



**SYNTHESIS AND *IN VITRO* BIOLOGICAL EXAMINATION OF  
DIOXOVANADIUM (V) MIXED- LIGAND COMPLEXES CONTAINING  
4-AMINO-5-MERCAPTO-3-PHENYL-1,2,4-TRIAZOLE AS PRIMARY  
LIGAND AND O-ANILINE DERIVATIVES AS CO-LIGANDS**

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**ABSTRACT**

Mixed-Ligand complexes are interesting compounds that have distinguished structural features and applications. In this report we synthesized new dioxovanadium (V) complexes from 4-amino-5-mercapto-3-phenyl-1,2,4-triazole ( $L_1$ ) as primary ligand and *o*-aniline derivatives as co-ligands ( $L_{2-4}$ ). Dioxovanadium (V) mixed-ligand complexes were synthesized in 1:1:1 ( $L_1$ :M: $L_{2-4}$ ) molar ratio. Structural elucidation was determined using different characterization and analytical techniques that support an octahedral geometry for the synthesized complexes with a general formula of  $[L_1VO_2L_{2-4}]$ . The molar conductance measurements showed electrolytic properties for the mixed-ligand dioxovanadium (V) complexes. The *in vitro* antimicrobial experiments indicated weak antibacterial potential and moderate antifungal capacity.

**Keywords: Dioxovanadium (V) complexes; 1,2,4-triazole, Mixed-ligand; Antimicrobial**

**1. INTRODUCTION**

Mixed-ligand complexes are a huge important family of coordination compounds that have interesting structural features.

Synthesis of mixed ligand complexes and their characterization have been an interest of many researchers since long far due to

their bioinorganic and pharmaceutical applications and significant role in biological process [1-2]. They are important models for metalloenzyme-substrate complexes and they are models for multimetal-multiligand species in biochemical systems [3]. They showed potential applications in promotion of oxidative cleavage of plasmid DNA [4-5]. And exhibit cytotoxicity by inducing apoptosis [6]. Some mixed metal complexes reported as potential anticancer agents and showed efficient DNA-cleaving ability [7]. They have dramatic influences on the catalytic properties of catalysts [8].

During the last few decades large number of mixed-ligand coordination compounds containing heterocyclic organic ligands have been reported [9]. It has been shown that it is very common a metal ion can be coordinated to more than one type of organic ligands at one time [8].

It is well established in the literature that 1,2,4-triazole derivatives are very adequate ligands for transition metals [10-11]. The compounds with 1,2,4-triazole nucleus was utilized as a scaffold to prepare somatotropin release inhibiting factor (SRIF) nonpeptide ligands [12]. These heterocyclic chemicals are an excellent scaffold due to amide bond isostere with possibly enhanced bioavailability and having multiple possible sites of attachment [12]. 1,2,4-triazole ligands show enormous coordination diversity, especially when

the triazole nucleus is substituted with additional donor groups [13]. This property together with their strong  $\sigma$  donor properties and the relative ease of synthesis make them very attractive for designing new metal complexes with interesting properties [10].

Literature survey revealed that heterocyclic compounds bearing triazole moiety possess significant therapeutic activities due to their conformational rigidity and improved physical properties, such as charge density or lipophilicity, metabolic stability and oral bioavailability [13]. Their biological activity is enhanced on coordination with metal ions [14-15]. Among the heterocyclic triazole derivative is 3-mercapto-1,2,4-triazole which is observed to have wide spectrum of biological activities and has the ability to coordinate metal ions [16].

Vanadium (V) is an important trace metal has some physiological roles in many biological systems as insulin-enhancing action and anticancer potential [17]. Vanadium Oxo moieties are found in the active sites of vanadium-dependent enzymes [18]. They are used by some ocean algae as cofactor and as an active center of enzymes in the haloperoxidase (e.g. vanadium bromoperoxidase) [19]. It is evident in producing naturally-occurring organobromine compounds and involved in the biosynthesis of many marine natural products [20-23]. Peroxovanadium (V)

complexes have been the focus of research due to their significance role in many biological systems. They are reported to have insulin mimetic effects, antitumor capacity as well as osteogenic and cardioprotective activity [22, 24-26]. Novel Medicinal applications of vanadium compounds since the beginning of the 21<sup>st</sup> century are geared towards chronic diseases like viral infections, HIV, leishmania and SARS [27]. Organic ligands assist and improve the bioavailability, transport and targeting mechanism of vanadium compounds [27].

Vanadium in the +5 oxidation state readily forms V–O bonds and comfortably binds N and S as well, forming chemically firm coordination compounds with flexible coordination geometries [28]. Many Vanadium (V) complexes with different coordination ligands have been investigated and studied for their applications in different fields [20, 29]. Recently we have published our work on Oxo/dioxo-vanadium (V) complexes with Schiff base ligands derived from 4-amino-5-mercapto-3-phenyl-1,2,4-triazole [15].

Choosing a compound with 1,2,4-triazole moiety as a basic primary ligand with o-aminophenol substituents as co-ligands could provide a worth coordination environment around the vanadium ion. In

addition, and in continuation to our work on ligands containing 4-amino-5-mercapto-3-phenyl-1,2,4-triazole and encouraged by the thorough literature survey, in the present study, our focus is an attempt to prepare and characterize mixed-ligand dioxovanadium (V) complexes with 4-amino-5-mercapto-3-phenyl-1,2,4-triazole as primary bidentate ligand and 2-aminophenol, 2-aminothiophenol or o-phenylenediamine as bidentate co-ligands. As the metal complexes formed by the combination of transition metal ion with some potent ligands are expected to be more biologically active than the metal salt or the ligands individually, therefore we tried to examine the antimicrobial capacity of the synthesized mixed-ligand vanadium complexes.

