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Oxo/dioxo-vanadium(V) complexes with Schiff base ligands derived from 4-amino-5-mercapto-3-phenyl-1,2,4-triazole

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ABSTRACT

Vanadium complexes containing Schiff base ligands are of great importance and have numerous applications. A series of Schiff base ligands derived from 4-amino-5-mercapto-3-phenyl-1,2,4-triazole and different aldehydes were synthesized and combined with ammonium metavanadate in 2:1 and 1:1 molar ration to yield oxo- and dioxo-vanadium(V) complexes $NH_4[VO(L_{a\text{-}f})_2]$ and $NH_4[VO_2(L_{g\text{-}h})_2]$, respectively. The structure of the synthesized compounds was confirmed by elemental analysis, UV, IR, NMR, MS and TGA. Complexes with bidentate and tridentate ligands were expected to possess a distorted square-pyramidal structure. The ligands and their complexes have been examined for antimicrobial activity against six types of bacteria and one kind of fungus that widely distributed in Albaha region, Kingdom of Saudi Arabia. The results indicate that some of the complexes were active against *C. albicans* fungus when used as powder, and no sound activity were shown against any type of tested bacteria.

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1. Introduction

Vanadium complexes have received intensive studies in many research laboratories in the recent decades due to their role in bio-coordination chemistry and they represent functional and structural models for biological systems [1]. Vanadium complexes containing pharmacologically interesting moieties have considerable interest in drug discovery. They have been reported to exhibit excellent role in the biological and pharmacological research studies *in vivo* and *in vitro* systems as antimicrobial, anti-carcinogenic and antileishmanial agents [2-6]. They show important role as enhancers of oxygen affinity by hemoglobin and myoglobin and they have insulin-mimetic activity [7-9].

Dioxodovanadium(V) complexes in particular have been reported to interact with biologically active organic molecules which allow them of a competent study of their action in biochemical processes [1]. VO_2(4-*n*-butyl-semicarbazone) complex reported to exhibit insulin-mimetic activity in the presence of ascorbic acid [9]. Also, vanadium dipicolinate complex $NH_4[VO_2(dipic)]$ was reported to be very effective in lowering blood glucose in animal studies and the effectiveness was dependent on the ligand and the vanadium oxidation state [10]. Oxovanadium(V) complexes reported to have potent dual anti-HIV and spermicidal activities [11]. In addition, Schiff bases and their metal complexes played a prominent role in the development of coordination chemistry. They represent an attractive field of research due to their structural features, special activities in pharmacology, biological systems and the wide range of applications [12,13].

Compounds incorporating the 3-substituted-4-amino-5-mercapto-1,2,4-triazoles substructure exhibit a wide spectrum of biological activity and contain an amino and mercapto groups which has the ability to coordinate metal ions [14].

The interaction of vanadium species with Schiff base ligands bearing therapeutic applications is of growing focus of attention and driven a considerable amount of research [15]. Various vanadium complexes with Schiff base ligands containing 1,2,4-triazole moiety are used in pharmacological and biological research studies found to exhibit important roles in biological applications [16]. It has been reported that many compounds containing 1,2,4-traizole moiety are having insecticidal, fungicidal and herbicidal activity [17].

In view of the facts mentioned before, we considered interesting to design new compounds in a trial to develop a molecule combining different pharmacophore fragments in one structure, which may lead to interesting biologically active agents.

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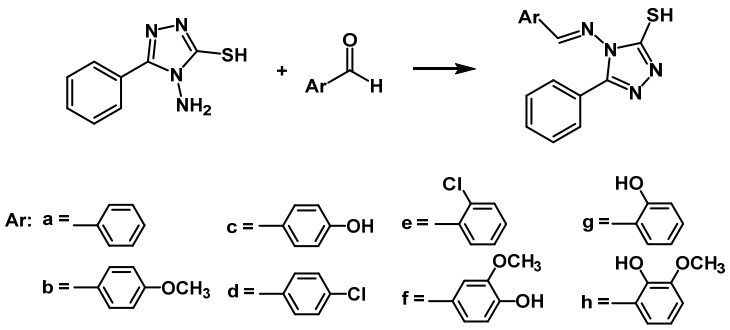


Scheme 1

We have synthesized a new oxo- and dioxovanadium (V) complexes from a series of bidentate and tridentate Schiff base ligands derived from 4-amino-5-mercapto-3-phenyl-1,2,4-triazole condensed with different aldehydes. The newly synthesized vanadium complexes were characterized by elemental analysis, spectroscopic and physicochemical methods. The microbial activities of the ligands and their corresponding complexes were tested 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. These microbes are widely distributed at Albaha region, Kingdom of Saudi Arabia.

