IJBPAS, May, 2019, 8(5): 939-959

ISSN: 2277–4998

International Journal of Biology, Pharmacy
and Allied Sciences (IJBPAS)
'A Bridge Between Laboratory and Reader'

www.ijbpas.com

MIXED-LIGAND OXO/ DIOXOVANADIUM (V) COMPLEXES INCORPORATING BIDENTATE AND TRIDENTATE DONOR HYDRAZONES AND o-PHENYLENEDIAMINE

ISRAA A. ALGHAMDI*, MOHAMED ABDELBASET[1, 2*], INES EL MANNOUBI[1]

*1: Chemistry Department, Faculty of Science, AlBaha University, Al-Baha, KSA

2: Chemistry Department, Faculty of Science, Al Azhar University, Assiut Branch, Assiut, Egypt

***Correspondence: M. Abdelbaset: baset1002002@yahoo.co.uk; Mobile: +966531974844;**

Israa A. Alghamdi: Osoo_1413@hotmail.com; Mobile: +9660558193973

Received 29th Nov. 2018; Revised 20th Dec. 2018; Accepted 30th Dec. 2018; Available online 1st May 2019

https://doi.org/10.31032/IJBPAS/2019/8.5.4704

ABSTRACT

A series of vanadium (V) complexes with some mixed ligands containing hydrazone moiety (L_1-L_4) and o-Phenylendiamine (L_5) have been synthesized. The synthesized ligands and their corresponding vanadium(V) complexes have been characterized by elemental analyses, IR, UV-Vis, ^{1}H-NMR, Mass spectra, molar conductance and thermal analysis. The analytical data showed that the stoichiometry of the Oxo/Dioxovanadium (V) mixed-ligand complexes were in 1:1:1 molar ratio. Structural elucidation was determined using different characterization and analytical data that supported an octahedral geometry for the synthesized vanadium (V) complexes. Some of the ligands and their vanadium (V) complexes have been screened for antimicrobial activity using different species of pathogenic bacteria and fungi. The results indicated that the ligands and their vanadium (V) complexes showed less antibacterial activity, while vanadium (V) complexes showed higher antifungal activity compared to the free ligands.

Keywords: Vanadium(V) complexes, Hydrazone derivatives, Mixed ligand, Antimicrobial Activity

1. INTRODUCTION

Mixed ligand complexes are reported to have an importance in the field of metalloenzymes and biological activities [1-3]. Due to the importance of such ligands, many scientific papers have been published on their coordination chemistry with transition metals [4, 5]. Hydrazones are important classes of ligands have played an important role in the development of coordination chemistry as they are readily form stable complexes with most transition metals [6]. Hydrazones and their metal complexes are having great pharmacological applications as anti-fungal, antiinflammatory, anti-bacterial and anti-cancer agents [7]. They are present in many of the bioactive heterocyclic compounds that are of a wide interest because of their diverse biological and clinical applications [8].

Vanadium chemistry has increasingly become the center of research attention, due to its role in biological system and has emerged as essential research topic in recent years [9]. The best evidence for a biological role of vanadium comes from bacteria and plants where it is present in certain vanadium dependent haloperoxidase and nitrogenase enzymes [10]. The structure and reactivity of vanadium complexes with biologically important ligands have been intensively studied [11-16].

From the importance mentioned above we are encouraged to prepare new vanadium complexes with some mixed ligands using hydrazone derivatives and o-phenylenediamine.

2. MATERIALS AND METHODS

2.1. Chemicals

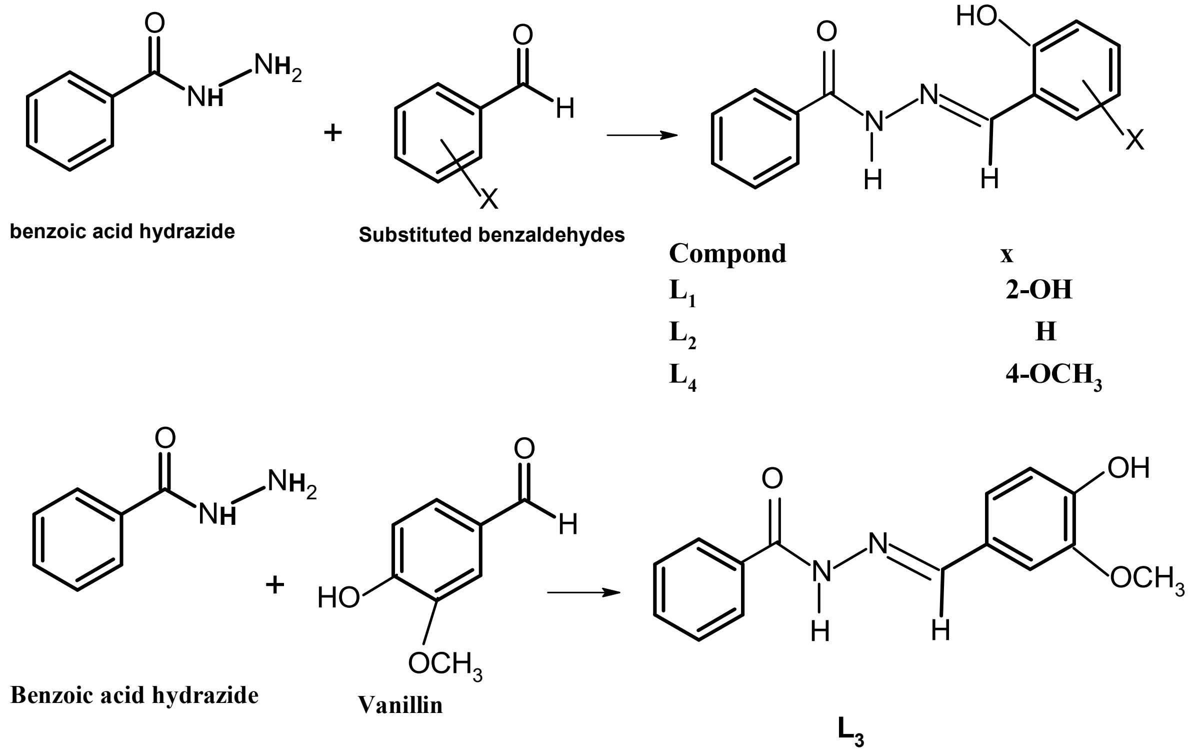
All chemicals used in this work NH_4VO_3, KVO_3, benzaldehyde, salicylaldehyde , anisaldehyde, vaniline, *o*-phenylenediamine (L_5), were purchased from Sigma-Aldrich and used as received without purification. The benzoic acid hydrazide and Hydrazone derivatives (L_1 – L_4) has been synthesized according to the reported methods [17].

2.2. Instruments

Melting points of the synthesized ligands and complexes were measured using Electrothermal (Cat NO. TA9100) melting point apparatus. Elemental analysis for C, H, N and S were carried out using Leco VTF-900 CHN-S-O 932 version 1.3x (ThermoFisher Scientific-USA) instrument. FT-IR spectroscopy was recorded on Nicolet IS50 FT-IR spectrophotometer in the spectra range of 400-4000 cm^{-1}. Electronic spectra of solutions of the complexes in DMF were recorded on Evolution 300 UV-vis Spectrophotometer. Mass spectra were recorded on a Thermo Fisher Exactive + TriversaNanomate mass spectrometer. Molar conductivities of freshly prepared DMF solutions of the complexes at a concentration of 0.001M were measured using Hanna instrument HI8633N Multi-range conductivity meter. Thermo gravimetric analysis (TGA) was recorded on Shimadzu analyzer 50 in a dynamic nitrogen atmosphere (100 ml/min) at a heating rate 10°C/min. The ^{1}HNMR spectra were obtained using Varian Mercury-400BB (400 MHz) spectrometer using TMS (^{1}H) as standard.

2.3. Synthesis of Hydrazone derivative ligands ($L_1 – L_4$)

The Hydrazone derivatives ($L_1 – L_4$) were prepared by the condensation of Benzoic acid hydrazide (1.36 g ,10 mmol) in 50 ml of ethanol with an aldehyde compound (benzaldehyde, salicylaldehyde, vaniline, anisaldehyde) (10 mmol) in absolute ethanol (l0 mL). Few drops of glacial acetic acid were added to the reaction mixture. The mixture was refluxed for 4 hours and was allowed to cool at room temperature. The precipitate was filtered and washed by ethanol. The obtained product was recrystallized using ethanol to get pure solid [17].



Compond	x
L_1	2-OH
L_2	H
L_4	4-OCH_3

Scheme 1: Hydrazone derivatives ligands

2.4. Preparation of vanadium (V) complexes

Preparation of the $NH_4[VO_2(L_n) L_5]. xH_2O$ complexes

An ethanolic solution of Hydrazone derivatives ($L_1 – L_4$) as a primary ligand (1mmol) and ethanolic solution of *o*-phenylenediamine (L_5) as a co-ligand (1mmol), were added slowly, into warm aqueous solution of NH_4VO_3 (1 mmol). The mixture was heated and refluxed with stirring for five hours where the complexes precipitated out from the solution. The precipitateswere filtered, washed with proper solvents and dried using desiccator.

Preparation of the $K[VO_2(L_n) L_5]. xH_2O$ complexes

KVO_3 (1 mmol) was dissolved in a solution of 5 ml H_2O and mixed with ethanolic solution of Hydrazone derivatives ($L_1 – L_4$) as a primary ligand (1mmol) and ethanolic solution of *o*-phenylenediamine (L_5) as a co-ligand (1mmol). The mixture was refluxed for 5 hours under stirred condition. The precipitate product formed was filtered and washed many times using ethanol, and finally dried in vacuo over P_2O_5.

2.5. Antimicrobial Activity

The microbial activities of the ligands and their complexes were examined against six pathogenic bacteria (Staphylococcus aureus, *Enterococcus faecalis*, and *Group B streptococcus* (GBS)) as Gram-positive bacteria, and (Proteus Mirabilis, *Escherichia coli*, *Klebsiella pneumoniae*) as Gram-negative bacteria, in addition to one kind of fungi (*Candida albicans*) to assess their antimicrobial properties.

