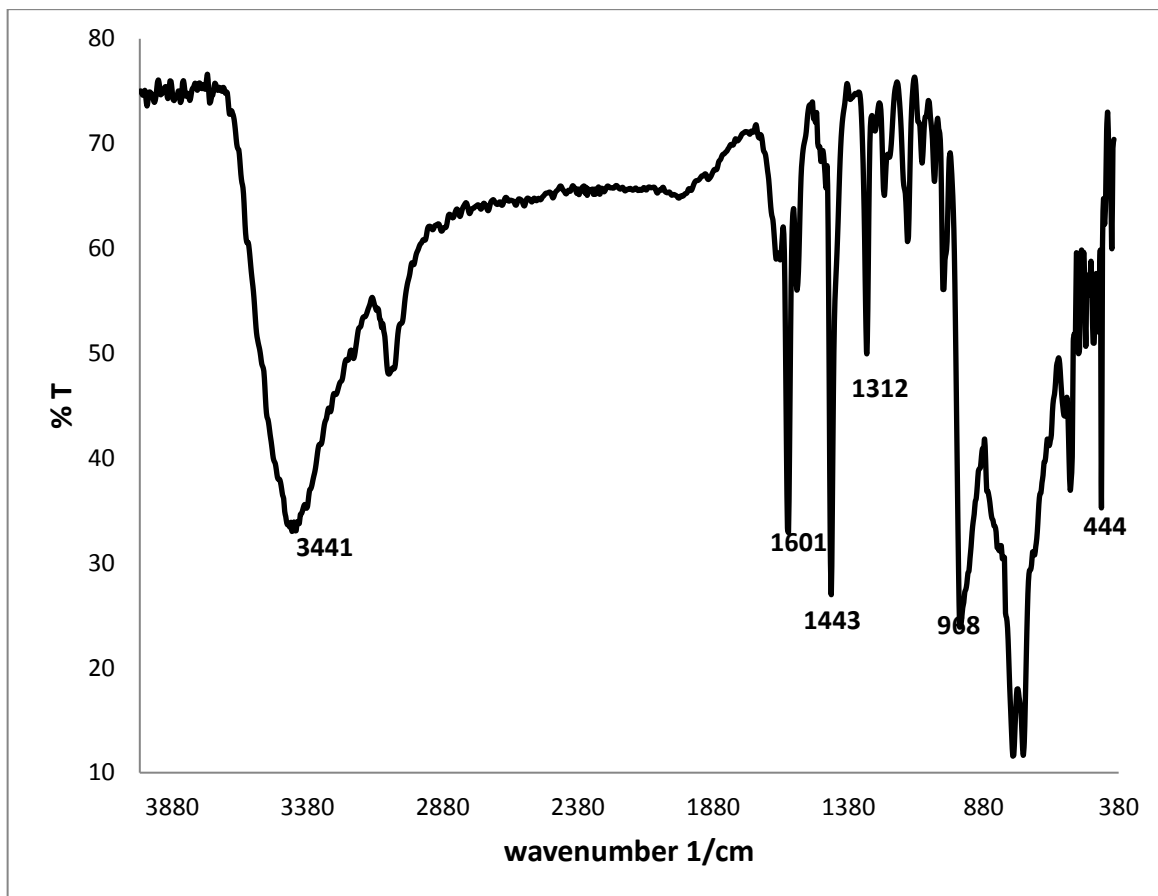
Fig. 6: The proposed structures of the VO(II) and V(V) complexes.