2. Experimental

2.1. Chemicals

All chemicals used in this work NH_4VO_3, benzaldehyde, salicylaldehyde, *o*-vaniline, anisaldehyde, vaniline, *p*-hydroxy benzaldehyde, 2-chlorobenzaldehyde, 4-chlorobenzaldehyde were purchased from Sigma-Aldrich and used as received without purification. The 4-amino-5-mercapto-3-phenyl-1,2,4-triazole has been synthesized according to the reported methods [18].

2.2. Preparation of Schiff base ligands

Schiff base ligands (L_a-L_h) were prepared from the condensation of the amino compound 4-amino-5-mercapto-3-phenyl-1,2,4-triazole and an aldehyde compound: benzaldehyde, salicylaldehyde, *o*-vaniline, anisaldehyde, vaniline, *p*-hydroxy-benzaldehyde, 2-chlorobenzaldehyde, *p*-chlorobenzaldehyde (1:1) molar ratio in an ethanolic solution and refluxing for nearly 3 hours in the presence of piperidine according to the reported method [19,20]. The solvent was evaporated partially and the yellow/orange precipitates were collected and dried under vacuum. Yield ranges between 70-85% (Scheme 1).

4-(Benzylideneamino)-5-phenyl-4H-1, 2, 4-triazole-3-thiol (**L_a**): Color: Yellow. Yield: 70%. M.p.: 190-192 °C. FT-IR (KBr, ν, cm^{-1}): 1600 (C=N), 2743 (SH). Anal. calcd. for $C_{15}H_{12}N_4S$: C, 64.26; H, 4.31; N, 19.99; S, 11.44. Found: C, 64.36; H, 4.28; N, 19.92; S, 11.26%.

4-((4-Methoxybenzylidene)amino)-5-phenyl-4H-1, 2, 4-triazole-3-thiol (**L_b**): Color: Brownish yellow. Yield: 85%. M.p.: 185-187 °C. FT-IR (KBr, ν, cm^{-1}): 1613 (C=N), 2642 (SH). Anal. calcd. for $C_{16}H_{14}N_4SO$: C, 61.92; H, 4.55; N, 18.05; S, 10.33. Found: C, 61.88; H, 4.49; N, 17.96; S, 10.27%.

4-(((3-Mercapto-5-phenyl-4H-1, 2, 4-triazol-4-yl)imino) methyl)phenol (**L_c**): Color: Yellow. Yield: 75%. M.p.: 175-177 °C. FT-IR (KBr, ν, cm^{-1}): 1602 (C=N), 2750 (SH), 3295 (OH). Anal. calcd. for $C_{15}H_{12}N_4SO$: C, 60.80; H, 4.08; N, 18.91; S, 10.82. Found: C, 60.62; H, 4.02; N, 18.86; S, 10.77%.

4-((4-Chlorobenzylidene)amino)-5-phenyl-4H-1,2,4-triazole-3-thiol (**L_d**): Color: Yellow. Yield: 80%. M.p.: 192-194 °C. FT-IR (KBr, ν, cm^{-1}): 1606 (C=N), 2756 (SH). Anal. calcd. for $C_{15}H_{11}N_4SCl$: C, 57.23; H, 3.52; N, 17.80; S, 10.18. Found: C, 57.14; H, 3.49; N, 17.82; S, 10.10%.

4-((2-Chlorobenzylidene)amino)-5-phenyl-4H-1,2,4-triazole-3-thiol (**L_e**): Color: Brownish yellow. Yield: 80%. M.p.: 180-182 °C. FT-IR (KBr, ν, cm^{-1}): 1620 (C=N), 2757 (SH). Anal. calcd. for $C_{15}H_{11}N_4SCl$: C, 57.23; H, 3.52; N, 17.80; S, 10.18. Found: C, 57.20; H, 3.49; N, 17.70; S, 10.12%.

