Oxovanadium(IV) Complexes of α-Amino Acid Schiff bases and Polypyridyl Ligands: Synthesis, Characterization and Antimicrobial Activity

Abstract

Oxovanadium(IV) complexes of the type [VO(L)(bpy)] (V-1 to V-5) have been synthesised and characterised by FTIR and UV-Vis spectra, molar conductance, melting points, and magnetic susceptibilities measurements, where L= N-salicylidene-β-alanine (sal-ala), N-salicylidene-glycine (sal-gly), N-salicylidene-DL-β-phenylalanine (sal-pheala), N-salicylidene-leucine (sal-leu), and N-salicylidene-DL-methionine (sal-met), and bpy are 2,2´-bipyridine. The infrared spectral data reveals that the tridentate nature of the amino acid-based Schiff base ligand and the coordination of theligand throughisomethine nitrogen, phenolic oxygen and carboxylate oxygen with vanadyl (VO^{2+}) ion. All of these complexes were determined to be non-electrolyte in nature, according to conductivity measurements. The magnetic moment measurements have been attributed that these complexes are paramagnetic and have d^1 configuration of vanadium(IV) ion. The antimicrobial activity of the synthesized complexes was evaluated against four pathogenic bacteria viz. *Escherichia coli*, *Proteus vulgaris*, *Bacillus subtilis*and*Staphylococcus aureus*. It has been observed that the complexes of phenanthroline, were more potent against all pathogens than their analogous bipyridine complexes.

Keywords: α-Amino Acid; Oxovanadium(IV) complexes**;** Schiff base; Polypyridyl Ligands;

1. Introduction

Vanadium coordination chemistry is a new area of interest since it was found to be an important trace element for some organisms[1,2] and a cofactor in some haloperoxidases[3] and nitrogenases.[4] Several studies have been conducted on vanadium complexes with oxidation states (IV) and (V), and several of these compounds have been found to be powerful anti-tumors[5], anti-leukemics[6], and insulin-mimics.[7,8]

Transition metal complexes are now being studied for their potential applications as DNA-dependent electron transfer, DNA structural probes and site-specific nucleic acid cleavage in the development of novel therapeutic and diagnostic agents.[9]DNA cleavage activity of transition metal complexes has been the subject of investigation[10-12], with the focus on the mid to late transition elements and comparatively little attention paid to the earlier members of the series. Among the latter, vanadium, with its three biologically accessible oxidation states (III, IV, and V) has begun to be recognized as having important biological role.[3,13–15] Our interest in developing novel oxovanadium(IV) complexes (Scheme 1) that potentially exhibit antimicrobial properties and possess unique physiochemical characteristics motivated the current research.

A.

where R = corresponding α-amino acids and N-N is polypyridyl ligands.

B.

C.

Scheme 1: Ternary structures of the oxovanadium(IV) complexes **(A)**, corresponding α-amino acids **(B)** andpolypyridyl ligands **(C)** used in the present study.

2. Experimental Methods

All chemicals and solvents were reagent grade and were used as received without further purification. The amino acid-based Schiff base tridentate ligands were synthesized according to published literature. The polypyridyl ligands 2,2′-bipyridine are commercially available. These complexes were synthesized by the template method.

Infrared spectra were recorded on a FTIR-8400, SHIMADZU, Japan using a KBr disc, at the Central Science Lab of Rajshahi University, UV-visible spectra of complexes were recorded on a SHIMADZU DOUBLE BEAM spectrophotometer

(model UV-1200) at the Department of Chemistry, Rajshahi University. The melting points or decomposition temperature of all the prepared metal complexes were observed with an electrothermal melting point apparatus. It was, however, not possible to measure the melting points beyond 300^{o}C.The conductance measurements were made at room temperature using a WPACM35 conductivity meter and a dip-cell with a platinized electrode. The SHERWOOD SCIENTIFIC magnetic susceptibility balance was used to probe the magnetic nature of the complexes.