3. RESULTS AND DISCUSSION

Oxovandium(V) complexes were synthesized by reaction of vanadium (V) metal salt with Hydrazone derivatives ($L_1 – L_4$) as primary ligands and o-phenylenediamine (L_5) as coligand. All the complexes produced were coloured and stable on prolonged exposure to air. The vanadium complexes were soluble in DMF and DMSO but insoluble in other common organic solvents. The primary ligands (L_2 –L_4) acts as a bidentate ligand and coordinate through free C=O and nitrogen of the azomethane C=N group. While the ligand (L_1) act as tridentate and coordinated through free C=O, nitrogen of the azomethane C=N and deprotonated OH groups. The coligand o-phenylenediamine act as bidentate and coordinate through the two nitrogen atoms of the amine groups.

Elemental analyses and other physical data of the vanadium complexes are listed in Table 1. The elemental analyses agree well with the proposed molecular formula of the complexes (Table 2). The sharp melting points show the purity of the ligands and their complexes. The presence of hydrated water was confirmed by TG analysis.

The molar conductivity for the vanadium (V) complexes **1-8** were measured in 1x10^{-3} M DMSO solutions and are listed in Table 2, The molar conductance measurements values lies in the range (65.6 – 96.8 ohm^{-1} cm^{2} mole^{-1}) indicates the electrolytic behavior of the prepared complexes [18]. The vanadium (V) complexes **1-8** are found to be 1:1 electrolytes. The molar conductance measurement for the vanadium complexes are compatible with the molecular formulae arrived from the analytical information.

3.1. Infrared Spectra

The significant bands observed in the infrared spectra of the ligands (L_{1-4}) and their complexes are shown in Table 3 and the representative spectra are shown in Figs. 1, and 2. The infrared spectra of the ligands (L_{1-4}) give bands in the region 3010–3050 cm^{-1}, 1600–1640 cm^{-1}, 1630 – 1690 cm^{-1} and 3210 -3260 cm^{-1} were assigned to N-H, C=N, C=O and OH stretching respectively. The main observation points are discussed below.

1- In the IR spectra of the vanadium complexes there was a band in the range of 1600-1630 of the characteristic υ(C=O) stretching vibration with a strong shift from the bands of the free ligands (1630 – 1690 cm^{-1}). This indicates that the ligands were coordinated to the metal centers [19-21].

2- The bands at 1600 - 1640cm^{-1} are assigned to υ(C=N) group of the free ligands. These bands of the υ(C=N) group in the vanadium (V) complexes were shifted to 1530 - 1590 cm^{-1} frequency, indicating the participation of nitrogen atom of υ(C=N) group in coordination in all metal complexes under investigation [22, 23].

3- The characteristic free ligands (L_1 and L_3) band of hydroxyl group υ(O-H) was observed at 3210 and 3260 cm^{-1} respectively. This band is absent in the spectra of the vanadium (V) complexes (**1** and **2**), indicating coordination through the deprotonated phenolic OH group [24].

4- The IR spectrum of the complexes showed a band in the regions 3350 cm^{-1} and 3200-3250 cm^{-1} which can be assigned to ν(NH_2) indicating that the N of the amino group in ligand 5 (L_5) were coordinated to the vanadium metal ion [25] .

5- The oxovanadium(V) complexes exhibit an additional strong absorption band in the region 930 - 990 cm^{-1}, which assigned to ν(V=O)[26].

6- The IR spectra of the complexes (1, 3, 5 and 7) showed band in the range 1440-1455 cm^{-1} which is correspondent to the deformation modes of the $\delta(NH_4^+)$ ion [26, 27].

7- The appearance of a medium broad band in the range 3140-3500 cm^{-1}, due to υ(OH) indicate the presence of an H_2O molecules in the crystal of hydrated complexes [28-30]. These bands are absent in the free ligands.

8- The appearance of new bands in the region 440-490 and 520-590 cm^{-1} can be assigned to υ(V–N) and υ(V–O) respectively [18,26, 31, 32]. This indicate that the ligands (L_2 – L_4 and L_5) act as bidentate and the ligand (L_1) act as tridentate and are coordinating with vanadium ions through the N and O atoms.

3.2. UV-Vis spectra

The UV-Vis spectra of the vanadium (V) complexes were recorded in 10^{-5} mol. L^{-1} in DMF in the range 200-800 nm. UV-Vis spectra (Figs 3 and 4) of the vanadium (V) complexes exhibit several absorption bands. The absorption band at the higher energy region 300-318 nm for the complexes are assigned to intraligand π-π^* transitions [33-35]. The absorption bands observed at wavelength 398 - 425 nm are assignable to the intramolecular ligand-to-metal charge transfer (LMCT) transitions from the P^{π} orbital on the nitrogen and oxygen to the empty d orbitals of the metal [36, 37].

3.3. ^{1}H NMR Spectra

^{1}HNMR spectra of ligands and vanadium (V) complexes were recorded in DMSOd6 using tetra methyl silence (TMS) as internal standard. The ^{1}H NMR spectral data are shown in Figs 5-7. The ^{1}H NMR spectra of some ligands (L_1 and L_3) exhibit an OH proton at δ11.34 ppm [26] which was disappeared in the spectrum of vanadium complexes (**1** and **2**) supporting the deprotonation of the hydroxyl group and coordination through the oxygen atom with the central vanadium ion. But in the complexes (**5** and **6**) these signals shifted to lower field in the spectra of the vanadium(V) complexes. Also, in the ^{1}H NMR spectrum of ligands showed a signal at δ 8.65 ppm which is caused by the NH group. In complexes this signal was shifted to higher field in the spectra [38, 39].

There are signals at 7.87 and 7.88 ppm in the ^{1}H NMR spectrum of ligands were assigned to azomethine proton (H-C=N) these signals shifted to upfield due to the participation of azomethine nitrogen in coordination with Vanadium ions [40] . Also, the signal of NH_2 protons appear at δ5.30 ppm, this signal was shifted to higher field in the ^{1}HNMR spectra of the Vanadium (V) complexes indicating bonding through nitrogen atom of the amine group to the central vanadium ion [41]. The ligand (L_3) showed signal for methoxy groups at 3.86 ppm, these signal shifted to higher field in the spectra of the Vanadium (V) complexes (**5** and **6**) [42] that the values of chemical shifts for the methoxy groups in the metal complexes supporting its participation in coordination to the Vanadium ion.

3.4. Thermogravimetric Analysis.

Thermal analysis studies were carried out for vanadium complexes to confirm the data obtained from infrared spectroscopy studies on the state of the water molecules in the complexes as well as for their decomposition patterns

*Thermal decomposition of $NH_4[VO (L_1) L_5]2H_2O$ (**1**) complex.*

The TG curve of the $NH_4[VO_2 (L_1) L_5] 2H_2O$ (**1**) complex represents three decomposition steps as illustrated in Fig. 8. The first step complex display a weight loss at around 100 °C that corresponds to two lattice water molecules present in complex (calcd. 7.70 %, found 7.00 %). In the second decomposition step within the temperature range 100–250 °C show mass loss of (calcd. 22.04 %, found 23.00 %) which is reasonably accounted by the removal of $C_6H_8N_2$ (o-phenylenediamine) from the complex. The final step exhibits completion of weight loss between 250 and 600 °C that is corresponds to the decomposition of the primary ligand (L_1) leading to the final residue at 600 °C as metal oxide ($0.5V_2O_5$) (calcd. 19.48 %, found 17.00 %) [43].

$NH_4[VO_2 (L_1) L_5]2 H_2O \rightarrow 0.5 V_2O_5 +$ volatile products

*Thermal decomposition of $NH_4 [VO_2 (L_3) L_5]2.5 H_2O$ (**5**)complex*

The TG curve of the $NH_4 [VO_2 (L_3) L_5]2.5 H_2O$ (**5**) complex shows three steps as shown in fig 9. The complex start decomposing at 60◦C and ended at 200 °C, corresponding to elimination of two and half lattice water molecules and NH_3 gas from the metal chelate, the observed weight loss of 11.50 % is close to the calculated value of 11.84% [26]. The next two steps exhibit completion the decomposition of the complex with weight loss between 200 and 600 °C leaving metal oxide (0.5 V_2O_5) as a final residue (obs. = 18.16%, calcd. = 17.38 %). [43].

Thermal decomposition of NH_4 [VO_2 (L_4) L_5]3 H_2O (7) complex

The thermal decomposition of NH_4 [VO_2 (L_4) L_5]3 H_2O (**7**) complex saw multistage process as shown in fig. 10. the first step started from 50 °C and ended at 130 °C, which attributed to the loss of three lattice water molecules (calcd. 10.44 %, found 10.50 %). The second step (130 °C to 230 °C) corresponds to the loss of the $C_6H_8N_2$ (o-phenylenediamine) and NH_3 gas from the complex [26] the observed weight loss of 23.50 % is close to the calculated value of 24.17%. The third step of decompostion occurs between 250–600 C, with a weight loss of the primary ligand (L_3) leaving metal oxide (0.5 V_2O_5) as a final product at 600 °C [43].

*Thermal decomposition of K[VO_2 (L_4) L_5] (**8**) complex*

The thermal decomposition behavior of K[VO_2 (L_4) L_5] (**8**) complex is slightly different from those of the above complexes (Fig. 11). This complex display two stages of weight loss and no mass loss was observed up to 150 C which indicates the absence water molecule. The first decomposition process occurs at about 150- 320 °C and is assigned to removal of organic moiety (primary ligand L_4) (obs. = 52 %, calcd. = 52.47 %). In the second step within the temperature range 400–600 C, completing decomposition of this complex ended with formation of metal oxide KVO_3 at 600 C (obs. = 25.48%, calcd. = 28.51 %).