4-(((3-Mercapto-5-phenyl-4H-1, 2, 4-triazol-4-yl)imino) methyl)-3-methoxyphenol (**L_f**): Color: Yellow. Yield: 70%. M.p.: 182-184 °C. FT-IR (KBr, ν, cm^{-1}): 1605 (C=N), 2810 (SH), 3265 (OH). Anal. calcd. for $C_{16}H_{14}N_4SO_2$: C, 58.88; H, 4.32; N, 17.17; S, 9.82. Found: C, 58.92; H, 4.20; N, 17.10; S, 9.76%.

2-(((3-Mercapto-5-phenyl-4H-1, 2, 4-triazol-4-yl)imino) methyl) phenol (**L_g**): Color: Brownish yellow. Yield: 70%. M.p.: 151-153 °C. FT-IR (KBr, ν, cm^{-1}): 1616 (C=N), 2759 (SH), 3289 (OH). Anal. calcd. for $C_{15}H_{12}N_4SO$: C, 60.80; H, 4.08; N, 18.91; S, 10.82. Found: C, 60.75; H, 4.10; N, 18.87; S, 10.80%.

2-(((3-Mercapto-5-phenyl-4H-1, 2, 4-triazol-4-yl)imino) methyl)-6-methoxyphenol (**L_h**): Color: Pale brown. Yield: 85%. M.p.: 206-208 °C. FT-IR (KBr, ν, cm^{-1}): 1643 (C=N), 2750 (SH), 3295 (OH). Anal. calcd. for $C_{16}H_{14}N_4SO_2$: C, 58.88; H, 4.32; N, 17.17; S, 9.82. Found: C, 58.82; H, 4.30; N, 16.98; S, 9.80%.

2.3. Preparation of metal complexes

To a hot magnetically stirred (50 mL) ethanolic solution of the triazole Schiff base (2 mmol), a solution of NH_4VO_3 (0.117g, 1 mmol) in 30 ml hot water was added slowly with stirring. The mixture was stirred and heated directly on a wire gauze for one hour during which a precipitated product was formed. The precipitates thus formed were filtered, washed with methanol, dioxane and then with diethyl ether and dried under vacuum. The yields obtained were in the range of 65-70%. All complexes were prepared following the same procedure using 2:1 and 1:1 (L:M) molar ratio in case of bidentate and tridentate Schiff bases, respectively.

2.4. Instrumentation

Elemental analyses (C, H, N, O and S) were performed using Leco VTF-900 CHN-S-O 932 version 1.3x (ThermoFisher Scientific-USA) instrument. Electronic spectra of solutions of the complexes in DMF were recorded on Evolution 300 UV-vis Spectrophotometer. FT-IR spectra (400-4000 cm^{-1}) were recorded as KBr discs using Nicolet IS50 FT-IR spectrophotometer. The mass spectra were carried out on LC-MS spectrometer of Thermo Scientific 3000 series. Thermogravimetric

analysis (TGA) was recorded on Shimadzu analyzer 50 in a dynamic nitrogen atmosphere (100 mL/min) at a heating rate 10 °C/min. Circular NMR spectra were obtained in CD_3OD solutions with a Varian Mercury-400BB (400 MHz) spectrometer using TMS (^1H) as standard.

2.5. Antimicrobial activity

The microbial activities of the ligands and their corresponding complexes were tested 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. These microbes are widely distributed at Albaha region, Kingdom of Saudi Arabia.