2.1 Synthesis and Characterization of Oxovadium(IV) Complexes of α-Amino Acid Schiff Bases and 2,2′-Bipyridine Ligands

2.1Preparation of [VO(sal-ala)(bpy)], (V-1)

The process used for producing oxovanadium(IV) complexes involved mixing α-amino acids, β-alanine (ala) (0.267 g, 3 mmol), and NaOH (0.100 g, 2.25 mmol) in 10 mL methanol with a methanolic solution of salicylaldehyde (sal) (0.3 mL, 3 mmol) in a round-bottom flask. Following an hour of refluxing, a methanolic solution of vanadyl sulphate (0.489 g, 3 mmol) was added to the mixing mixtureAfter refluxing the mixture for an hour, a light blue precipitate formed. A solution of 2,2'-bipyridine (bpy) (0.469 g, 3 mmol) in 10 mL methanol was added to the mixture.After refluxing the mixture for an additional hour, a dark brown precipitate formed. Subsequently, the precipitate underwent filtration through a Buchner funnel, methanol washing, and subsequent drying in a vacuum desiccator over anhydrous $CaCl_2$.

Yield: 0.740 g (59%), Λ_M = 10.0 ohm^{-1} cm^2 mol^{-1} in DMF at 31 °C. IR (KBr phase, cm^{-1}): 3471br, 1619vs, 1544m (C=N), 1316m, 959s (V=O), 614m, 456m (br, broad; vs, very strong; s, strong; m, medium; w, weak). UV-Vis (DMSO), λ/nm (ε/M^{-1} cm^{-1}): 268−301 (3436−3462), 364 (2572),377sh (2312) (sh, shoulder). μ_{eff} =1.57 B.M. at 303 K.

Complexes **V-2 to V-5** were prepared by the procedure as described for complex **V-1**using DL-β-phenylalanine (phyala) (0.495 g, 3 mmol), leucine (leu) (0.393 g, 3 mmol), glycine (gly) (0.225 g, 3 mmol) and DL-methionine (met) (0.447 g, 3 mmol) respectively instead of β-alanine (ala).

2.2Preparation of [VO(sal-pheala)(bpy)], (V-2)

Yield: 0.851 g (57%), Λ_M = 19.3 ohm^{-1} cm^2 mol^{-1} in DMF at 31 °C. IR (KBr phase, cm^{-1}): 3435br, 1621vs, 1540s (C=N), 1310m, 942s (V=O), 614m, 445m. UV-Vis (DMSO), λ/nm (ε/M^{-1} cm^{-1}): 267−302 (3675−3524), 364 (2181),376sh (2161). μ_{eff} =1.60 B.M. at 303 K.

2.3Preparation of [VO(sal-leu)(bpy), (V-3)

Yield: 0.870 g (63%), Λ_M = 16.1 ohm^{-1} cm^2 mol^{-1} in DMF at 31 °C. IR (KBr phase, cm^{-1}): 3453w, 1620w, 1530w, 1310w, 961s (V=O), 618m, 460w. UV-Vis (DMSO), λ/nm (ε/M^{-1} cm^{-1}): 268–301 (3662−3325), 364 (2027),374sh (2008). μ_{eff} =1.55 B.M. at 303 K.

2.4Preparation of [VO(sal-gly)(bpy)], (V-4)

Yield: 0.693 g (57%), Λ_M = 16.1 ohm^{-1} cm^2 mol^{-1} in DMF at 31 °C. IR (KBr phase, cm^{-1}): 3414br, 1654s, 1535s (C=N), 1312m, 963s (V=O), 803s, 617s, 463m. UV-Vis (DMSO), λ/nm (ε/M^{-1} cm^{-1}):270−303 (3462−3311), 364 (2459),375sh (2364). μ_{eff} =1.54 B.M. at 303K.