## 2. MATERIALS AND METHODS

### 2.1 Materials and Starting Compounds Synthesis

4-amino-5-mercapto-3-phenyl-1,2,4-triazole was synthesized according to the reported procedure [15, 30]. All other chemicals used in this study were of analytical grade purchased from local market and used directly without purification.

### 2.2 General Procedure for Preparation of Mixed-ligand Dioxovanadium (V) Complexes

The dioxovanadium (V) mixed-ligand complexes were synthesized following general procedure according to scheme 1 shown below. All complexes were prepared

using 1:1:1 ( $L_1:M:L_{2-4}$ ) molar ratio. To a mixture of hot ethanolic solution of 4-amino-5-mercapto-3-phenyl-1,2,4-triazole ( $L_1$ ) (0.01mol) and *o*-phenylenediamine ( $L_2$ ), or 2-aminophenol ( $L_3$ ), or 2-aminothiophenol ( $L_4$ )(0.01mol), an aqueous hot solution of ammonium metavanadate ( $NH_4VO_3$ ) or potassium metavanadate ( $KVO_3$ )(0.01mol) was added slowly dropwise with continuous stirring and refluxing for 5 hours. The complexes precipitated out from the solution were filtered washed with proper solvents and dried in open air. The purity of the compounds was checked with TLC paper where one spot was observed confirming the formation of single complex. All the synthesized complexes were colored solid powders with reasonable yield and melting points above 300 °C.

$NH_4[VO_2(L_1)(L_2)].0.5H_2O$ (**1**) :solid black powder, % yield = 80%; elemental analysis calculated (found) C:41.07 (41.50 ); H:4.88 (4.98); N: 23.96 (24.65); O: 9.77(10.25); S: 7.82(8.12); V: 12.46 (12.55). IR data ( $cm^{-1}$ ): 990  $\nu(V=O)$ , 500  $\nu(V-N)$ , 440  $\nu(V-S)$ , 1440  $\nu(NH^+)$  , 3120  $\nu(H_2O)$ .

$NH_4[VO_2(L_1)(L_3)].3.5H_2O$ (**2**): solid black powder, % yield = 75%; elemental analysis calculated (found) C: 36.28 (40.35); H: 36.28 (40.35); N: 18.14(19.80); O: 22.46(14.95); S: 6.91(8.10); V:

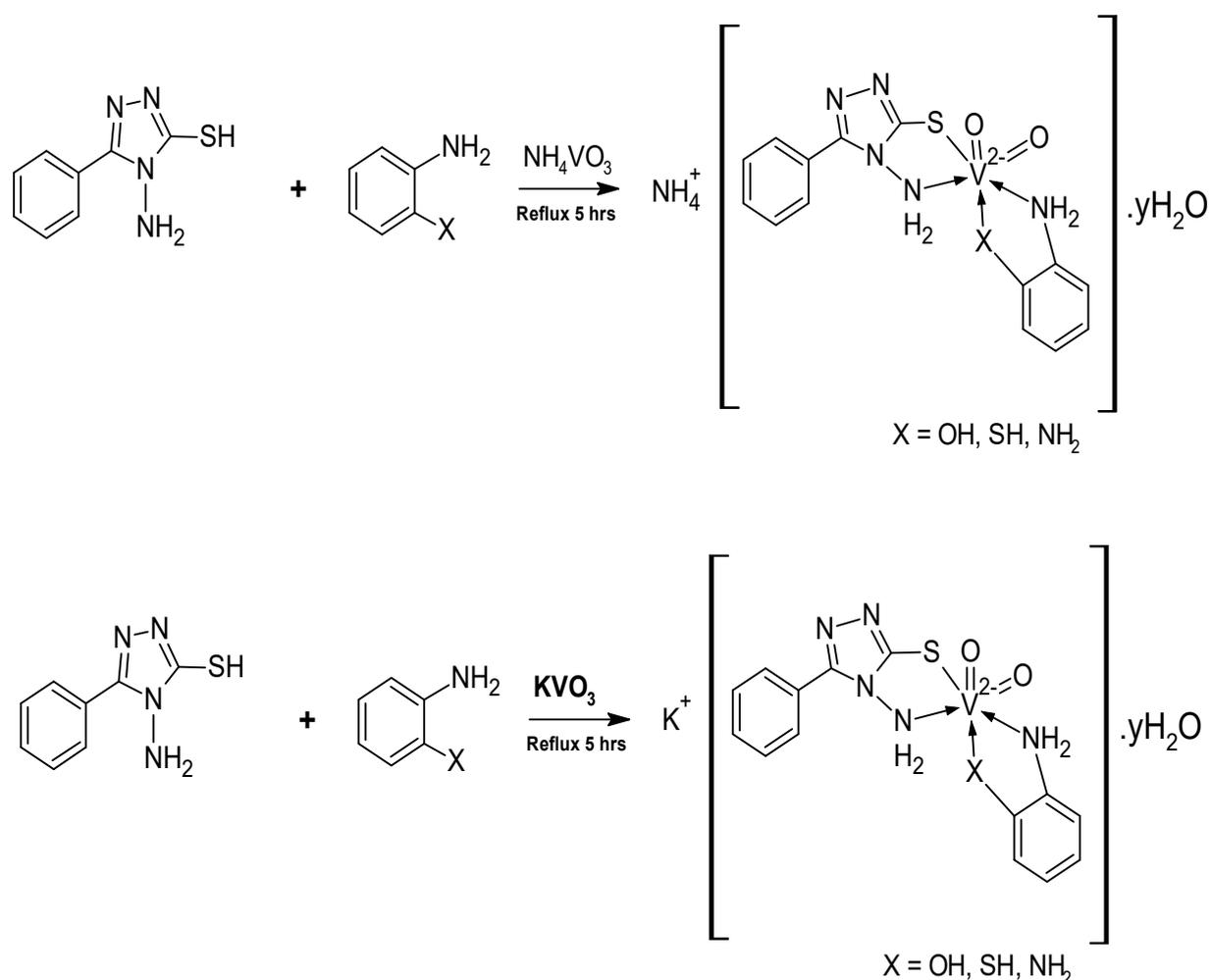
11.01(11.85). IR data ( $cm^{-1}$ ): 993  $\nu(V=O)$ , 595  $\nu(V-O)$ , 505  $\nu(V-N)$ , 445  $\nu(V-S)$ , 1455  $\nu(NH^+)$  , 3150  $\nu(H_2O)$ .