3.5. Mass spectra

The mass spectral studies of ligands (L_1 – L_4) and some of the representative vanadium (V) complexes to confirm the structures and molecular weights (Figs. 12 – 15). In mass spectrum for the ligand (L_1) the observed peak was at 241.17 m/z which is matches the theoretically calculated molecular weight (240.25 m/z). The observed mass spectra for the ligand (L_2) is appear at 225.08 m/z confirming the formula weight for this ligand (calculated 224.25 m/z). For the ligand (L_3) the observed peak was at271.08 m/z which matches the theoretically calculated molecular weight (272.28 m/z). Also, in mass spectrum for the ligand (L_4) appear signal at 255.08 m/z confirming the formula weight for this ligand (calculated 254.28 m/z). The molecular ion peak for the complex K[VO (L_1) L_5] 6H_2O (**2**) a peak was observed at 462.62 m/z confirming the formula weight for this complex (calculated 461.52 m/z). For the K[VO_2 (L_2) L_5] H_2O (**4**) the mass spectra shows a peak at 471 m/z, which is equivalent to its calculated molecular weight (472.22m/z). Also for the complex K[VO_2 (L_3) L_5] 2.5H_2O (**6**) appears at 545.08 m/z which is equivalent to its calculated molecular weight (545.5 m/z).

Looking on the results, we concluded that the hydrazone derivatives ligands (L_2 –L_4) acts as a bidentate ligand coordinating through free C=O and nitrogen of the azomethane C=N group forming stable five membered ring, while ligand (L_1) act as tridentate forming stable five and six membered rings. Also, the coligand o-phenylenediamine act as bidentate and coordinate through nitrogen atom of the amine group forming five membered ring.

On the basis of the previous observations, it is suggested that the complexes (**3-8**) with bidentate ligands (L_2-L_4) have dioxo-group in the *cis*-configuration attached to the vanadium center show an octahedral geometries. While, The vanadium (V) complexes (1 and 2) with tridentate ligand (L_1) were having one oxo group (V=O), and their structure are expected to be octahedral geometry.

The proposed structure of the complexes **1–8** are shown below. (See scheme 2).

3.6 Antimicrobial activity

The organic ligand (L_1) and their prepared corresponding vanadium (V) complexes (1 and 2) were assessed for microbial susceptibility against three strain Gram-positive bacteria Staphylococcus aureus, *Enterococcus faecalis*, and *Group B streptococcus* (GBS) and three Gram-negative bacteria Proteus Mirabilis, *Escherichia coli*, *Klebsiella pneumonia* in addition, to one kind of pathogenic fungus *Candida albicans*. The screening of the tested compounds were carried out at fixed concentration of 10^{-3} g/mL in DMSO solvent. After the incubation period, the microbial susceptibility were monitored by measuring the zones (in mm) around each hole at which the visible growth was completely inhibited. The observations are listed in table 4. The results indicated that organic ligand (L_1) did not show any activity against nearly all types of bacteria (Gram-positive bacteria and Gram-negative bacteria) Also, there is less activity was noticed with ligand (L_1) against the fungus *C. albicans* (inhibition zone of 9 mm)

The tested metal complexes (**1** and **2**) showed antifungal activity against the pathogenic fungus *C. albicans* with highest sensitivity with an inhibition zone = 18 and 20 mm respectively. The increased antifungal activity of the prepared vanadium complexes may returned to chelation that increases the permeability of the chemicals and may be returned to the presence of vanadium ion (V^{5+}) [26].

The results indicated that most of the vanadium complexes (**1** and **2**) did not show antibacterial activity against all types of Gram-negative bacteria and Gram-positive bacteria except complex ($K[VO (L_1) L_5] 6H_2O$ (**2**)) have moderate activity against the Gram-positive *Enterococcus faecalis (inhibition zone of 13 mm) and complex* $NH_4[VO (L_1) L_5]2 H_2O$ (**1**) have less activity against the Gram-positive *Staphylococcus epidermidis* and S.a: *Staphylococcus aureus (inhibition zone of 13 mm).*

Table 1: The physical data of the Hydrazone derivatives ligands (L_1-L_4) and their Vanadium (V) Complexes

Compound	Mol. Formula	Yield %	Colour	M. P. (°C)	Mol. Wt.
L_1	$C_{14}H_{12}N_2O_2$	82%	Pale yellow	179	240.25
L_2	$C_{14}H_{12}N_2O$	60%	brownish yellow	195	224.25
L_3	$C_{15}H_{14}N_2O_3$	102%	Brownish yellow	124	270.28
L_4	$C_{15}H_{14}N_2O_2$	92%	white	157	254.28
$NH_4[VO (L_1) L_5]2 H_2O$ (1)	$C_{20}H_{27}N_5O_5V$	62%	Dark brown	>300	468.4
$K[VO (L_1) L_5] 6H_2O$ (2)	$C_{20}H_{31}N_4O_9KV$	162%	Dark brown	> 300	561.25
$NH_4 [VO_2 (L_2) L_5] 3H_2O$ (3)	$C_{20}H_{30}N_5O_6V$	62%	Dark brown	> 300	487.42
$K[VO_2 (L_2) L_5] H_2O$ (4)	$C_{20}H_{22}N_4O_4KV$	81%	Dark brown	> 300	472.22
$NH_4 [VO_2 (L_3) L_5]2.5 H_2O$ (5)	$C_{21}H_{31}N_5O_{7.5}V$	55%	Dark brown	> 300	524.16
$K[VO_2 (L_3) L_5] 2.5H_2O$ (6)	$C_{21}H_{27}N_4O_{7.5}KV$	45%	Dark brown	> 300	545.5
$NH_4 [VO_2 (L_4) L_5]3 H_2O$ (7)	$C_{21}H_{32}N_5O_7V$	41%	Dark brown	> 300	517.17
$K[VO_2 (L_4) L_5]$ (8)	$C_{21}H_{22}N_4O_4KV$	41%	Dark brown	> 300	484.20

Table 2: Elemental analysis and molar conductance for the mixed ligand vanadium (V) complexes

Compound	Cald(Found)%					Molar conductivity $ohm^{-1} cm^{2} .mol^{-1}$
	C	H	N	O	V	
$NH_4[VO (L_1) L_5]2 H_2O$ (1)	51.28 (51.53)	5.81 (5.62)	14.95 (14.64)	17.07 (16.85)	10.87 (10.73)	67.4
$K[VO (L_1) L_5] 6H_2O$ (2)	42.77 (42.32)	5.56 (5.73)	9.97 (9.84)	25.64 (25.35)	9.07 (9.41)	74.6
$NH_4 [VO_2 (L_2) L_5] 3H_2O$ (3)	49.28 (49.46)	6.20 (5.94)	14.36 (14.78)	19.69 (19.88)	10.45 (10.69)	73.8
$K[VO_2 (L_2) L_5] H_2O$ (4)	50.84 (51.12)	4.69 (5.13)	11.85 (11.45)	13.54 (13.96)	10.78 (10.39)	85.5
$NH_4 [VO_2 (L_3) L_5]2.5 H_2O$ (5)	48.05 (48.22)	5.91 (5.64)	13.34 (13.65)	22.88 (22.74)	9.72 (9.35)	75.7
$K[VO_2 (L_3) L_5] 2.5H_2O$ (6)	46.19 (45.85)	4.94 (5.13)	10.26 (10.54)	21.99 (21.68)	9.34 (9.14)	88.4
$NH_4 [VO_2 (L_4) L_5]3 H_2O$ (7)	48.74 (48.39)	6.23 (6.61)	13.53 (13.85)	21.64 (21.37)	9.84 (9.55)	65.6
$K[VO_2 (L_4) L_5]$ (8)	52.06 (51.82)	4.57 (4.36)	11.56 (11.79)	13.21 (12.92)	10.51 (10.73)	96.8

Table 3: IR Spectroscopic data (cm^{-1}) of ligands and their vanadium (V) complexes.

Compound	H_2O	OH	NH_2	NH	C=N	C=O	V=O	V–O	V–N
L_1		3260	-	3050	1600	1680	-	-	-
$NH_4[VO(L_1)L_5]2H_2O$ (1)	3230	-	3460 3440	3050	1590	1630	980 930	540	480
$K[VO(L_1)L_5]6H_2O$ (2)	3500	-	3350 3360	3050	1540	1600	930	590	460
L_2	-		-	3050	1600 1640	1690	-	-	-
$NH_4[VO_2(L_2)L_5]3H_2O$ (3)	3150b	-	3150b	3030	1530	1605	930	560	450
$K[VO_2(L_2)L_5]H_2O$ (4)	3150	-	3370 3350	3045	1580	1610	950	520	440
L_3		3210	-	3030	1600	1640	-	-	-
$NH_4[VO_2(L_3)L_5]2.5H_2O$ (5)	3160b	3160b	3160b	3030	1580	1600	980	560	460
$K[VO_2(L_3)L_5]2.5H_2O$ (6)	3200b	3200b	3200b	3050	1570	1610	990 970	550	490
L_4	-		-	3010	1600	1630	-	-	-
$NH_4[VO_2(L_4)L_5]3H_2O$ (7)	3140b	3140b	3140b	3030	1530	1620	950	560	480
$K[VO_2(L_4)L_5]$ (8)	-	-	3150	3020	1590	1620	940	540	490