The antibacterial and antifungal activities of the ligands and their corresponding vanadium complexes were tested by Well Diffusion Assay method as the susceptibility testing method [21,22]. The antibacterial and antifungal activities were tested for their *in vitro* growth inhibitory activity against the investigated pathogenic bacterial and fungal strains cultured on the surface of a sterile Muller-Hinton agar as a microbiological growth medium. The stock solution of the compounds was prepared by dissolving 0.02 g of each compound in 5 mL DMSO as solvent. The solvent (DMSO) was used as a control in a similar manner to the prepared solutions of the tested compounds. Using sterile cork borer (6 mm) a small hole in the middle of each dish was made. Then, solutions of the ligands and the corresponding complexes in DMSO were poured into the holes made in the cultured Muller-Hinton agar medium and incubated for a period of 24 hours at 37 °C. After the incubation period, the microbial susceptibility was monitored by measuring the zones (in cm) around each hole at which the visible growth was completely inhibited. Each sample was repeated in triplicate, and statistical analyses were performed with SPSS 16.0 for windows. For statistical analysis $p < 0.05$ were considered statistically significant. Data were presented as mean ± standard deviation (SD).

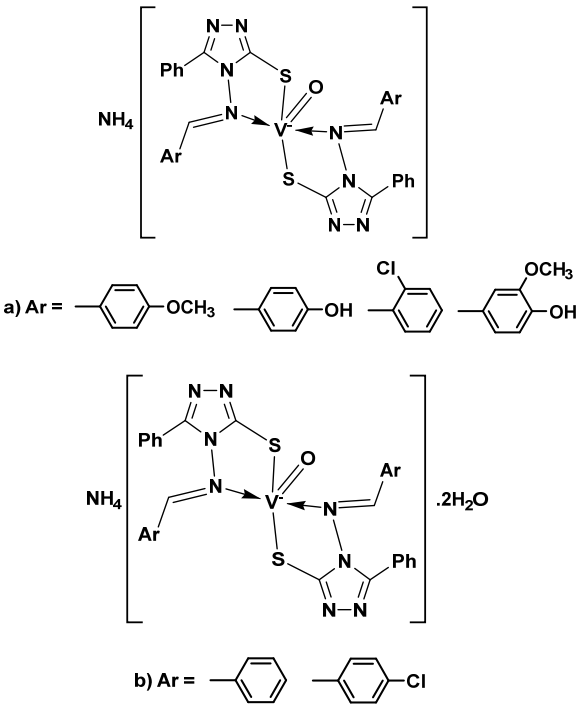
Also, we have performed the antifungal susceptibility against *Candida albicans* of the organic Schiff base ligands and their corresponding dioxidovanadium complexes using the solid form of the compounds by spreading the solid powder (0.02 g) on the surface of the agar medium.

3. Results and discussion

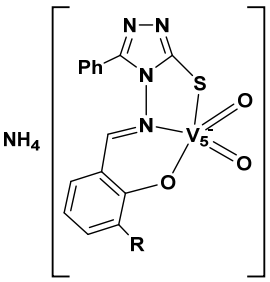
3.1. Synthesis, elemental analysis and structural description

Our task was constructing vanadium(V) complexes containing Schiff base ligands with 1,2,4-triazole moiety having mercapto (-SH) group. We have selected these ligands for our investigation because such ligands have N, S and/or O as donor atoms and are expected to have/or enhance antimicrobial activity. The synthesis of the designed Schiff base ligands were successfully achieved by the condensation of the amino compound 4-amino-5-mercapto-3-phenyl-1,2,4-triazole with different aldehydes: salicylaldehyde, *o*-vaniline, anisaldehyde, benzaldehyde, vaniline, *p*-hydroxybenzaldehyde, 2-chlorobenzaldehyde, *p*-chlorobenzaldehyde in the 1:1 molar ratio in an ethanolic solution and refluxing for nearly 2 hours [19,20]. Scheme 1 illustrates our attempt to design suitable starting materials to be used as ligands (L_a-L_h). The melting points and colours of the isolated organic ligands are shown in Section 2.2.

The structures of the isolated Schiff bases were supported by elemental analysis and spectroscopic measurements. The oxovanadium(V) Schiff base complexes were obtained by the reaction of the bidentate Schiff base ligands in ethanolic solution and ammonium metavanadate (NH_4VO_3) salt in hot water solution using 1:1 [L:M] molar ratio. While, the dioxovanadium(V) Schiff base complexes were obtained by the reaction of the tridentate ligands and NH_4VO_3 salt using 1:1 [L:M] molar ratio. The coloured air stable mononuclear vanadium complexes were isolated. The proposed structures (1 and 2) are shown in Scheme 2.