$NH_4[VO_2(L_1)(L_4)]$  (**3**) : solid black powder, % yield = 68%; elemental analysis calculated (found) C: 40.38 (40.80); H: 4.12 (4.45); N: 20.20 (20.62); O: 7.69 (8.12); S: 15.37 (15.65); V: 12.24 (12.65). IR data ( $cm^{-1}$ ): 950  $\nu_{as}(V=O)$ , 820  $\nu_s(V=O)$  , 500  $\nu(V-N)$ , 470  $\nu(V-S)$ , 1450  $\nu(NH^+)$ .

$K[VO_2(L_1)(L_2)]$  (**4**) : solid dark brown powder, % yield = 72%; elemental analysis calculated (found) C: 39.89 (40.22); H: 3.59 (3.25); N: 19.95 (20.36); O: 7.60 (7.86); S: 7.59 (7.95); V: 12.10 (12.45). IR data ( $cm^{-1}$ ): 975  $\nu_{as}(V=O)$ , 860  $\nu_s(V=O)$  , 500  $\nu(V-N)$ , 460  $\nu(V-S)$ .

$K[VO_2(L_1)(L_3)].H_2O$  (**5**) : solid shiny black powder, % yield = 65%; elemental analysis calculated (found) C: 38.26 (37.85); H: 3.44 (3.75); N: 15.94 (16.26); O: 14.57 (15.74); S: 7.28 (6.96); V: 11.60 (12.05). IR data ( $cm^{-1}$ ): 980  $\nu_{as}(V=O)$ , 832  $\nu_s(V=O)$  , 590  $\nu(V-O)$ , 540  $\nu(V-N)$ , 480  $\nu(V-S)$ , 3300  $\nu(H_2O)$ .

$K[VO_2(L_1)(L_4)]$  (**6**) : solid dark green powder, % yield = 74%; elemental analysis calculated (found) C: 38.44 (38.64); H: 3.00 (2.86); N: 16.02 (15.75); O: 7.32 (6.85); S: 14.63 (14.45)V: 11.65 (11.86). IR data ( $cm^{-1}$ ): 990  $\nu(V=O)$ , 520  $\nu(V-N)$ , 470  $\nu(V-S)$ .



Scheme 1

### 2.3 Characterization and Analysis Techniques

Melting points of the synthesized complexes were measured using Electrothermal (Cat NO. TA9100) melting point apparatus. Elemental analysis for C, H, N and S) were carried out in our laboratory 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  $\text{cm}^{-1}$ . Evolution 300 UV-visible double beam Spectrophotometer was used to record UV-visible spectra using DMF as solvent. Mass spectra were recorded on a Thermo Fisher Exactive + Triversa Nanomate mass spectrometer. Molar conductivities of freshly prepared DMF solutions of the vanadium (V) complexes at a concentration of 0.001M were measured using Hanna instrument HI8633N Multi-range conductivity meter. For determining the magnetic susceptibility at room

temperature we used Gouy's method apparatus balance (Holmarc's Magnetic Susceptibility –Gouy's Method Apparatus (Model No: HO-ED-EM-08)) and with  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant.

$^1\text{H}$  NMR spectra were recorded in  $\text{DMSO-d}^6$  using 300 MHz Varian NMR spectrometer (Micro-analytical Center, Cairo University, Egypt). The molar conductivity measurements were made in DMF solution ( $10^{-3}$  M) using a Tacussel conductometer type CD6N. Thermal analysis (DTA/TGA) were obtained out by using a Shimadzu DTA/TGA-50 thermal analyzer (Micro analytical Center, Cairo University, Egypt) with a heating rate of  $10^\circ\text{C}/\text{min}$  in nitrogen atmosphere in the temperature range  $25\text{--}800^\circ\text{C}$  using platinum crucibles.