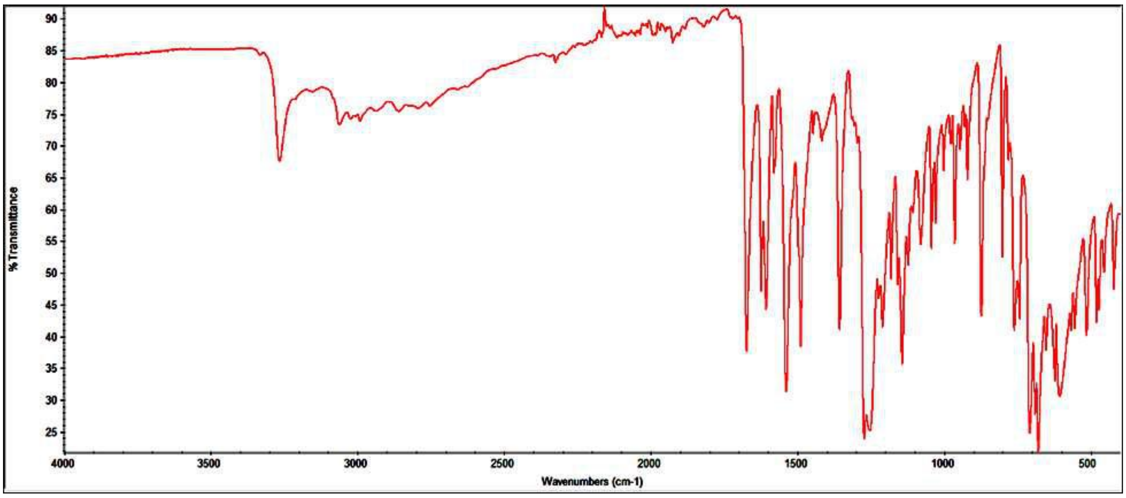


Fig. 1. IR spectrum for ligand (L_1)

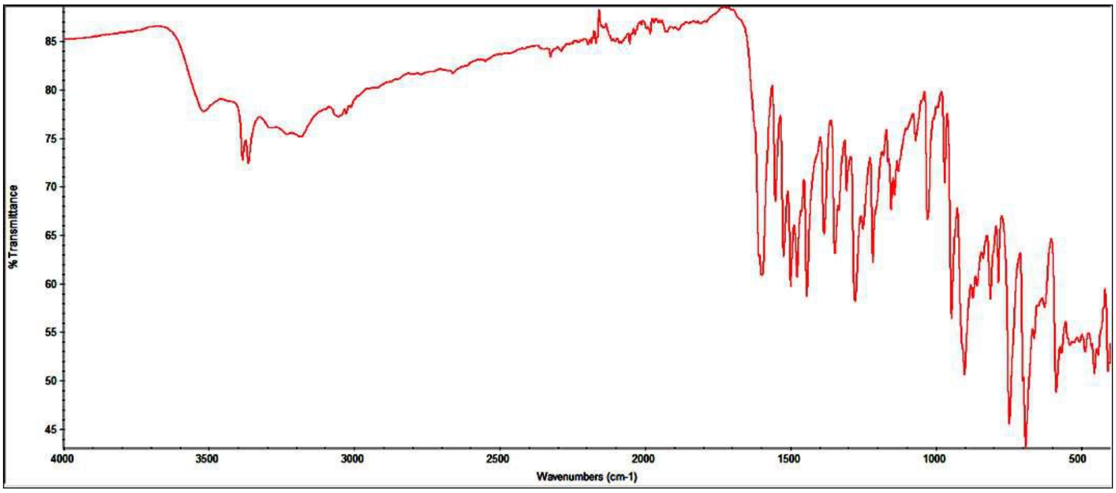


Fig. 2. IR spectrum for $K[VO(L_1)L_5]6H_2O$ (2) complex

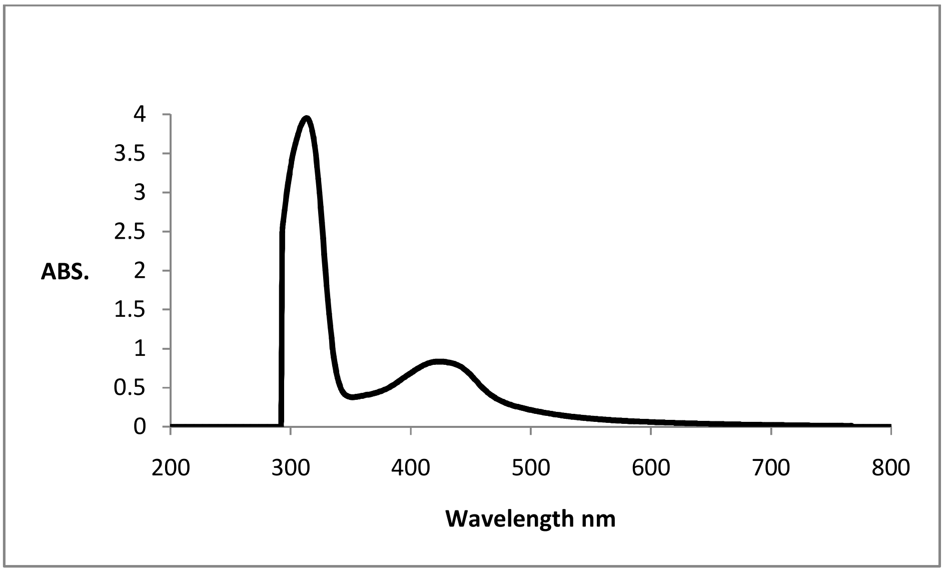


Fig. 3. The electronic spectrum of K[VO_2 (L_2) L_5] H_2O (4) complex

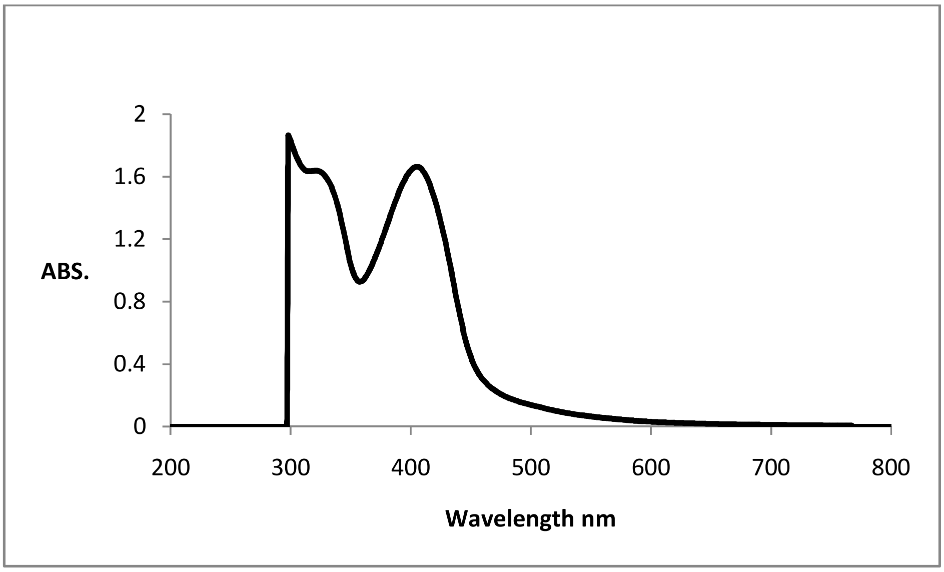
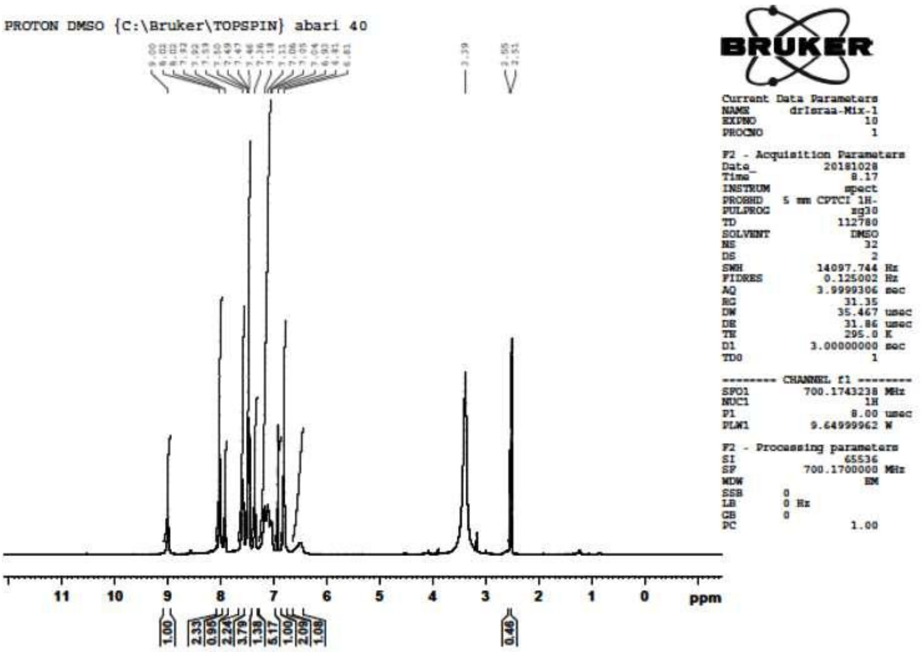