2.5Preparation of [VO(sal-met)(bpy)], (V-5)

Yield: 0.862 g (60%), Λ_M = 7.9 ohm^{-1} cm^2 mol^{-1} in DMF at 31 °C. IR (KBr phase, cm^{-1}): 3412br, 1618s, 1535s (C=N), 1312m, 959vs (V=O), 616m, 451m. UV-Vis (DMSO), λ/nm (ε/M^{-1} cm^{-1}): 269−307 (3263−3325), 363 (3175),388sh (2709). μ_{eff} =1.80 B.M. at 303 K.

3 Results and Discussion

The complexes were prepared in a high yield according to the template method. All the complexes of oxovanadium(IV) are soluble in DMF and DMSO but insoluble in common organic solvents such as methanol, ethanol, benzene, chloroform. The molar conductance of the complexes , as indicated in Table 1, varies between 7.9 and 19.3 ohm^{-1} cm^2 mol^{-1} when measured in DMF at a concentration of 10^{-3} M. The readings are lower than someone would expect for an electrolyte. As predicted, molar conductance measurements show that the complexes are non-electrolytes in nature.Magnetic moments of oxovanadium(IV) complexes were measured at room temperature and the values are given in **Table1**.

The magnetic moments of complexes were in the range 1.54–1.80 B.M., which correspond to a single electron of the d^1 system of oxovanadium(IV) center and paramagnetic in nature.Melting point gives an approximate idea about the nature of the complexes and can suggest whether it is covalent or ionic. The melting point of the complexes prepared for this study is given in **Table 1**.

Table 1: Physical Properties of the prepared oxovanadium(IV) complexes

Complex Symbol	Complex	Color	Melting point/De °C	Molar conductance $ohm^{-1} cm^2 mol^{-1}$	μ eff in B.M
V-1	[VO(sal-ala)(bpy)]	Dark brown	214–217(De)	10.0	1.57
V-2	[VO(sal-pheala)(bpy)]	Orange	182–186(De)	19.3	1.60
V-3	[VO(sal-leu)(bpy)]	Ash	225–228(De)	16.1	1.55
V-4	[VO(sal-gly)(bpy)]	Blackish red	252–255(De)	16.1	1.54
V-5	[VO(sal-met) (bpy)]	Brown	212–215(De)	7.9	1.80

3.1 IR spectral studies

The IR spectral data of oxovanadium(IV) complexes show a broad band in the 3413–3472 cm^{-1} region which is possibly due to the hydrated water molecule in the complexes.[50] The complexes exhibit ν(C=O) bands at 1619–1654 cm^{-1} and ν(C–O) bands at 1310–1316 cm^{-1} which are significantly lower than the values for respective bands of uncoordinated amino acids. Further, the appearance of ν(V–O) modes at around 618 cm^{-1} confirms the coordination of carboxylate ion to the central metal ion.[51] The ν(O–H) band usually appeared at 3600 cm^{-1} for the phenolic –OH is absent in the present complexes which supports the coordination of phenolic oxygen to vanadyl ion. The bands appeared at around 1540 cm^{-1} may be assigned to ν(C=N) stretching frequency suggesting the coordination of the azomethine nitrogen and heterocyclic nitrogen to the VO^{2+} moiety. The coordination of nitrogen of azomethine and heterocyclic nitrogen is further evident by the appearance of ν(V–N) modes at 446–463 cm^{-1} region.[52] The present

oxovanadium(IV) complexes exhibit the ν(V=O) stretching frequency in the 942–964 cm^{-1} region characteristic of metal-oxygen multiple bond, thus ruling out the possibility of polymeric nature of the complexes since the polymeric oxovanadium(IV) complexes exhibit one or more broad absorption bands below 900 cm^{-1} due to bridging vanadyl group, –V–O–V–.[53] The present complexes exhibit medium intense band in the region ~960 cm^{-1} indicating the monomeric nature of the complexes.[54]

The IR spectra of oxovanadium(IV) complexes (V-**1 to V-5**) are shown in the Figures **1–5**.