#### 2.4 Assessment of Antimicrobial Capacity

The antimicrobial capacity of the prepared mixed-ligand vanadium (V) complexes was tested against one local Gram-positive bacteria isolates *Staphylococcus aureus* and one local Gram-negative bacteria strains *Escherichia coli*. Moreover, the activities were examined against one local fungal isolate *Candida albicans*. The investigation was carried out in Blood Bank Centre at Albaha city-KSA, utilizing disc-diffusion standard technique using Mueller Hinton Agar (MHA) as growth medium following the Clinical and

Laboratory Standards Institute (CLSI) for bacteria and yeasts testing [15]. 0.01gm of each tested compound was dissolved in 5 mL DMSO solvent and used as stock solution. The concentration used for each test was  $10^{-3}$  g/mL. Sterile cork-borer (10mm) was used to make holes in the agar medium plates that were seeded with the test organism. The plates were kept in the refrigerator at nearly  $5^\circ\text{C}$  for one hour to allow the tested compounds to diffuse in the agar medium. The plates were then incubated at  $37^\circ\text{C}$  for 24 hours for bacteria and at  $30^\circ\text{C}$  for 72 hours in case of fungal strains. The bacterial and fungal potential activity was monitored by measuring the zones of completely growth inhibition (in mm) around the holes after the incubation period. Each test was repeated twice and means values were calculated.

### 3. RESULTS AND DISCUSSION

#### 3.1 Chemistry, Elemental Analysis and Mass Spectra

Dioxovanadium (V) Complexes were prepared using two bidentate ligands, 4-amino-5-mercapto-3-phenyl-1,2,4-triazole ( $\text{L}_1$ ) as primary ligand and o-aniline derivatives ( $\text{L}_{2-4}$ ) as secondary ligands. The yields obtained were in reasonable range of 65 -80%. All complexes were prepared following the same procedure using 1:1:1 ( $\text{L}_1$ : M:  $\text{L}_{2-4}$ ) molar ratio. The stoichiometry for the complexes have been manifested from the elemental analysis observations. It

confirms that the vanadium complexes were 1:1:1 (ligand: Metal: co-ligand). Moreover, the elemental analysis data get on well with the proposed structural formulae of the dioxovanadium (V) complexes as shown in the materials and methods section (scheme 1). All obtained compounds were dark-colored solid powders with melting points above 300 °C. They were stable at room temperature, insoluble in water and common organic solvents, but soluble in DMF, DMSO and acetonitrile solvents.

The mass spectra were recorded in order to confirm the theoretically calculated molecular weight according to the proposed structure. For the complex  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_2)] \cdot 0.5 \text{H}_2\text{O}$  (**1**) the observed peak was at 409.83 (figure 1) which is matches the theoretically calculated molecular weight of (409.08). The mass spectrum for  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_3)] \cdot 3.5\text{H}_2\text{O}$  (**2**) show a peak at 462.75 (figure 2) which is equivalent to the calculated M.Wt. (463.0). For  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_4)]$  (**3**) the observed peak was at 416.25 that is equivalent to the calculated M. Wt. (416.0).

The observed peak for  $\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_2)]$  (**4**) was at 421.73 matches the calculated M.Wt. (421.0), for the complex  $\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_3)] \cdot \text{H}_2\text{O}$  (**5**) the observed peak was at 438.25 matches the theoretical M.Wt. (439.0). Finally for the complex  $\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_4)]$  (**6**) the observed mass spectrum peak at 437.40 that equivalent to

the calculated M.Wt. (437.0). The recorded mass spectrum as mentioned before were identical with the theoretically calculated molecular weights according to the proposed structures and this proves and supports the proposed structures.

### 3.2 Molar conductance

The molar conductance of the complexes in  $10^{-3}$  M DMSO solution was measured at room temperature (23.6 °C) and the observed results are shown in table 1. The molar conductance values lies in the range (76.1–108.2  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ ) indicates the electrolytic behavior of the prepared complexes [31]. This indicates that the dioxovanadium (V) complexes are 1:1 electrolytic in nature and supports the presence of ions outside the coordination sphere of the vanadium complexes.

### 3.3 IR Spectroscopic Measurements

IR spectra were recorded for all complexes in order to determine the coordination sites that may involve in chelation to the vanadium central atom. The important data of the recorded IR spectra of the synthesized mixed-ligand metal complexes are shown in the materials and methods section. Figures 3-4 shows a representative IR spectrum recorded for the complexes.

In the IR spectrum of the complexes there are intense bands in the region range 440-480, 500-540 and 595-590  $\text{cm}^{-1}$ , which can be assigned to  $\nu(\text{V-S})$ ,  $\nu(\text{V-N})$  and  $\nu(\text{V-O})$

respectively [15, 31]. This proves the coordination of the ligands to vanadium metal through N, O, and S atoms present in the ligands.

In the IR spectra of the solid complexes a strong bands appeared at the range 950-990  $\text{cm}^{-1}$  and broadened bands in the region 820-860  $\text{cm}^{-1}$ . These bands may be assigned to asymmetric and symmetric  $\nu(\text{O}=\text{V}=\text{O})$  stretching vibrations of *cis*- $\text{VO}_2$  groups which agree within the expected band range for dioxovanadium (V) compounds having such coordination geometry [18, 31-36]. In some complexes the appearance of one single peak in the spectra indicates that the two  $\text{V}=\text{O}$  groups are indistinguishable. The low frequency of symmetric  $\text{VO}_2$  stretch may be attributed to the intra-molecular hydrogen bonding and the coordination of Oxo groups to the ammonium or potassium cations [37].