Fig. 4. The electronic spectrum of NH_4 [VO_2 (L_2) L_5] $3H_2O$ (3) complex



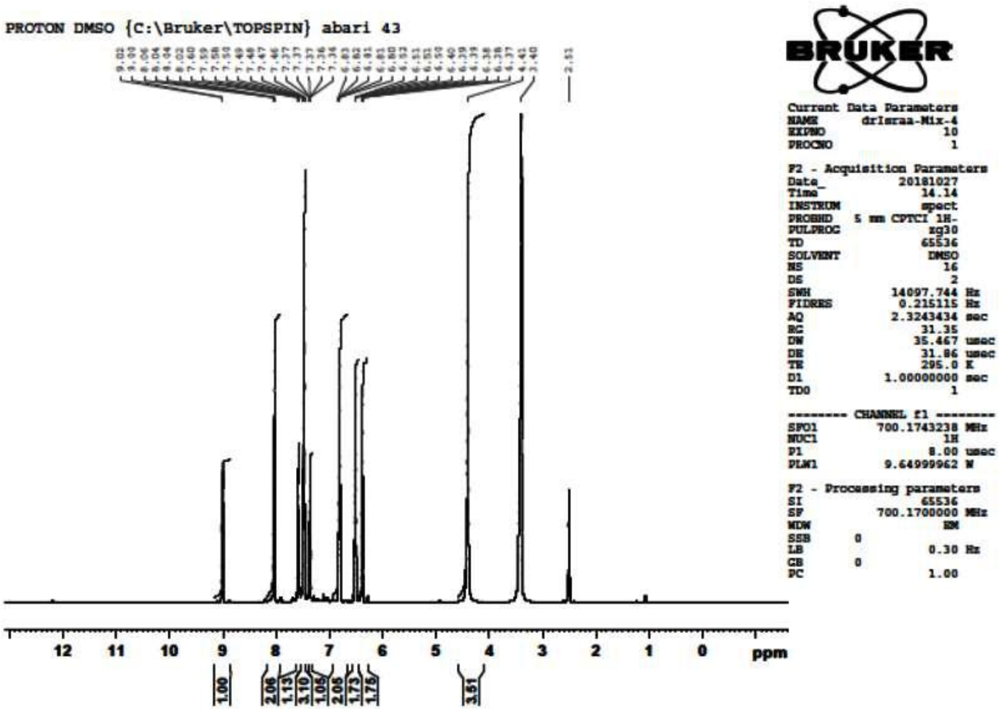
```
Current Data Parameters
NAME          drIsraa-Mix-1
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20181028
Time                   8.17
INSTRUM               spect
PROBHD   5 mm CPTCI 1H-
PULPROG                zg30
TD                   112780
SOLVENT                DMSO
NS                       32
DS                        2
SWH              14097.744 Hz
FIDRES            0.125002 Hz
AQ               3.9999306 sec
RG                    31.35
DW                   35.467 usec
DE                    31.86 usec
TE                    295.0 K
D1              3.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         700.1743238 MHz
NUC1                     1H
P1                     8.00 usec
PLW1            9.64999962 W

F2 - Processing parameters
SI                    65536
SF           700.1700000 MHz
WDW                      EM
SSB        0
LB         0 Hz
GB         0
PC                     1.00
```

Fig.5.^{1}H NMR spectrum of $NH_4[VO$ (L_1) $L_5]2$ H_2O (1) complex



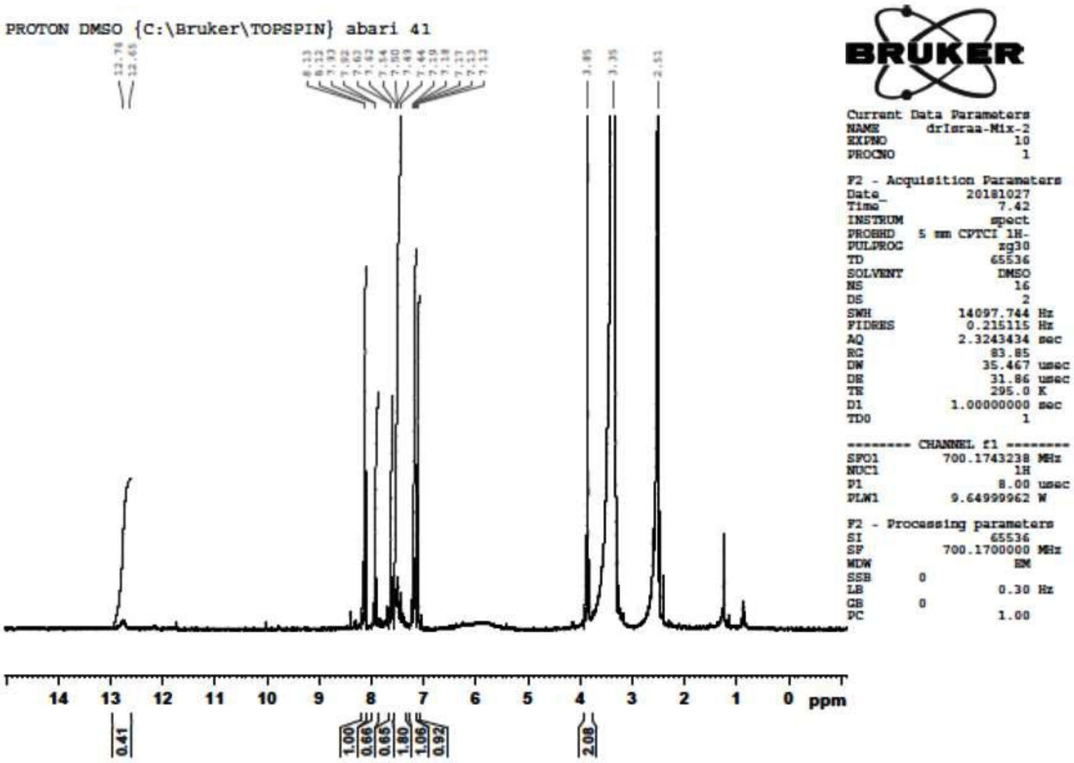
```
Current Data Parameters
NAME          drIsraa-Mix-4
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20181027
Time                  14.14
INSTRUM               spect
PROBHD   5 mm CPTCI 1H-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH              14097.744 Hz
FIDRES            0.215115 Hz
AQ               2.3243434 sec
RG                    31.35
DW                   35.467 usec
DE                    31.86 usec
TE                    295.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         700.1743238 MHz
NUC1                     1H
P1                     8.00 usec
PLW1            9.64999962 W

F2 - Processing parameters
SI                    65536
SF           700.1700000 MHz
WDW                      EM
SSB        0
LB                     0.30 Hz
GB         0
PC                     1.00
```