Structure 1



Structure 2

Scheme 2

General structures 1 and 2 give the perspective view of expected vanadium(V) complexes with the bidentate and tridentate Schiff base ligands, respectively (Scheme 2). Structure 1 represent complexes with bidentate ligands (L_a-L_f) having imino N (azomethine nitrogen) and mercapto S (of the -SH) atoms as donor sites. The elemental analysis measurements revealed that one NH_4^+ molecules are associated with the complex for each monomeric unit in all complexes obtained. The elemental analysis results (Table 1) also revealed that two complexes $NH_4[VO(L_a)_2].2H_2O$ and $NH_4[VO(L_d)_2].2H_2O$ were having two crystal H_2O molecules associated with each unit of these complexes (Structure 1b, Scheme 2). The V atoms in the bidentate ligand complexes are in square-pyramidal coordination environment with one oxo (O) atom present at the vanadium center.

Table 1. Elemental analysis result of the synthesized vanadium complexes.

Formula	Mol. Wt.	Calcd. (Found) %			
		C	H	N	S
$NH_4[VO(L_a)_2].2H_2O$ $C_{30}H_{30}N_9O_3S_2V$	679.68	53.01 (53.12)	4.44 (3.96)	18.54 (18.30)	9.43 (9.51)
$NH_4[VO(L_b)_2]$ $C_{32}H_{30}N_9O_3S_2V$	703.71	54.61 (54.72)	4.29 (4.60)	17.91 (17.85)	9.11 (8.80)
$NH_4[VO(L_c)_2]$ $C_{30}H_{26}N_9O_3S_2V$	675.65	53.32 (52.90)	3.87 (3.55)	18.65 (18.56)	9.49 (9.20)
$NH_4[VO(L_d)_2].2H_2O$ $C_{30}H_{28}N_9O_3S_2VCl_2$	748.57	48.13 (48.61)	3.77 (4.10)	16.84 (16.58)	8.56 (8.74)
$NH_4[VO(L_e)_2]$ $C_{30}H_{24}N_9OS_2VCl_2$	712.54	50.56 (50.15)	3.39 (3.80)	17.69 (17.92)	9.00 (8.60)
$NH_4[VO(L_f)_2]$ $C_{32}H_{30}N_9O_5S_2V$	735.09	52.24 (51.96)	4.11 (4.48)	17.13 (16.95)	8.71 (8.94)
$NH_4[VO_2(L_g)]$ $C_{15}H_{14}N_5O_3SV$	395.30	45.57 (45.85)	3.57 (3.65)	17.71 (17.94)	8.11 (7.85)
$NH_4[VO_2(L_h)]$ $C_{16}H_{16}N_5O_4SV$	425.33	45.18 (45.24)	3.79 (3.96)	16.46 (16.72)	7.53 (7.41)

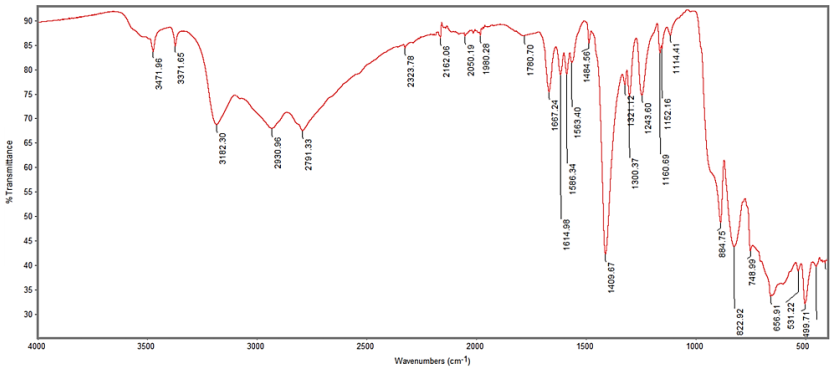


Figure 1. IR spectrum for $NH_4[VO(L_b)_2]$ complex.

In structure 2, the vanadium atom is in square-pyramidal coordination with the tridentate ligands (L_g-L_h) through its azomethine nitrogen, mercapto S atom and deprotonated phenolic oxygen atom (Scheme 2). The coordination sphere completed by two oxo ligands at *cis*-position [9].