In the IR spectra of some complexes a strong band and in some others medium band appeared in the range 1440-1455  $\text{cm}^{-1}$  which are correspondent to the deformation modes of the  $\delta(\text{NH}_4^+)$  ion [15, 38].

The broad bands at 3120, 3320 and 3300  $\text{cm}^{-1}$  in the complexes **1,2** and **5** respectively suggest the presence of lattice water in these complexes [15].

It is well known that Vanadium (V) prefer hexa-coordination rather than penta-coordination that is the driving force towards the coordination with two Oxo groups. The

vanadium(V) atom is hexa-coordinated with two bidentate ligands through the N and S atoms of the primary bidentate ligand ( $\text{L}_1$ ) and the N and O or S or N atoms of the co-ligands ( $\text{L}_2 - \text{L}_4$ ), in addition to two Oxogroups in *cis*-position to each other to complete the octahedral sphere [39-40]. The results also are in agreement with the fact that coordination chemistry of  $\text{V}^{5+}$  is dominated by the relatively stable dioxovanadium coordination complexes [41].

### 3.4 Electronic spectra and Magnetic Susceptibility

The electronic absorption bands in the spectra of the complexes recorded in  $10^{-3}$  M DMSO solution at room temperature. The UV-Visible spectrum of complexes display peaks at 430, 425, 440 and 435 nm which are assigned to ligand-to-metal charge transfer (LMCT) transitions from the  $\text{P}^\pi$  orbital on the nitrogen, oxygen and sulfur to the empty d orbitals of the metal [28, 35]. Whereas the other bands in the higher energy region (300–315 nm) for the complexes are likely to be due to intra-ligand  $\pi-\pi^*$  transitions [28, 35]. There was no d-d transition bands appeared in the UV-visible spectrum of the complexes as it is expected for dioxovanadium (V) complexes which is in agreement with the vanadium(V) oxidation state ( $\text{V}^{+5}$ ) because they have a  $3d^0$  configuration and there are no d electrons [40, 42].

The magnetic moment measurements showed that the synthesized complexes are diamagnetic in nature, which is evident for vanadium (V) complexes [ $d^0$  vanadium(V)] [35, 40].

### 3.5 $^1\text{H-NMR}$ spectra

$^1\text{H-NMR}$  spectra of the ligands and their vanadium (V) complexes (complexes **1** and **6**, figures 5) have been recorded in  $\text{DMSO-d}_6$  using tetramethyl silane (TMS) as internal standard. The  $^1\text{H NMR}$  spectra of the ligand show the  $-\text{SH}$  proton at 10.18 ppm, which was disappeared in the spectrum of the vanadium complexes supporting the deprotonation of the thiol group and coordination through the sulphur atom with the central metal ion [43-44]. Also, in the  $^1\text{H NMR}$  Spectra the signals of  $\text{NH}_2$  protons appear at  $\delta 5.14$  ppm, these signals shifted to high field in the spectra of the Vanadium (V) complexes indicating bonding through the nitrogen atom of the amine group to the central vanadium ion [45].

### 3.6 TGA Analysis

In order to support the proposed structures of the synthesized complexes we have performed TGA analysis. The thermogravimetric analysis for  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_2)] \cdot 0.5\text{H}_2\text{O}$  (**1**) complex (Figure 6). For the decomposition of this complex two weight loss steps were observed in the curve, the first ended at nearly  $100^\circ\text{C}$ ,

corresponding to the loss of 2.56 % that is closed to the calculated value of 2.22% of the sample which may be due to the presence of lattice water molecule that take place in the first step. This weight loss is in good agreement with the removal of half water molecule ( $0.5\text{H}_2\text{O}$ ). The thermogram exhibits completion of weight loss between  $100$  and  $600^\circ\text{C}$  that is may be due to the decomposition of the ligands leading to the final residue at  $600^\circ\text{C}$  as metal oxide ( $\text{V}_2\text{O}_5$ ). The remaining weight (obs./cal. 49.85/44.5) corresponds to a mixture of metal oxide in nitrogen atmosphere and some ashes as ultimate pyrolysis product. The results show good agreement with the formulae suggested from the analytical data.

### 3.7 Antimicrobial activity

Antimicrobial activities of the prepared mixed-ligand vanadium complexes were examined against *S. aureus* (G +ve) and *E. coli* (G -ve) bacterial strains, and *C. albicans* as fungal strain. The screening of the compounds were carried out at fixed concentration of  $10^{-3}$  g/mL in DMSO solvent. Zones of inhibition were measured in mm after 24 hours incubation period in case of bacterial strains and after 72 hours in case of fungal strains. The observations shown in table 2 indicate weak antibacterial and moderate antifungal activities.