Fig.6.^{1}H NMR spectrum of $K[VO$ (L_1) $L_5]$ $6H_2O$ (2) complex



```
PROTON DMSO {C:\Bruker\TOPSPIN} abari 41
```

```
Current Data Parameters
NAME        drIsraa-Mix-2
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20181027
Time                 7.42
INSTRUM             spect
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH             14097.744 Hz
FIDRES           0.215115 Hz
AQ              2.3243434 sec
RG                  83.85
DW                 35.467 usec
DE                  31.86 usec
TE                  295.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          700.1743238 MHz
NUC1                   1H
P1                   8.00 usec
PLW1           9.64999962 W

F2 - Processing parameters
SI                  65536
SF            700.1700000 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

Fig.7.^{1}H NMR spectrum of NH_4 [VO_2 (*L_4*) L_5]3 H_2O (7) complex

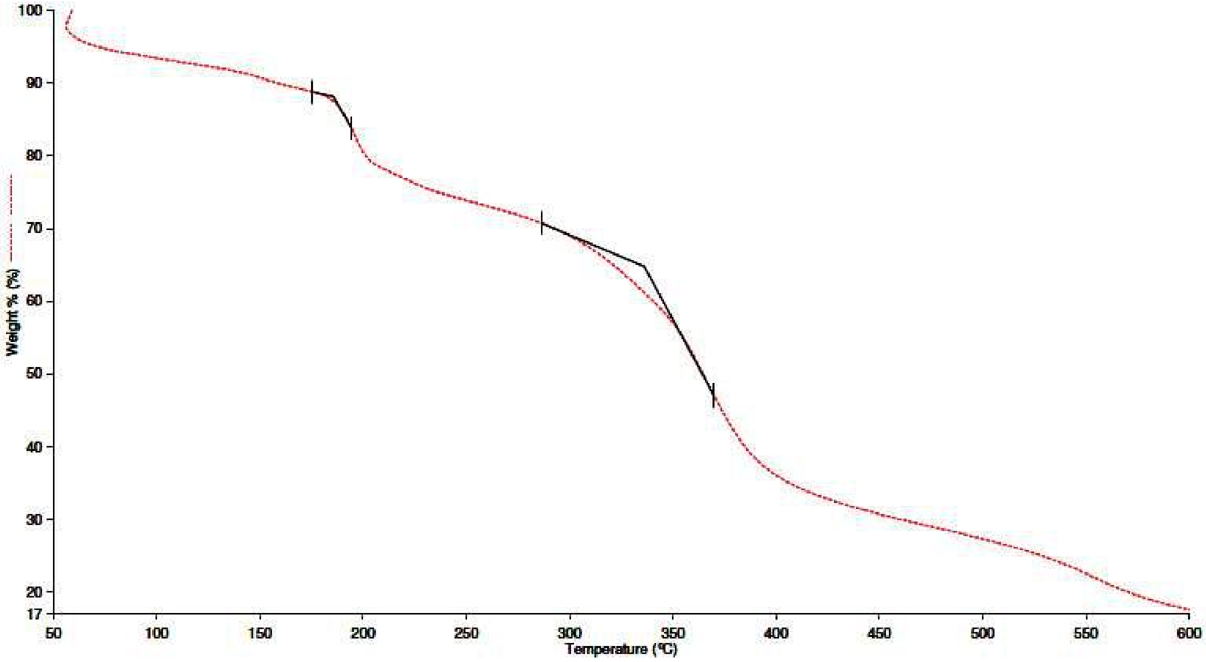


Fig.8.Thermogravimetric (TGA) curve of NH_4[VO (*L_1*) L_5]2 H_2O (1) complex

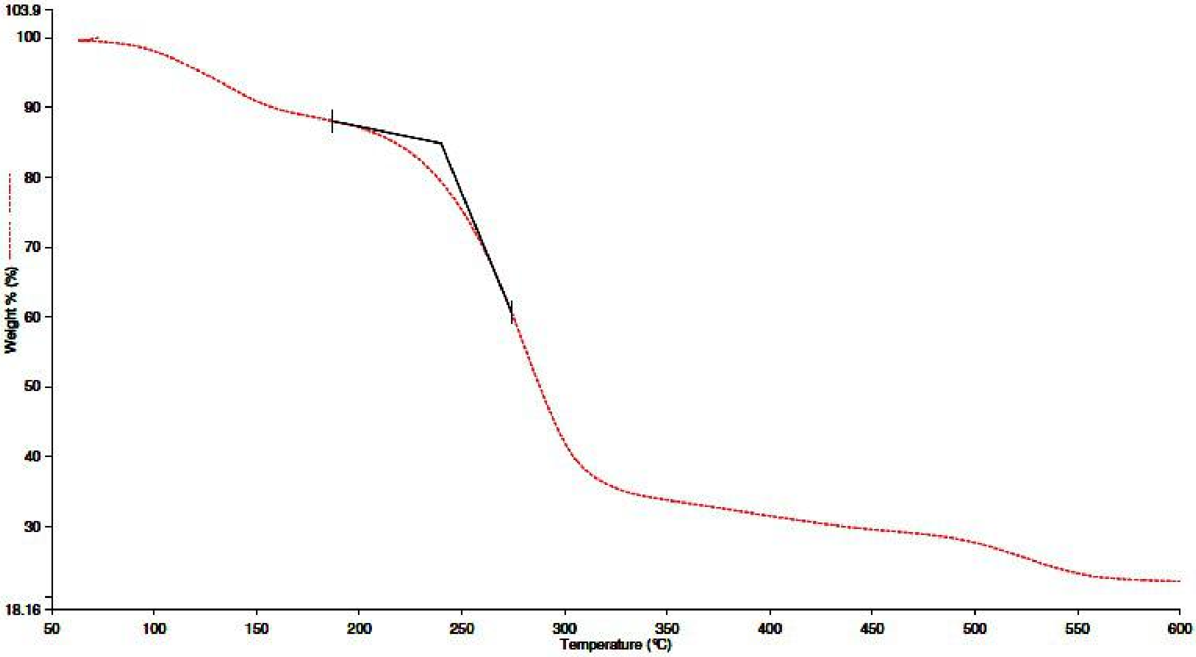


Fig.9.Thermogravimetric (TGA) curve of NH_4 [VO_2 (L_3) L_5]2.5 H_2O (5) complex

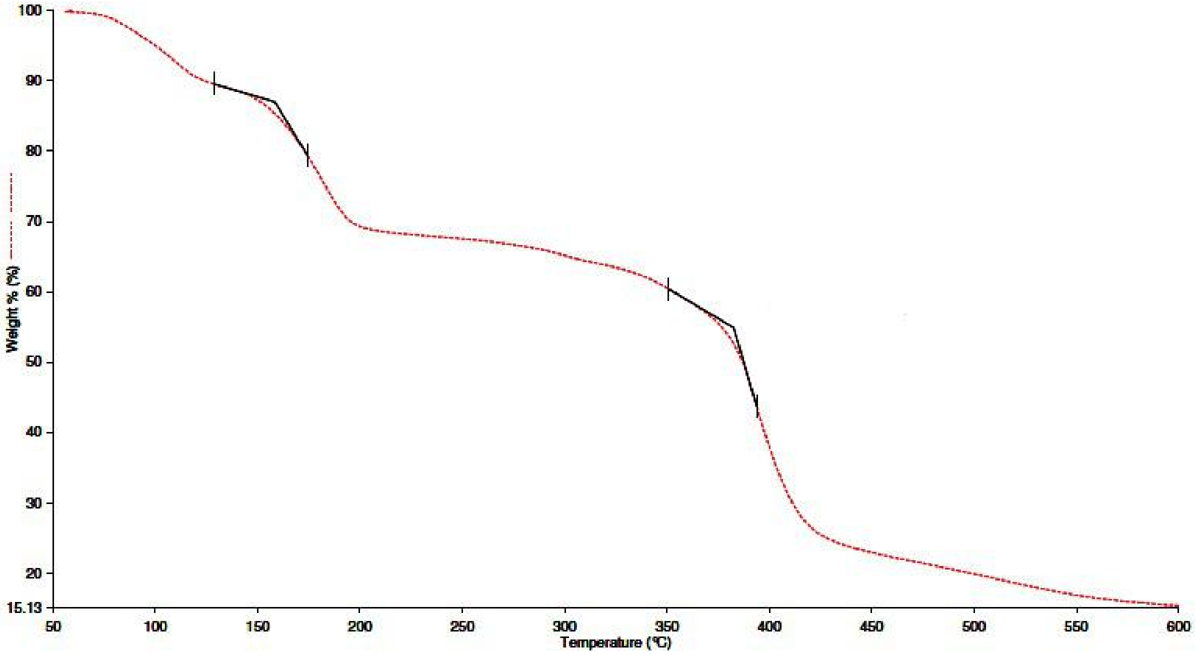


Fig.10.Thermogravimetric (TGA) curve of NH_4 [VO_2 (L_4) L_5]3 H_2O (7) complex

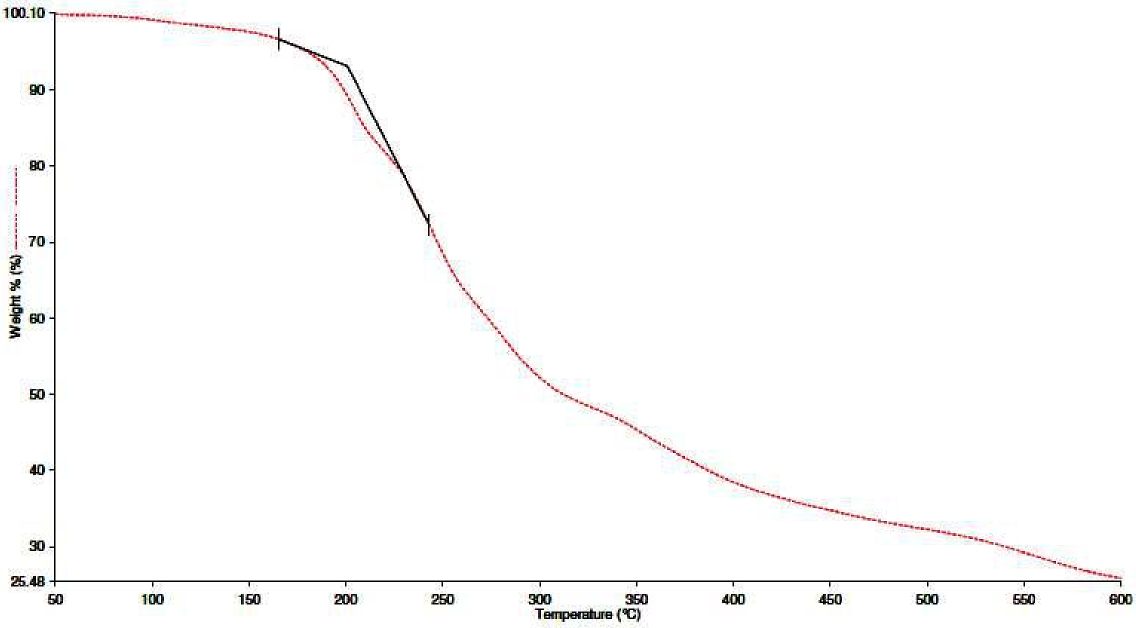


Fig.11.Thermogravimetric (TGA) curve of K[VO_2 (L_4) L_5] (8) complex

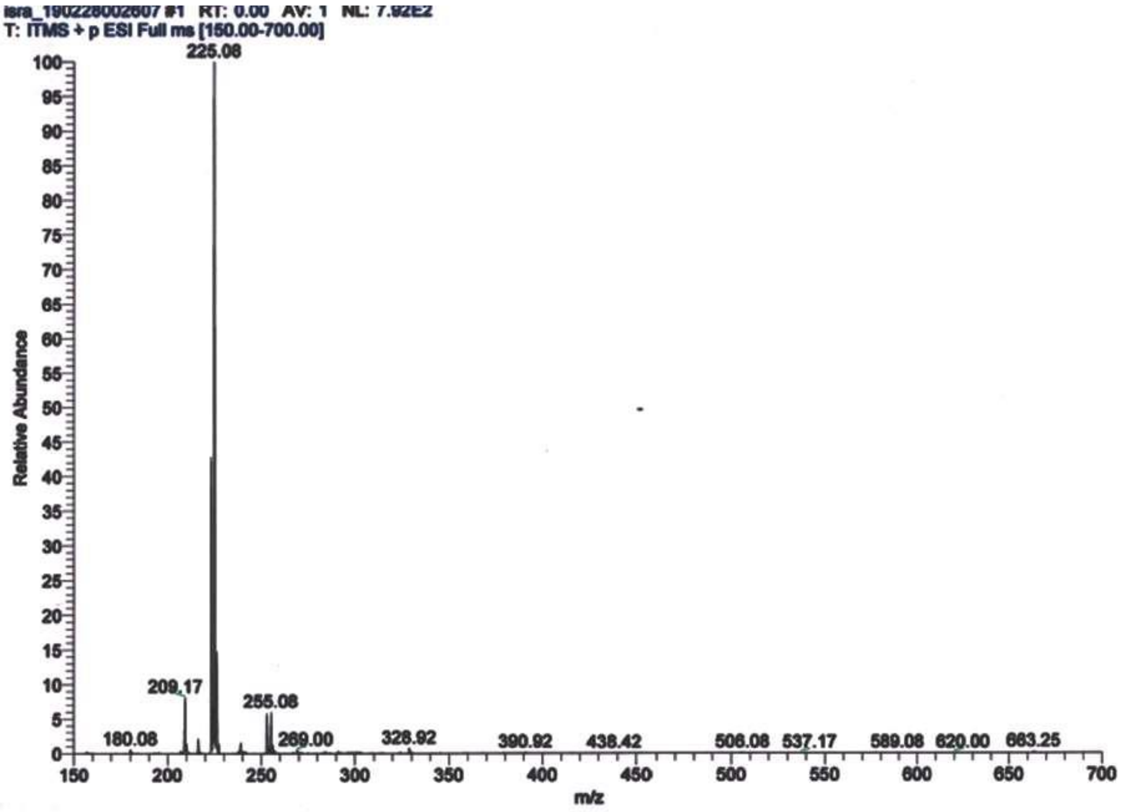


Fig.12. Mass spectra for Ligand (L_2)

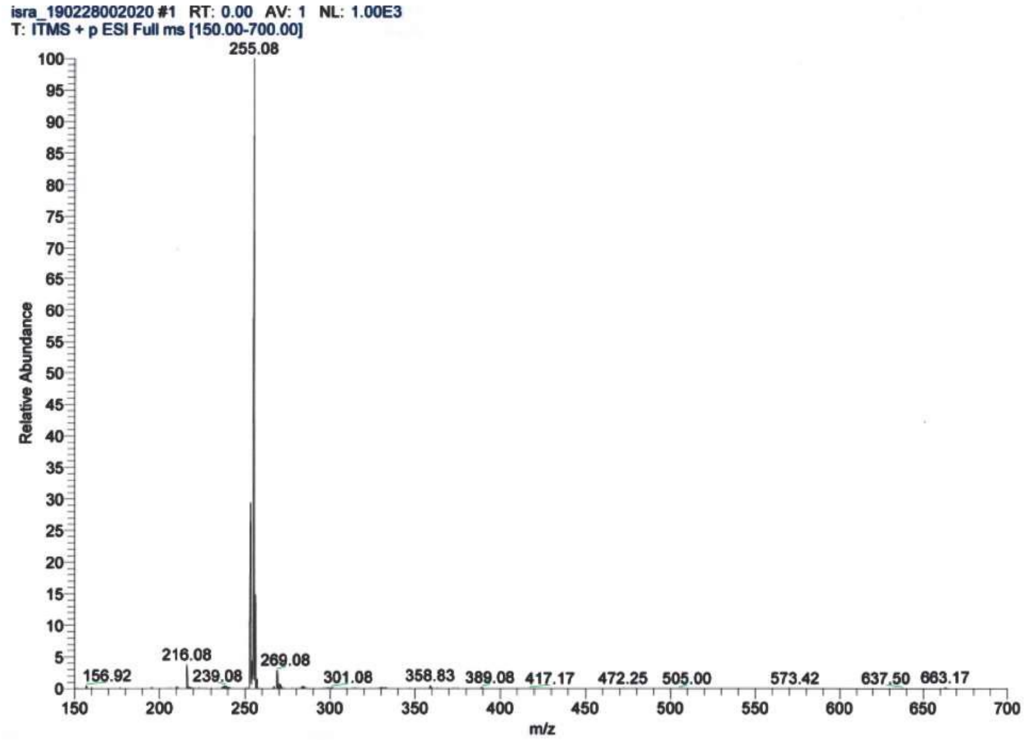


Fig.13. Mass spectra for Ligand (L_4)

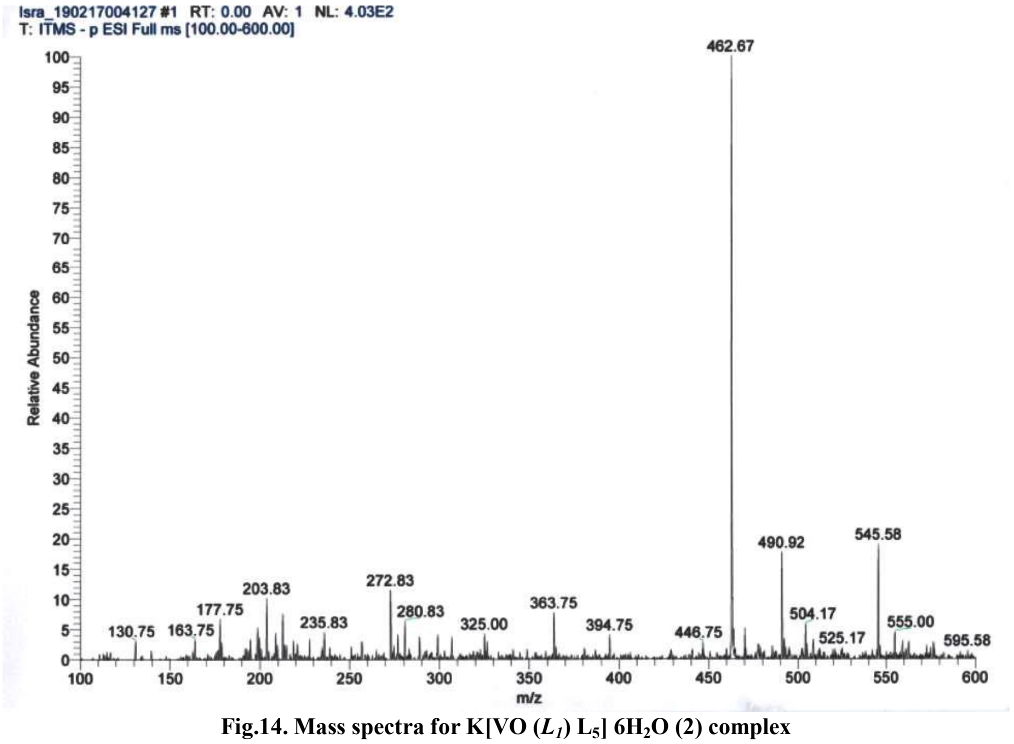


Fig.14. Mass spectra for K[VO (*L_1*) L_5] $6H_2O$ (2) complex

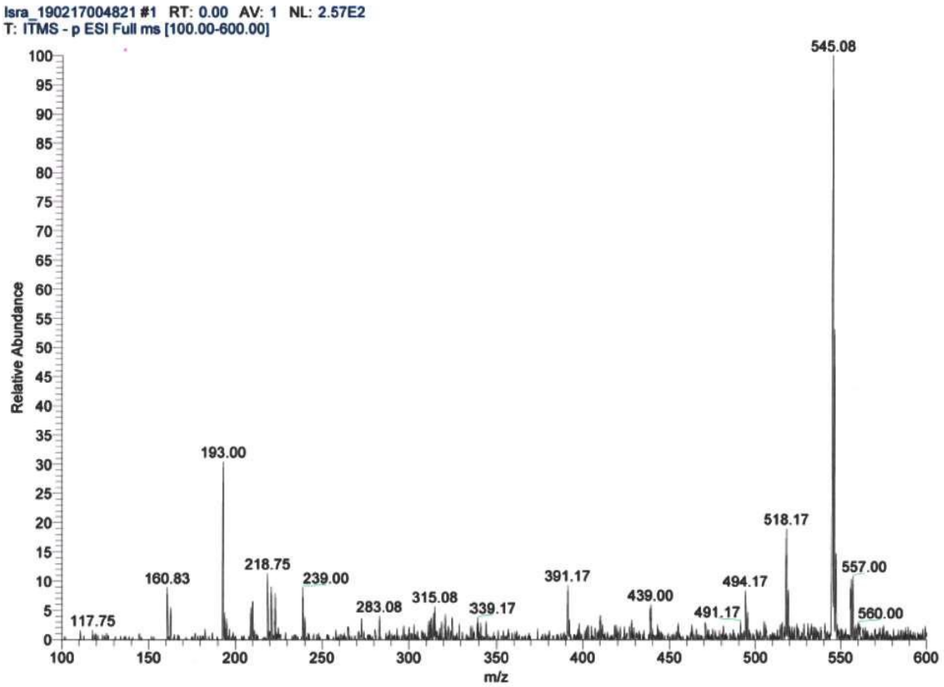
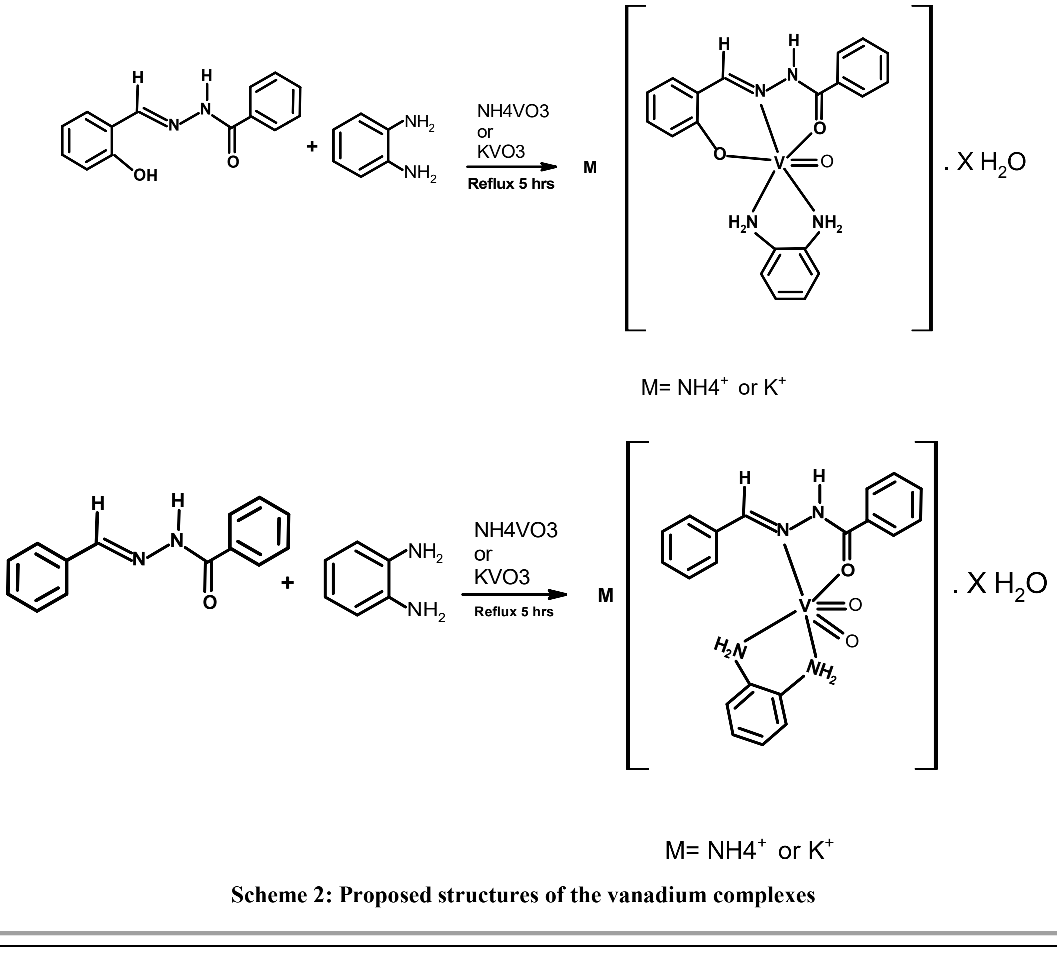


Fig.15. Mass spectra for $K[VO_2\ (L_3)\ L_5]\ 2.5H_2O$ (6) complex



Scheme 2: Proposed structures of the vanadium complexes

Table 4: Antimicrobial activity of the ligand (L_1) and Vanadium (V) Complexes

Antibacterial Activity 200 (100) µg/disc							Antifungal Activity
Compound	**Gram Positive Bacteria**			**Gram Negative Bacteria**			**Yeast**
	S.e	**S. a**	**E. f**	**E. a**	**P. m**	**P.a**	**C. a**
L_1	**0**	**0**	**0**	**0**	**0**	**0**	**9**
$NH_4[VO(L_1)L_5]2H_2O$ (1)	**7**	**7**	**0**	**0**	**0**	**0**	**18**
$K[VO(L_1)L_5]6H_2O$ (2)	**0**	**0**	**13**	**0**	**0**	**0**	**20**

S.e: *Staphylococcus epidermidis* (ATCC 12228); S.a: *Staphylococcus aureus* (ATCC 25923); E.f: *Enterococcus faecalis* (ATCC 29212); E.c: *Escherichia coli* (ATCC25922); P.m: *Proteus merabilis* (ATCC 13376); P.a: *Pseudomonas aerugenosa* (ATCC 27853); C.a: *Candia albican*(ATCC10231).

CONCLUSION