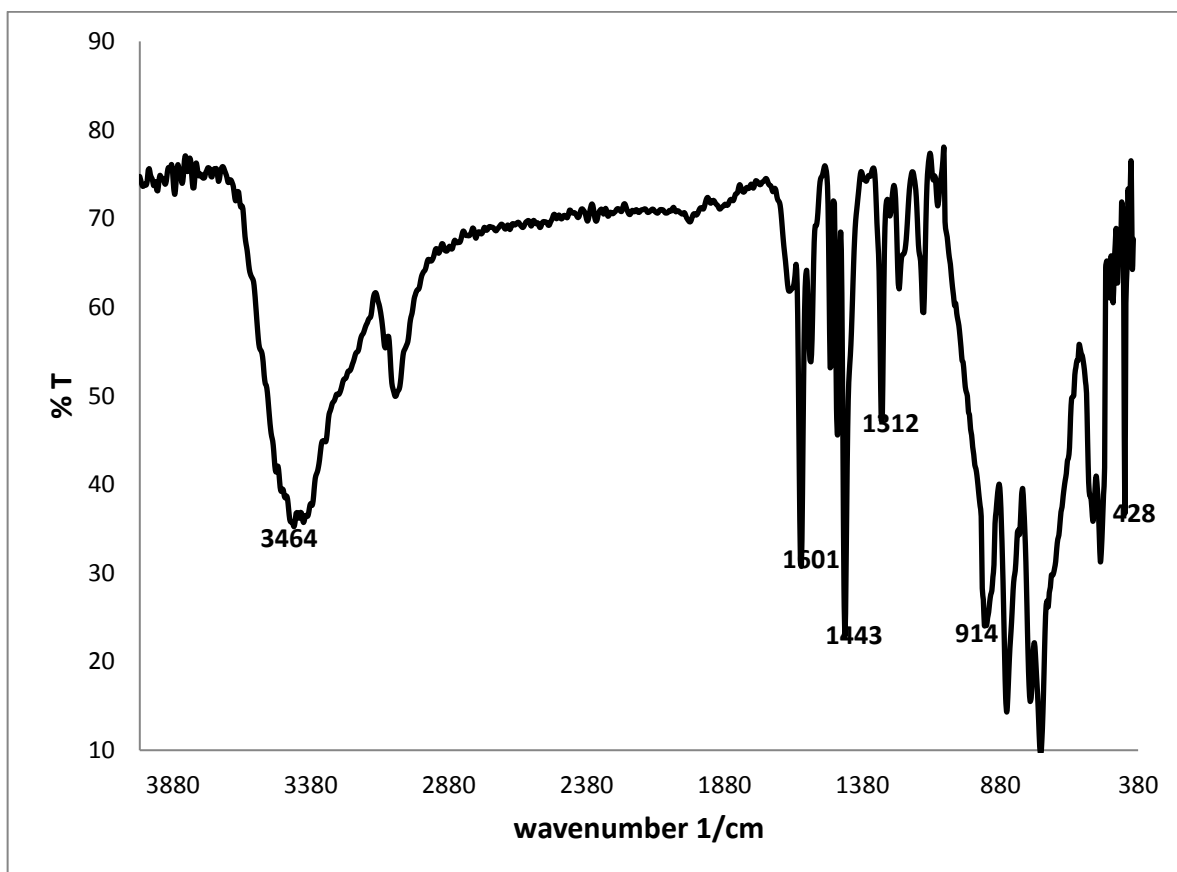
Supplementary fig. 1: The FT-IR spectrum of 2,2'-bipyridine (L).