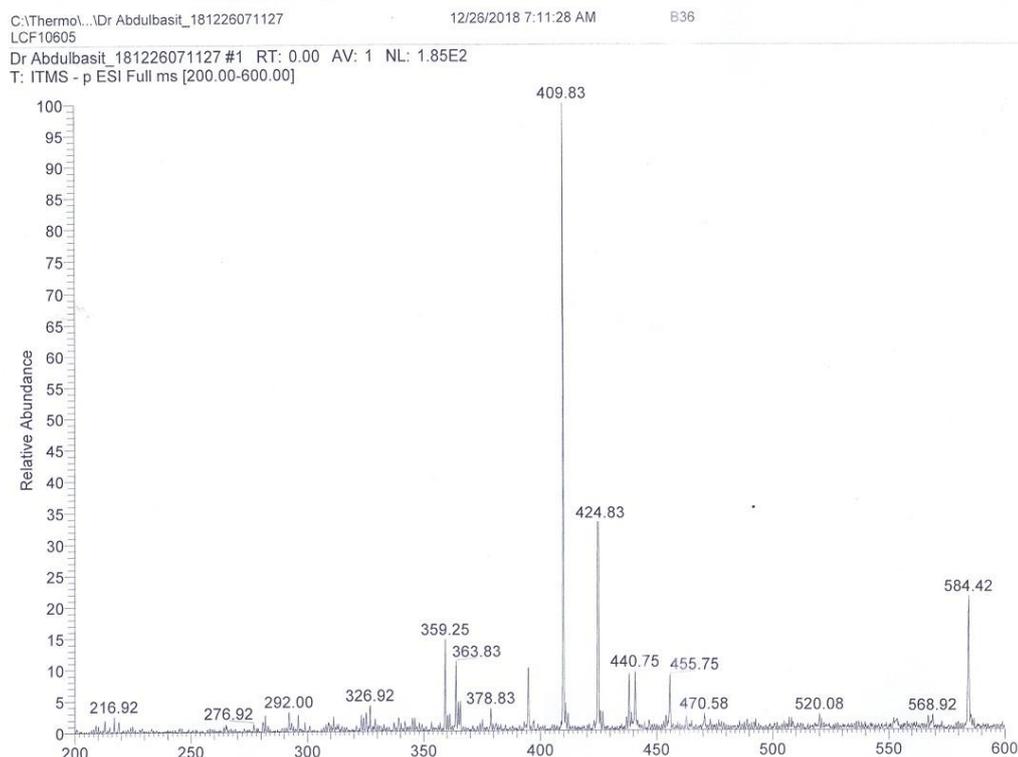
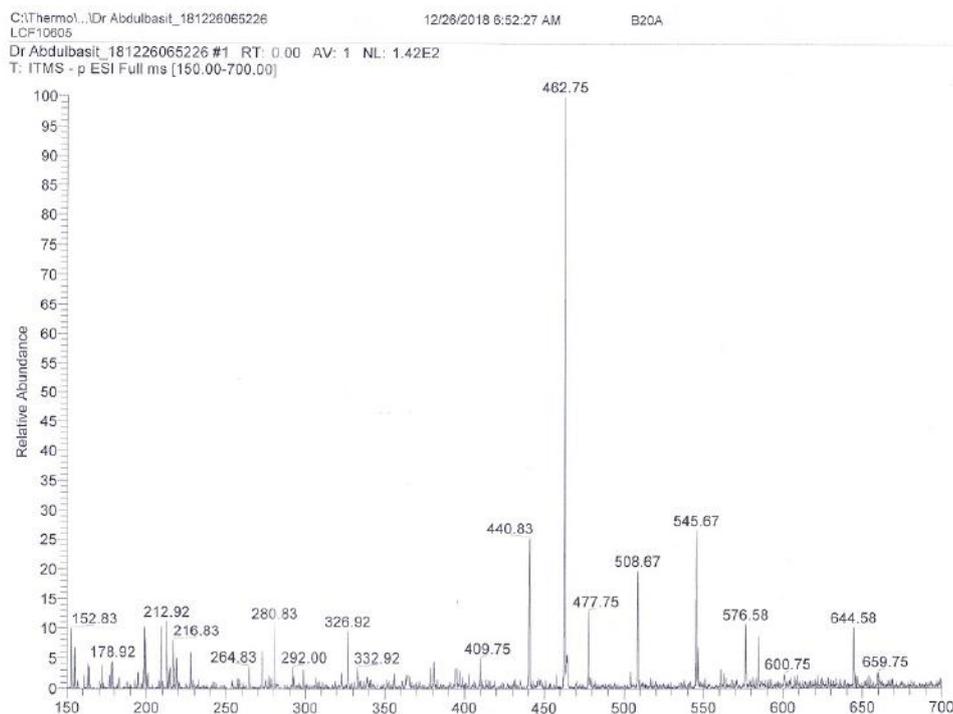
Figure 1: mass spectra for  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_2)] 0.5 \text{H}_2\text{O}$  (1)Figure 2: Mass spectra for  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_3)] 3.5\text{H}_2\text{O}$  (2)

Table 1: The molar conductance measurements for the prepared dioxovanadium (V) Complexes

Compound	Molar conductance( $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )
$\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_2)] 0.5 \text{H}_2\text{O}$ (1)	92.2
$\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_3)] 3.5\text{H}_2\text{O}$ (2)	86.4
$\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_4)]$ (3)	76.1
$\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_2)]$ (4)	98.6
$\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_3)] \cdot \text{H}_2\text{O}$ (5)	108.2
$\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_4)]$ (6)	97.0