Elemental analyses of the complexes obtained are in good agreement with the chemical formulae proposed for the compounds (Table 1).

The mass spectra were performed for some of the obtained complexes to determine the molecular weights. A molecular peak for the complex $NH_4[VO(L_b)_2]$ was observed at 702.08 *m/z* which is equivalent to its calculated molecular weight (703.71 *m/z*). For the complex $NH_4[VO_2(L_g)]$ a peak was observed at 396.04 *m/z* confirming the formula weight for this complex (calculated 395.317 *m/z*). This confirms the formula proposed for these complexes.

3.2. Spectroscopic characterization of the ligands and complexes

3.2.1. Infrared spectra

The IR spectra of Schiff base ligands and metal complex compounds were recorded and a representative IR spectrum is shown in Figure 1. The infrared spectra of the ligands (L_a-L_h) exhibit bands characteristic of the stretching vibrations of SH (2642-2800 cm^{-1}) and C=N (1600-1666 cm^{-1}) (Table 2) [23,24].

The significant bands observed in the IR spectra of the complexes are given in Table 2 and the main points are discussed below:

i) Free ligands characteristic band of the thiol group ν(SH) at 2642-2800 cm^{-1} for these bands are absent in the metal complexes indicating deprotonation of the thiol group and complexation of sulfur atom with metal ions. A new low frequency band appears in the metal chelates in the region 436-499 cm^{-1} (assigned to ν(V-S)) confirms the vanadium-sulfur bond formation [25,26].

ii) The strong sharp bands appeared in the range 1600-1666 cm^{-1} are assigned to azomethine group ν(C=N) of the free ligand. These bands were shifted to lower frequency and reduced intensity on complex formation, suggesting the participation of nitrogen atom of azomethine group in coordination [20]. This is further supported by the presence of a new low frequency band in the region 491-531 cm^{-1} in the IR spectra of the vanadium complexes assigned to ν(V-N) [25,26].

iii) The spectra of the bidentate complexes show a sharp strong band in the range 949-979 cm^{-1} indicative of the presence of ν(V=O) stretch [27].

iv) Two strong bands identified in the vanadium complexes with tridentate ligands spectra in the range 949-968 and 968-979 cm^{-1} can be assigned to symmetrical ν(O=V=O) and asymmetrical ν(O=V=O) stretching vibrations, respectively [28]. This clearly indicates the dioxo nature of these complexes [24,29-31]. The frequencies for O=V=O bonds in all tridentate complexes were nearly similar which is an indication that all tridentate complexes have VO_2^+ groups. These are well within the range expected for dioxo-vanadium(V) compounds and in agreement with the other results [27].

v) The IR spectrum of tridentate ligands (L_g-L_h) exhibit ν(C-O) (phenolic) stretches at 1645 and 1580 cm^{-1}. On coordination, these bands shifted to higher energy by ~25 cm^{-1} that indicates coordination through phenolic oxygen [19].

Table 2. Characteristic IR bands of the Ligands (L_a-L_h) and their vanadium complexes.

Compound	C=N	OH	SH	VO/VO_2	V-N	V-S
L_a	1600	-	2743	-	-	-
$NH_4[VO(L_a)_2].2H_2O$	1622	3514	2750	975	499	450
L_b	1613, 1666	-	2642	-	-	-
$NH_4[VO(L_b)_2]$	1614, 1667	-	2791	950	531	499
L_c	1602	3295	2750	-	-	-
$NH_4[VO(L_c)_2]$	1567	3300	2800	979	520	491
L_d	1606	-	2756	-	-	-
$NH_4[VO(L_d)_2].2H_2O$	1650, 1592	3400	2806	972	491	436
L_e	1620	-	2757	-	-	-
$NH_4[VO(L_e)_2]$	1616	-	2805	972, 957	506	490
L_f	1605	3272	2800	-	-	-
$NH_4[VO(L_f)_2]$	1606	3265	2810	958, 977	506	470
L_g	1616	3289	2759	-	-	-
$NH_4[VO_2(L_g)_2]$	1617	-	2801	973	500	450
L_h	1600, 1643	3295	2750	-	-	-
$NH_4[VO_2(L_h)_2]$	1598, 1688	-	2748	949, 968	527	473