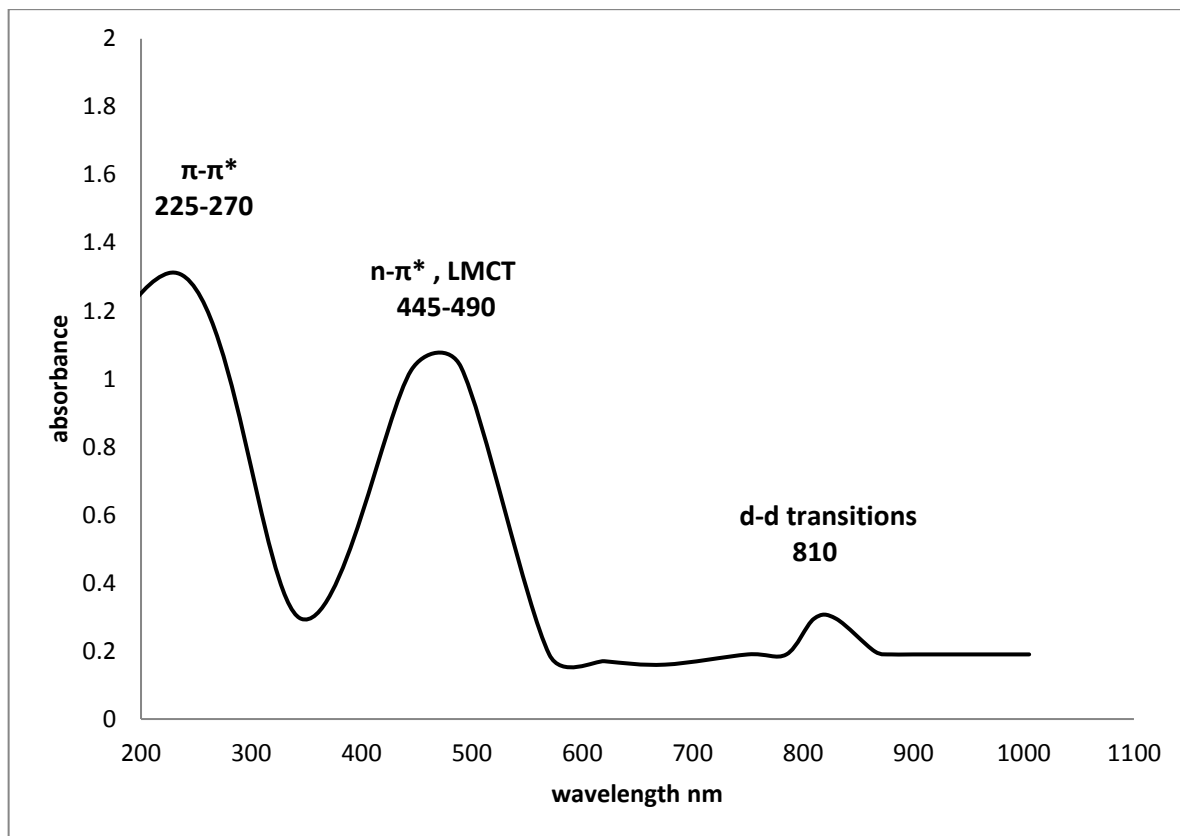
Supplementary fig. 2: The FT-IR spectrum of complex (2)



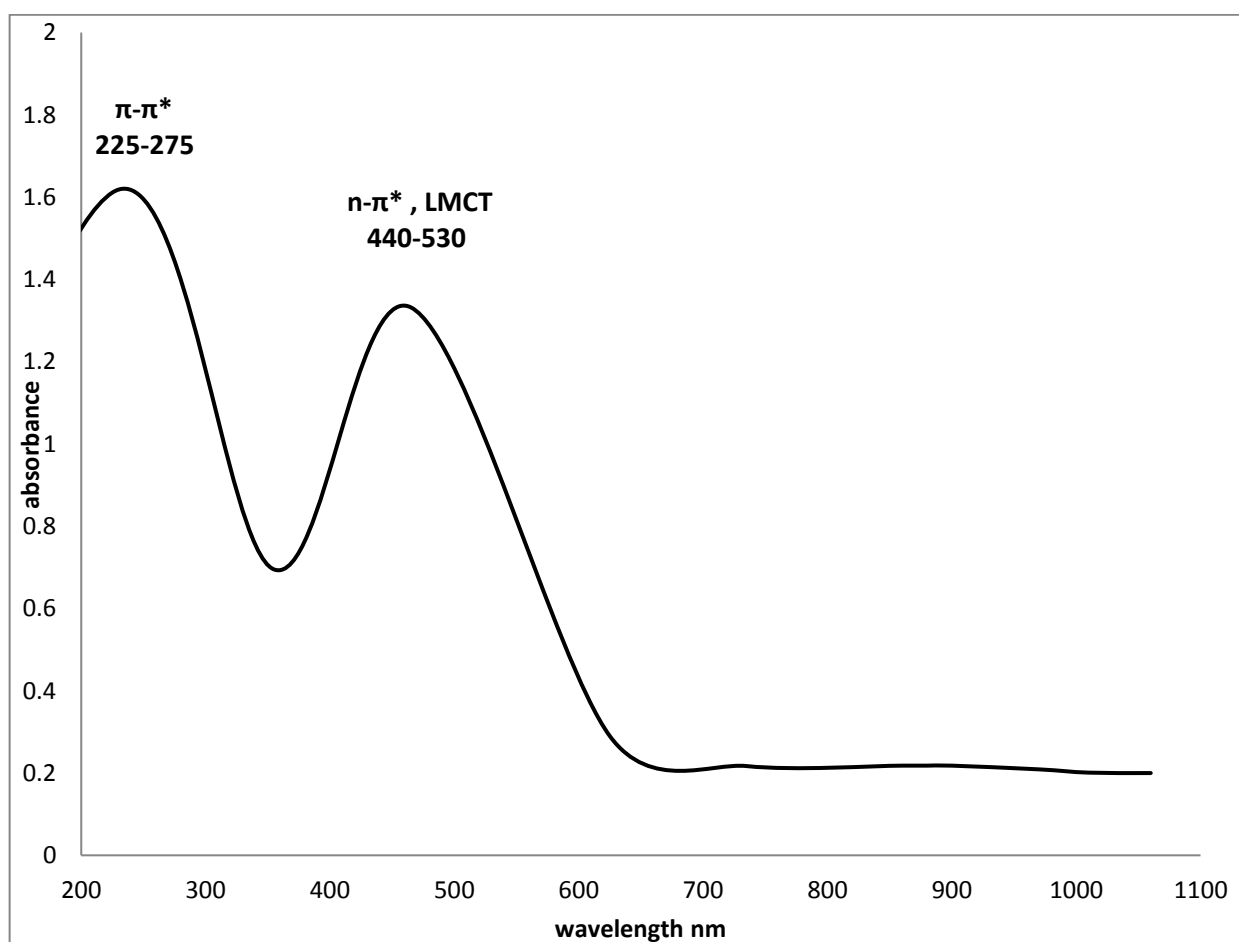
Supplementary fig. 3: The FT-IR spectrum of complex (3)



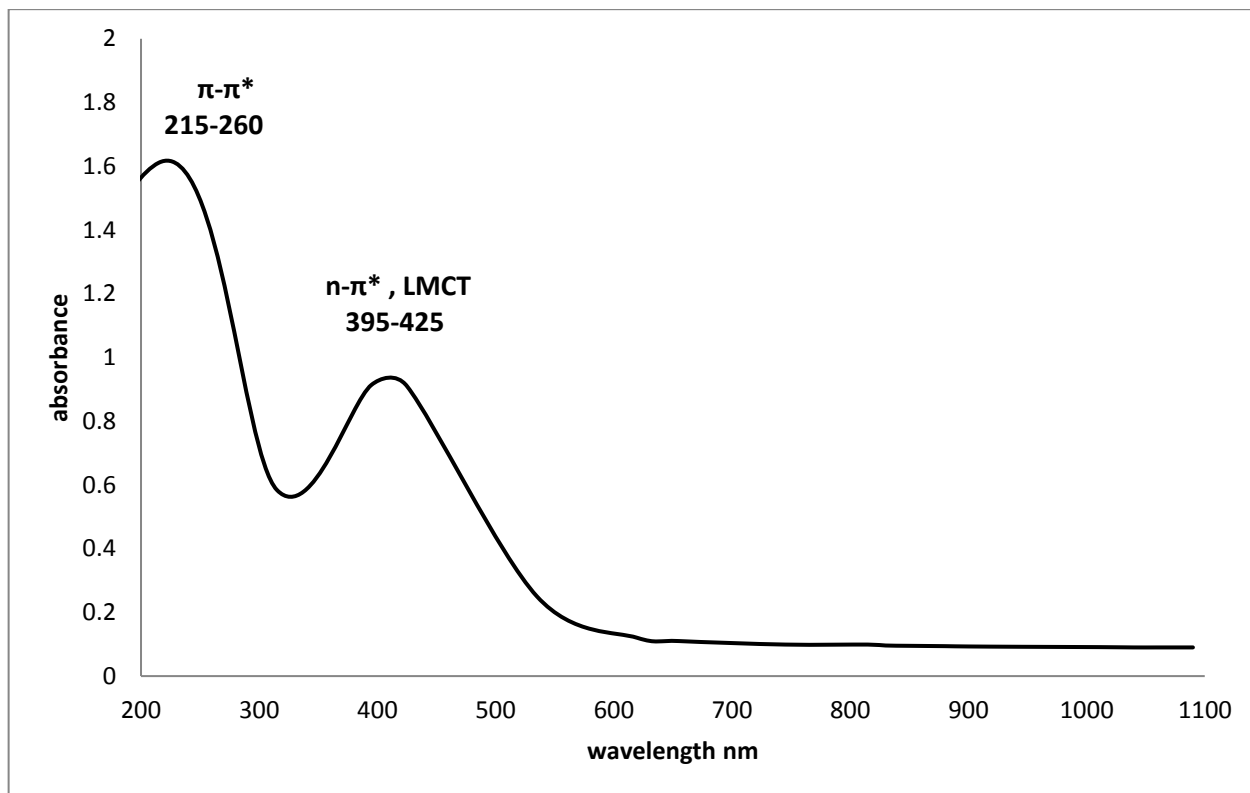