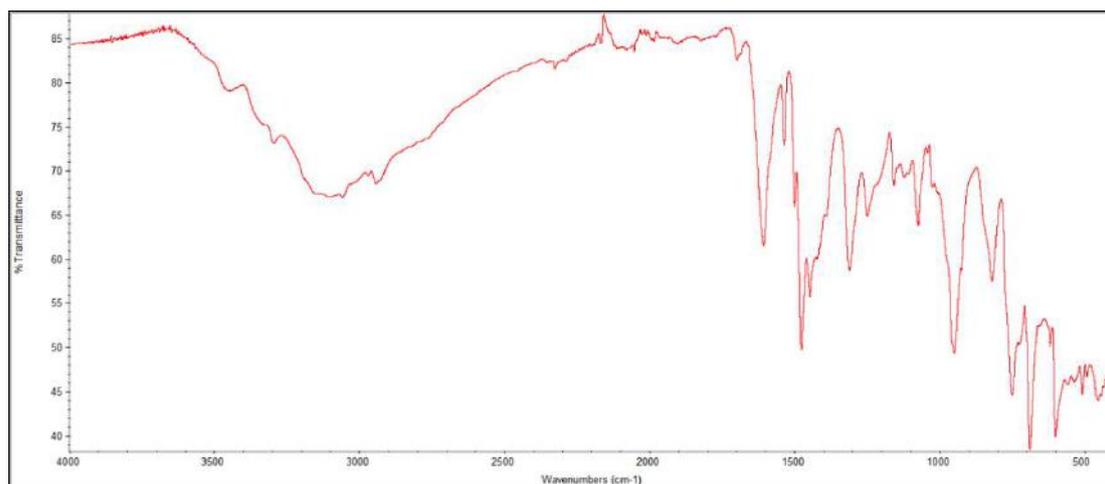


Fig. 3: IR spectrum for  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_3)] \cdot 3.5\text{H}_2\text{O}$  (2) complex

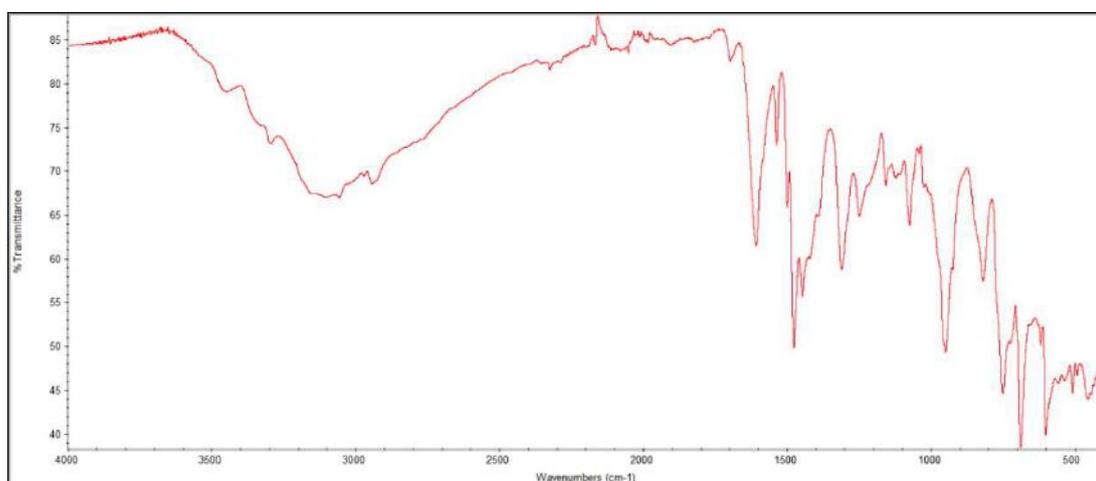


Fig.4: IR spectrum for  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_4)]$  (3) complex