New vanadium (V) complexes with some mixed ligands containing hydrazone moiety and o-phenylenediamine have been synthesized. The ligands (L_2-L_4) and vanadium (V) complexes have been characterized by Elemental analyses, IR, UV-Vis, ^{1}H-NMR, Mass spectra, molar conductance and thermal analysis. On the basis of the observed data we found that the ligands (L_2-L_6) behave as bidentate ligands while the ligand(L_1) behaves as tridentate ligand. Also, The analyses data of the mixed ligand vanadium (V) complexes suggested that the complexes (3-8) with bidentate ligands (L_2-L_4) have dioxo-group in the *cis*-configuration attached to the vanadium center and show an octahedral geometries. While, The vanadium (V) complexes (1 and 2) with tridentate ligand(L_1) were having one oxo group attached to the vanadium center and their structure are expected to be octahedral geometry. The antibacterial results show that the ligands show less antibacterial activity, on the other hand the antifungal activity of vanadium (V) complexes showed higher activity compared to the free ligands.

ACKNOWLEDGEMENTS

The authors are thankful to King Abdulaziz City for Science and Technology (KACST), Riyadh, Saudi Arabia for providing the financial support to this project (Grant No. 1-17-01-013-0004) and Albaha University for providing the necessary facilities to Department of Chemistry.

4. REFERENCES

[1] Anjaneyulu Y., Swamy R.Y. and Rao R. P., Proc. Indian Acad. Sci. (Chem. Sci.) 93(2) (1984) 131-138.

[2] Ali M. A., Kabi M. H., Uddin M. N., Majumder S. M. M., Tarafder M. T. H. And Khair M. A., Indian J. Chem., 27A (1988) 1064.

[3] Reddy K. H., Reddy P. S. and Babu P. R., Transition Met. Chem., 25(3) (2000) 505-510.

[4] Dawood Z. F., Sci. & Tech., 17 (2002). 35-38.

[5] Dawood Z. F., Hussein S. H. and Al-Shama'a M. A., Sci. & Tech. A.21 (2004) 71-75.

[6] Abeer T. Abdelkarim International Journal of Pharma Sciences 5(1) (2015) 839-851.

[7] Kachare A. A., Kumbalpuri S. A., Shankarwar S. G. and Chondhekar T. K., Der ChemicaSinica, 6(7) (2015) 87-92,

[8] Borhadeshobha, JPSI 1(3) (2012)18-22.

[9] Wever R., Kustin K., in: Advances in Inorganic Chemistry: Vanadium, a Biologically Relevant Element; Sykes, A. G. Ed.; Academic Press, New York, (1990) Vol. 35, p. 103.

[10] Butler A., Science 281 (1998) 207.

[11] Sigel H. and Sigel A., (Eds.), Vanadium and its Role in Life. Metal Ions in Biological Systems, Marcel Dekker, New York, Basel, Hong Kong, 1995.

[12] Ahmed M., Schwendt P., Marek J., Sivák M., Polyhedron 23 (2004) 655.

[13] Abdelbaset M., Zabin S. A., Int. J. Adv. Res. 4(12) (2016) 1861-1871.

[14] Gahlan A. A., El-Sayed A. Y., Marouf M. A. and Tawfik M.M., Int. J. Adv. Res. 3(1) (2015) 630-642.

[15] Abdelbaset M., Zabin S. A., Alorabi A. Q., IJBPAS, 8 (3) (2019) 627-644.

[16] Nechay B. R., Nanninga L. B., Nnechay P. S. E., Post R. L., Granthem J. J., Macara I. G., Kubena L. F., Phillips T. D., and Nielsen F. H., Fed. Proc. 45 (1986) 123.

[17] Jubie S, Ashish W, Sabaritha K, Nishanthini P, Anupriya Thomas, Jibi Antony, J. Pharm. Sci. & Res. 8(7), (2016), 582-585

[18] Yaul A., Pathe G., Deshmukh R., Aswar A. Vanadium complexes with quadridentate Schiff bases: Synthesis, Characterization, thermal and catalytic studies. J. Therm. And Calorim., 113: (2013) 745-752.

[19] Monfareda H.H., Lalami N.A., Pazio A., Wozniak K., Janiakc C., Dinuclear Vanadium, Copper, Manganese And Titanium Complexes Containing O,O,N-Dichelating Ligands: Synthesis, Crystal Structure And Catalytic Activity. Inorg. Chim. Acta. 406 (2013) 241-250.