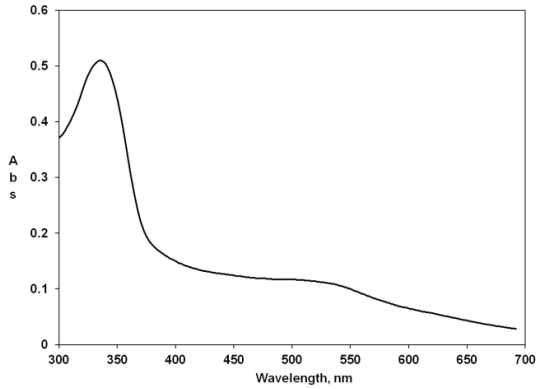


Figure 2. The electronic spectrum of $NH_4[VO_2(L_h)_2]$.

vi) A band centered in the range of 3110-3155 cm^{-1} is due to ammonium stretching mode while cation NH_4^+ deformation modes appear at 1615 and 1430 cm^{-1} [32,33].

vii) In the IR spectra of some complexes a broad band appear at 3400-3514 cm^{-1} due to ν(OH) which is an evident for the presence of water molecules in the complexes [34].

3.2.2. Electronic spectra

The electronic spectra of the complexes were recorded in 1×10^{-5} mol/L in DMF in the range 200-800 nm. The absorption observed at the wavelength 365 and 430 nm (Figure 2) are assignable to the intramolecular ligand-to-metal charge transfer (LMCT) transitions from the π orbital on the nitrogen and sulfur to the empty *d* orbitals of the metal. Whereas the other bands in the higher energy region (220-263 nm) for the complexes are likely to be due to intra-ligand π-π* transitions [24]. The shoulder at about 270-274 nm for complexes corresponds to LMCT band of V=O [35]. It was observed that all bands of the free ligands shift to lower energy in complexes indicating the coordination of ligands to the metal ions.

The possible structures of the synthesized oxovanadium(V) complexes are presumed by elemental analysis. The complexes contains two chelating ligands bidentate and tridentate with a ratio of 1:2 and 1:1 (M:L), respectively. The complexes with bidentate ligands have one oxo-group attached to the vanadium center (Structure 1a and b, Scheme 2) with one NH_4 molecule in all complexes and two H_2O crystalline molecules in some complexes. The structure is expected to be distorted square-pyramidal for the complexes with the bidentate ligands. Similarly, a distorted square-pyramidal structure for complexes with tridentate ligands in which the VO_2 in the *cis*-configuration for the monovanadium(V) complexes, $[VO_2(L_{g\text{-}h})_2]$ [27].

3.2.3. ^{1}H NMR spectra data

^{1}H NMR spectra of ligands and metal complexes were recorded in DMSOd6 using tetra methyl silane (TMS) as internal standard. The ^{1}H NMR spectra of Schiff bases show the -SH proton at δ 13.2-13.7 ppm. Disappearance of this signal of the -SH proton in the metal complexes supports the deprotonation of the thio-group and this supported the coordination of ligands through sulphur atom to the central vanadium metal ion [25]. The spectra of some free ligands exhibit an OH (phenolic) proton at δ 11.80 ppm. The absence of this signal in the complexes is in accordance with iminolization and subsequent replacement of H by the metal ion. The singlet at δ 9.13 and 8.71 ppm in the spectrum of the ligands were assigned to azomethine proton (H-C=N) [36]. When the metal is coordinated, the deshielding effect of the metal atom is apparent in some protons, causing a downfield shift of the corresponding ^{1}H NMR peaks. A significant downfield shift for the azomethine (CH=N) proton signal in the complexes with respect to the corresponding free ligands confirms the coordination of the azomethine nitrogen atom.

3.2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) data (Figure 3) shows that complexes undergo multistage decomposition. Figure 3 shows the TGA measurement of the complex $NH_4[VO(L_d)_2].2H_2O$ which was performed in the temperature range of 0-800 °C. The scanning rate was 10 °C/min to 800 °C in the presence of nitrogen gas flow. The thermal decomposition of $NH_4[VO(L_d)_2].2H_2O$ complex consists mainly of three stages.