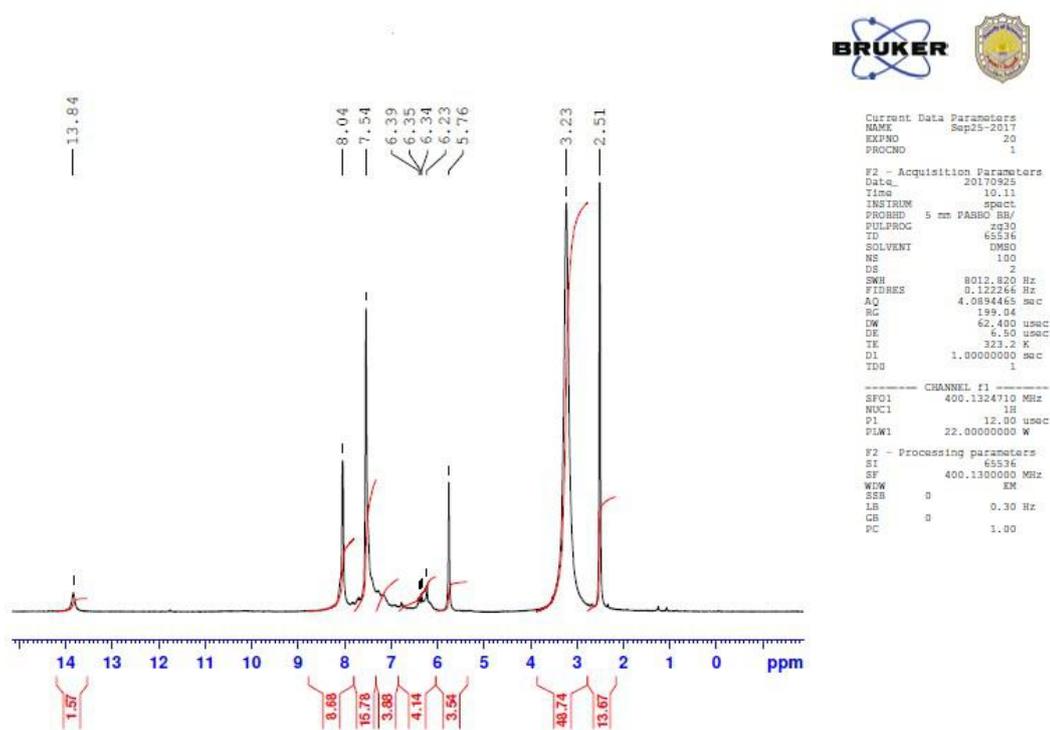


Figure 5:  $^1\text{H}$  NMR spectrum of  $\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_4)]$  (6) complex

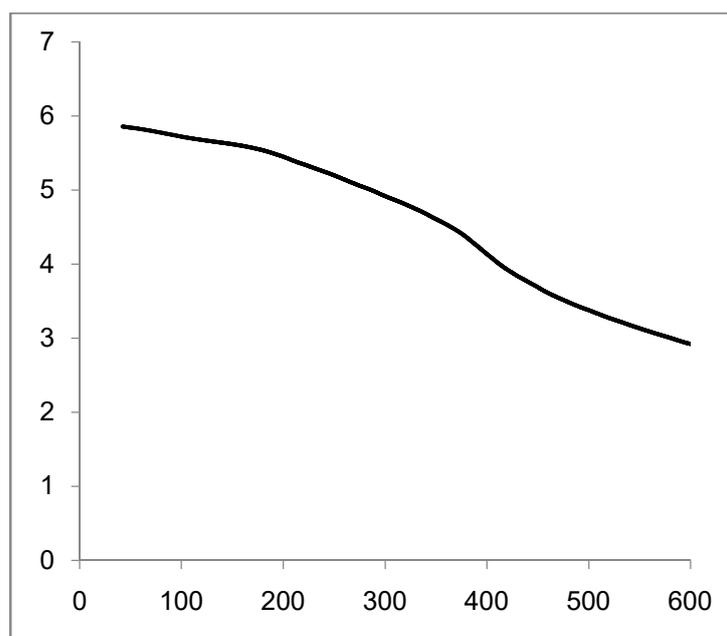


Figure 6: Thermogravimetric (TGA) curve of  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_2)] \cdot 0.5\text{H}_2\text{O}$  (1) complex

Table 2: Antibacterial and antifungal activity of the ligands and their Cu (II), Ni(II) and Zn(II) complexes

Compound	Zone of inhibition (mm)		
	<i>S.aureus</i> (G +ve)	<i>E.col</i> (G -ve)	<i>C. albicans</i>
$\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_2)] \cdot 0.5 \text{H}_2\text{O}$ (1)	7.5	8.0	13.6
$\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_3)] \cdot 3.5\text{H}_2\text{O}$ (2)	8.6	8.0	13.5
$\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_4)]$ (3)	10.2	8.8	16.0
$\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_2)]$ (4)	9.6	9.2	14.3
$\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_3)] \cdot \text{H}_2\text{O}$ (5)	11.5	9.0	13.4
$\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_4)]$ (6)	12.4	11.6	17.4

Among the tested complexes the compounds with the co-ligand ( $\text{L}_4$ ) containing thiol groups showed better activity than other complexes. This may be due to the presence of two thiol groups in these complexes. The effectiveness of these complexes (3 & 6) were further confirmed by determining the minimum inhibitory concentration (MIC) values in mg/mL against *S. aureus* bacterial strains and *C. albicans* fungal strain using liquid dilution method and observing the effective lowest concentrations [46]. The MIC experimentation results are showed moderate MIC values in the range of (20-25 mg/mL) against the bacteria *S. aureus* and MIC

values in the range of 16-20 mg/mL against the fungal strain *C. albicans*. The compound  $\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_4)]$  (6) showed best activity against the bacterial strain *S. aureus* with MIC value of 25 mg/mL and against the fungal strain with MIC value of 20 mg/mL.

These observations suggest that the prepared vanadium mixed metal complexes were having similar activity compared to our reported work earlier on vanadium complexes with triazole moiety [15].

## CONCLUSION

The targeted mixed-ligand Dioxido-vanadium (V) complexes containing bidentate ligands were synthesized in reasonable yield. The satisfactory analytical

data presented above suggest that the synthesized mixed-ligand dioxovanadium (V) complexes were of having the general formulae  $\text{NH}_4[\text{VO}_2(\text{L}_1)(\text{L}_{2-4})] \cdot y5\text{H}_2\text{O}$  or  $\text{K}[\text{VO}_2(\text{L}_1)(\text{L}_{2-4})] \cdot y\text{H}_2\text{O}$  with *cis*-dioxo groups attached to the vanadium central metal. The structures were proposed based on elemental analysis, mass spectra, IR, UV-visible, magnetic moment, molar conductance, TGA and  $^1\text{H}$ NMR measurements. The synthesized mixed-ligand dioxovanadium (V) complexes were monomeric with octahedral geometry. X-ray crystallographic studies, which might confirm the proposed structures, could not be carried out, as suitable crystals were not obtained.

The antibacterial investigation revealed that the synthesized complexes were weakly active against bacterial strains and showed moderate activity against the fungal strains.

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