[20] Armstrong C. M., Bernhardt P. V., Chin P., Richardson D.R., Structural Variations and Formation Constants Of First-Row Transition Metal Complexes Of Biologically Active Aroylhydrazones. Eur. J. Inorg. Chem., (2003) 1145-1156.

[21] Hosseini-Monfared H., Bikas R., Mayer P., Homogeneous Green Catalysts for Olefin Oxidation By Mono Oxovanadium(V) Complexes Of Hydrazone Schiff Base Ligands. Inorg. Chim. Acta, 363 (2010) 2574-2583.

[22] Abdelkarim A. T., International Journal of Pharma Sciences 5(1) (2015) 839- 851.

[23] Sarkar, A.; Pal, S. Polyhedron, 26 (2007) 1205.

[24] Sahoo S. K., Baral M., Kanungo B. K., Polyhedron 25 (2006) 722-736.

[25] Singh, K.; Kumar, Y.; Puri, P.; Singh, G. Bioinorg Chem. Appl. 2012 (2012) 9.

[26] Zabin, S. A. and Abdelbaset, M. "Oxo/ dioxo-vanadium (V) complexes with Schiff base ligands derived from 4-amino-5-mercapto-3- phenyl-1, 2,4- triazole". European Journal of Chemistry, 7(3) (2016) 322-328.

[27] Barakat A. S., Gaballa A. S., Mohammed S.F., Teleb S.M. Vibrational and thermal studies of the complexes $(NH_4)[VO(O_2)_2(phen)]\cdot 2H_2O$ and $(NH_4)[V(O_2)_3(phen)]\cdot 2H_2O$. Spectrochimica. Acta Part A., 62 (2005) 814–818.

[28] Silvertistein R. M., Bassler G. C. and Morrill T.C, “Spectormetirc Identification of Organic Compounds”, 4th Ed., John Wiley and Sons, 1981.

[29] Shakir M., Parveen S., Begum N., and Azim Y., Polyhedron, 22(24) (2003) 3181.

[30] Shakir M., Parveen S., Begum N., and Chingsubam P., Transition Metal Chemistry, 29 (2004) 196.

[31] Hammam A. M., EL-Gahami M. A., Khafagi Z. A., AL-Salimi M. S. and Ibrahim S. A., J. Mater. Environ. Sci. 6 (6) (2015) 1596.

[32] Kalshetty B. M., Gani R. S., Karabasannavar S. S. & Kalashetti M. B., Global Journal of Science Frontier Research Chemistry, 13 (2) (2013). Version 1.0

[33] Zhao P. S., Ming Xu J., Zhang W. G., Jian F. F., and Zhang L., Struct. Chem.18 (2007) 993.

[34] Shaghaghi Z. SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy, 131 (2014) 67-71.

[35] Anacona J., Rodriguez J., Camus J. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 129 (2014) 96-102.

[36] Maurya M. R., Khurana S., Zhang W., Rehder D., J. Chem. Soc., Dalton Trans., 2002, 3015– 3023.

[37] Mahajan S., Singh B., Sheikh H. N., Kalsotra B. L. ChemSci Trans., 1(1) (2012) 23.

[38] Subhapradha D., Dharmendra K., Pramod N., Swathi K., IJAPR 6(07) (2015) 192 – 200.

[39] Mitić D. M., Miodragović Đ. U., Sladić D. M., Vitnik Ž J., Miodragović Z. M., Anđelković K. K., Radulović M. Đ., Juranić N. O.. J. Serb. Chem. Soc. 73 (8–9) (2008) 815–824.

[40] Krishnamoorthy P., Sathyadevi P., Butorac R. R., Cowley A. H., Bhuvanesh N. S. P., Dharmaraj N., Dalton Trans., 41 (2012) 4423–4436.

[41] Haddad R., Yousif E., Ahmed A., Springer Plus 2 (2013) 510.

[42] Bogdan M., Floare C. G., Pîrnău A., Journal of Physics: Conference Series 182 (2009) 012002.

[43] Barakat A. S., Sadeek S. A., International Journal of Advanced Research 2 (11) (2014), 300-314.