Supplementary fig. 4: The FT-IR spectrum of complex (4)



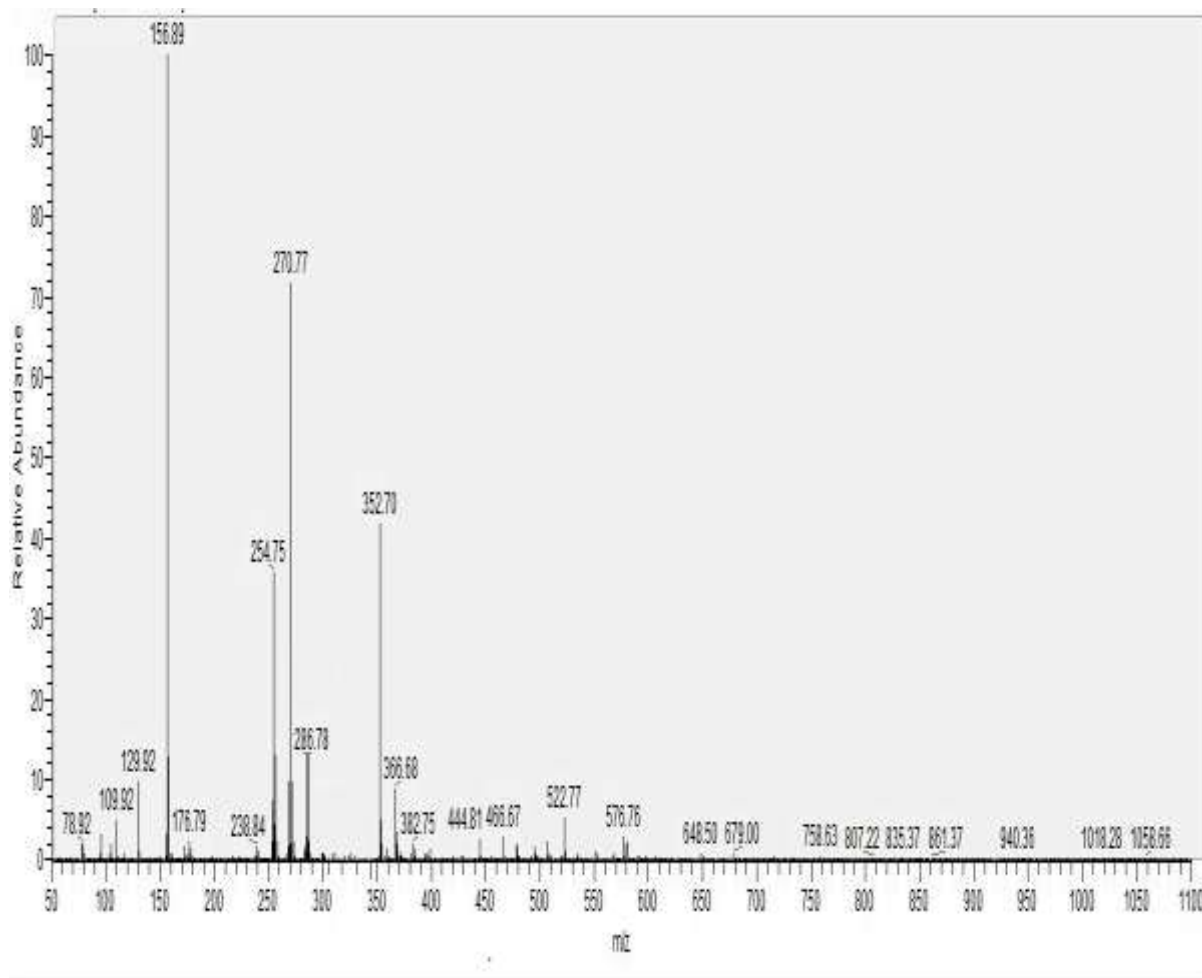
Supplementary fig. 5: The UV-Vis. spectrum of complex (2)



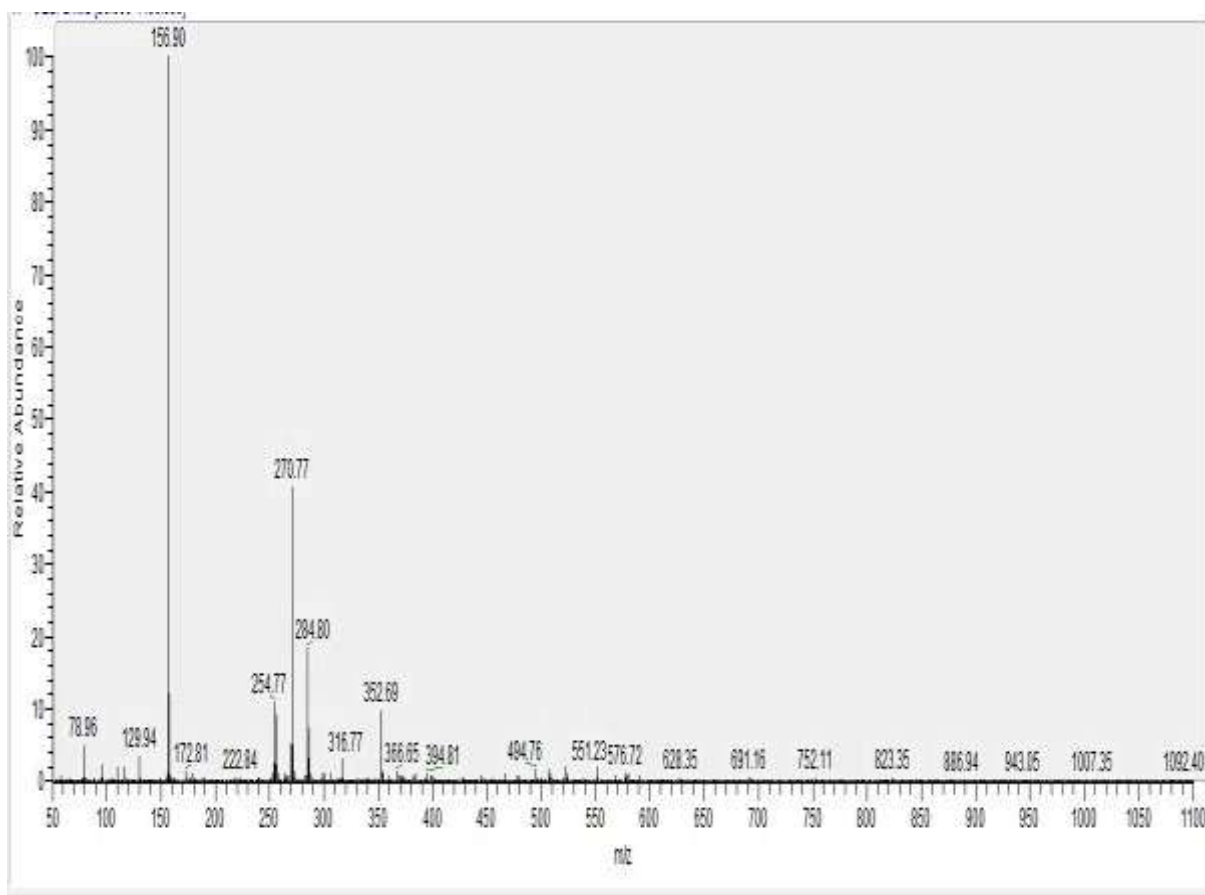
Supplementary fig. 6: The UV-Vis. spectrum of complex (3)



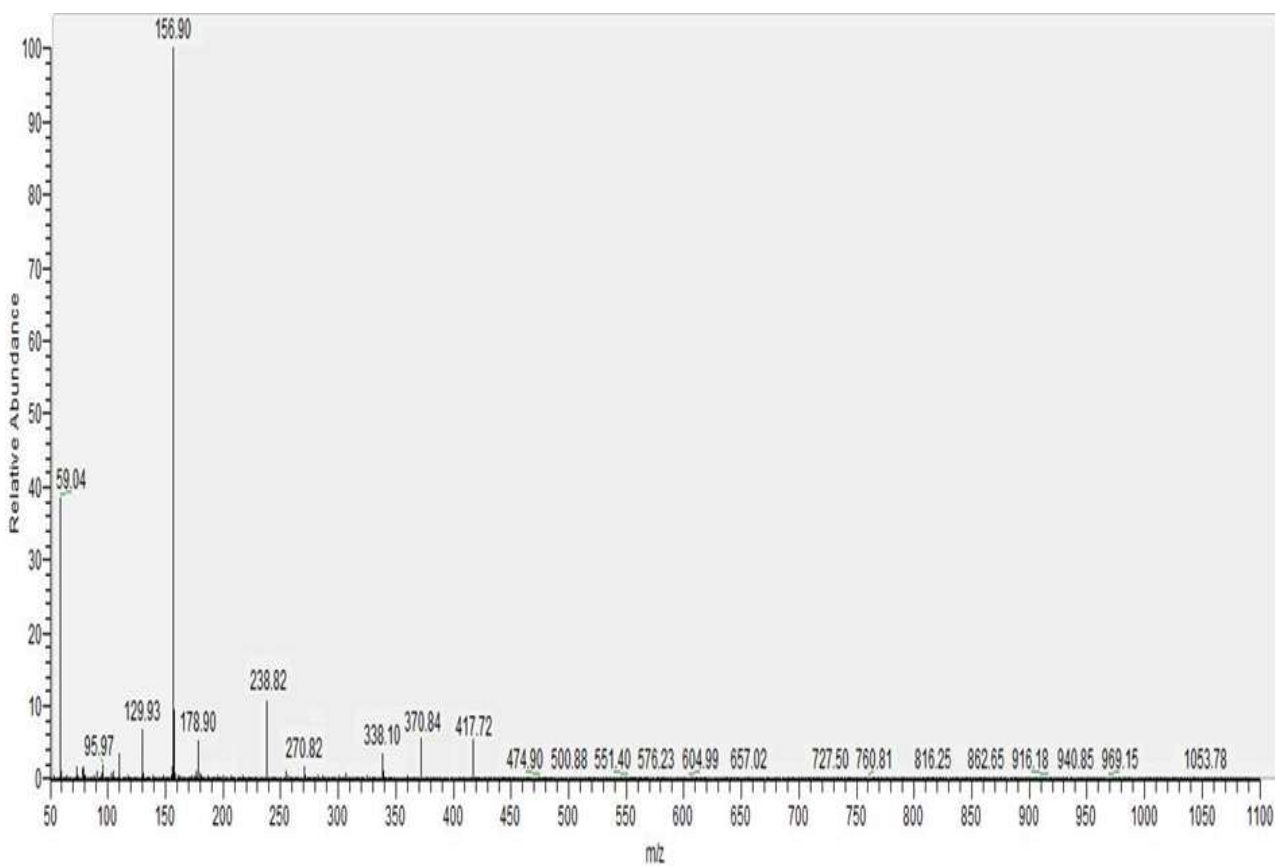