The first step complex display a weight loss at around 100 °C that corresponds to two lattice water molecules present in complex (calcd. 4.8%, found 4.87%). The second TG step at 100-350 °C represents a mass loss (calcd. 35.53%, found 35.36%) corresponding to the removal of organic moiety [$C_{14}H_{10}Cl_2$] and NH_3 gas. The final step corresponds to decomposition of triazole molecules at 350-800 °C of the ligand leading to the final residue at 800 °C as metal oxide. The results show good agreement with the formulae suggested from the analytical data [37,38]. The total decomposition process can be represented as:

$$NH_4[VO(L_d)_2].2H_2O \rightarrow V_2O_5 + \text{Volatile products} \quad (1)$$

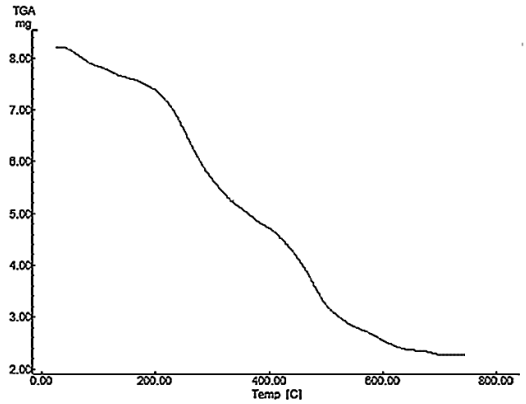


Figure 3. Thermogravimetric (TGA) curve of $NH_4[VO(L_d)_2].2H_2O$ complex.

3.3. Anti-microbial activity

The synthesized organic Schiff base ligands and their corresponding vanadium(V) complexes 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* and *Klebsiella pneumonia* in addition, to one kind of pathogenic fungus *Candida albicans*. These bacteria and fungus types are selected because they are widely distributed at Albaha region, Kingdom of Saudi Arabia, the place where this study was carried out. Well Diffusion method was used as testing method for microbial susceptibility using DMSO as solvent and as a control. After the incubation period, the microbial susceptibility was monitored by measuring the zones (in cm) around each hole at which the visible growth was completely inhibited. The results indicated that most of the compounds did not show any activity against all types of bacteria except compound ($NH_4[VO_2(L_c)_2]$) have moderate activity against the Gram-positive Group B *Streptococcus bacteria* (inhibition zone of 1.15 cm). The tested vanadium complex compounds showed antifungal susceptibility when used in the powder form against the pathogenic fungus *C. albicans* with highest sensitivity was of compound ($NH_4[VO_2(L_a)_2].2H_2O$) with an inhibition zone = 1.65 cm. The organic Schiff base ligands did not show any antifungal susceptibility against *C. albicans* fungus. In general metal complexes have some moderate antifungal activity compared to the free ligands and did not show sound antibacterial activity. The moderate antifungal activity of the complexes may be due to chelation tended to make the ligands more active as fungicides due to factors like solubility and permeability. These factors are influenced by the presence of vanadium ion that might be the possible reason for increasing activity. These results are in accordance with reports of earlier workers [37].

4. Conclusion

Two series of bidentate and tridentate Schiff's base ligands containing triazole moiety were synthesized and combined with ammonium metavanadate in 2:1 and 1:1 (L:M) molar ratio in case of bidentate ligands and tridentate ligands, respectively. Two types of monomeric vanadium(V) complexes (oxo- and dioxo-) were formed. The complexes with bidentate ligands were having one oxo group (V=O), while complexes with tridentate ligands were having two oxo-groups (V=O). The possible structures of the synthesized oxo/dioxvanadium(V) complexes are presumed by elemental analysis, IR, UV-visible, NMR, MS and TGA. The structure is expected to have a distorted square pyramidal geometry for all the complexes. The compounds were tested for their antibacterial and antifungal activity. Observations indicated that the synthesized vanadium complexes were moderately active against *C. albicans* fungus where, the metal complexes are more active compared to the free ligands. The ligands and their vanadium complexes did not show any antibacterial activity.

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