Supplementary fig. 7: The UV-Vis. spectrum of complex (4)



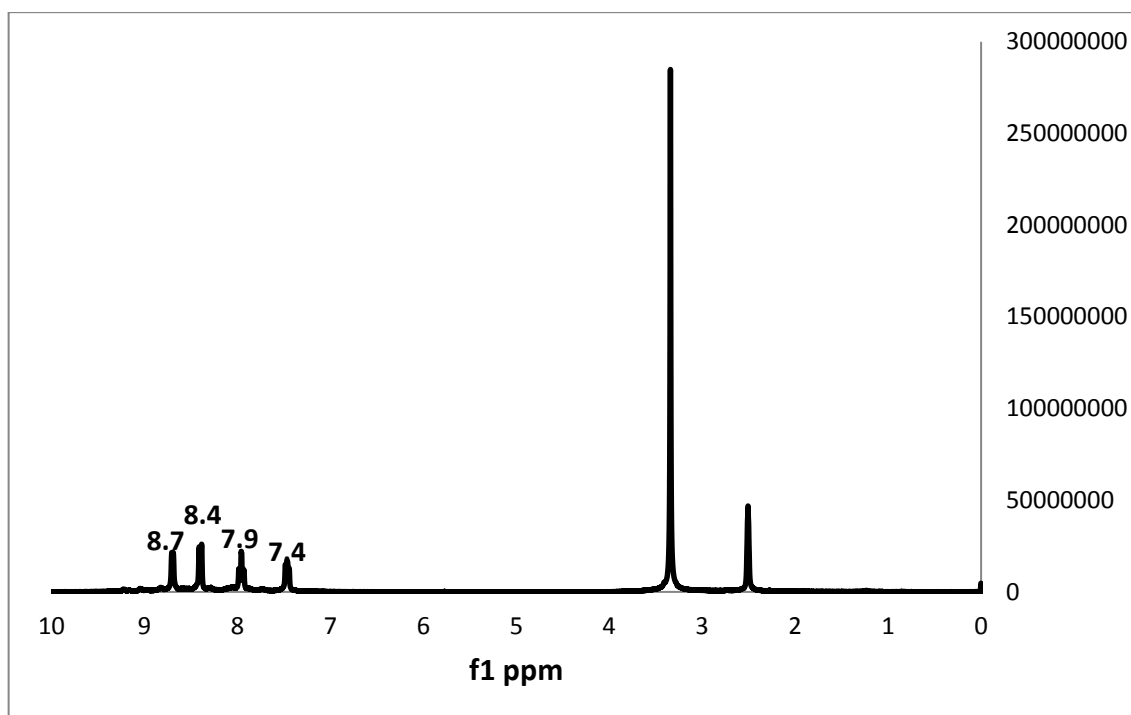
Supplementary fig. 8. The mass spectrum of complex (2)



Supplementary fig. 9: The mass spectrum of complex (3)



Supplementary fig. 10: The mass spectrum of complex (4)



Supplementary fig. 11: The ^1H -NMR spectrum of complex (4) recoded in DMSO-d_6 .

Conclusion

The 2,2'-bipyridine ligand is used to prepare complexes with VO(II) and V(V). The prepared complexes have been characterized by different techniques. This ligand behaves as N_2 donors. The binary and ternary complexes with vanadyl VO(II) and V(V) in the molar ratio (1:1 and 1:2) have square pyramidal and octahedral geometry respectively. The presence of V=O bands and the shifts of C=N bands in all complexes suggested the bonding of VO(II) and (V) ions with the ligand through its nitrogen atoms. ^1H -NMR spectra of vanadate complexes showed suitable shifts of the ligand protons which indicated the coordination of the ligand with the vanadate (V).

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