Table 2: Important FTIR frequencies of complexes (**1**–**5**)

Sl. No.	**Complex**	**ν(OH)** cm^{-1}	**ν(C=O)** cm^{-1}	**ν(C–O)** cm^{-1}	**ν(C=N)** cm^{-1}	**ν(V–N)** cm^{-1}	**ν(V–O)** cm^{-1}	**ν(V=O)** cm^{-1}
V-1	[VO(sal-ala)(bpy)]	3472	1619	1316	1544	457	614	959
V-2	[VO(sal-pheala)(bpy)]	3435	1621	1310	1540	446	619	942
V-3	[VO(sal-leu)(bpy)]	3453	1621	1310	1530	460	618	961
V-4	[VO(sal-gly)(bpy)]	3414	1654	1312	1536	463	618	964
V-5	[VO(sal-met)(bpy)]	3413	1643	1312	1536	452	616	960

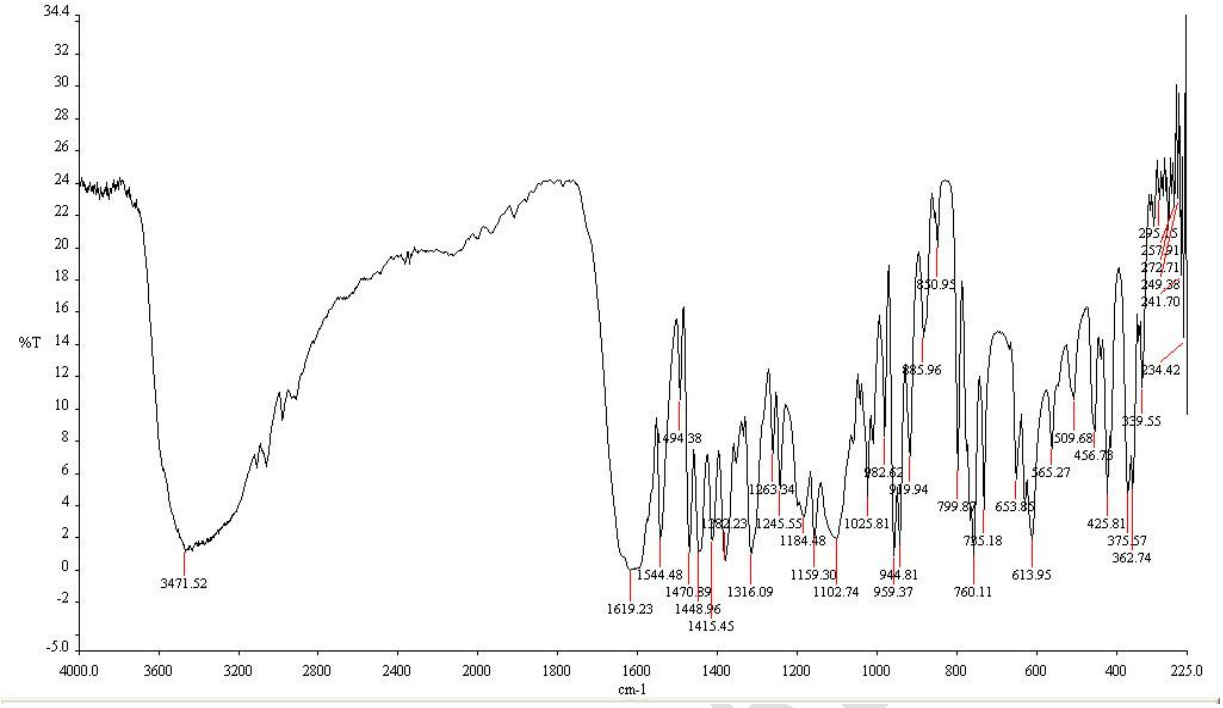

Figure 1: IR spectrum of [VO(sal-ala)(bpy)] complex, V-1

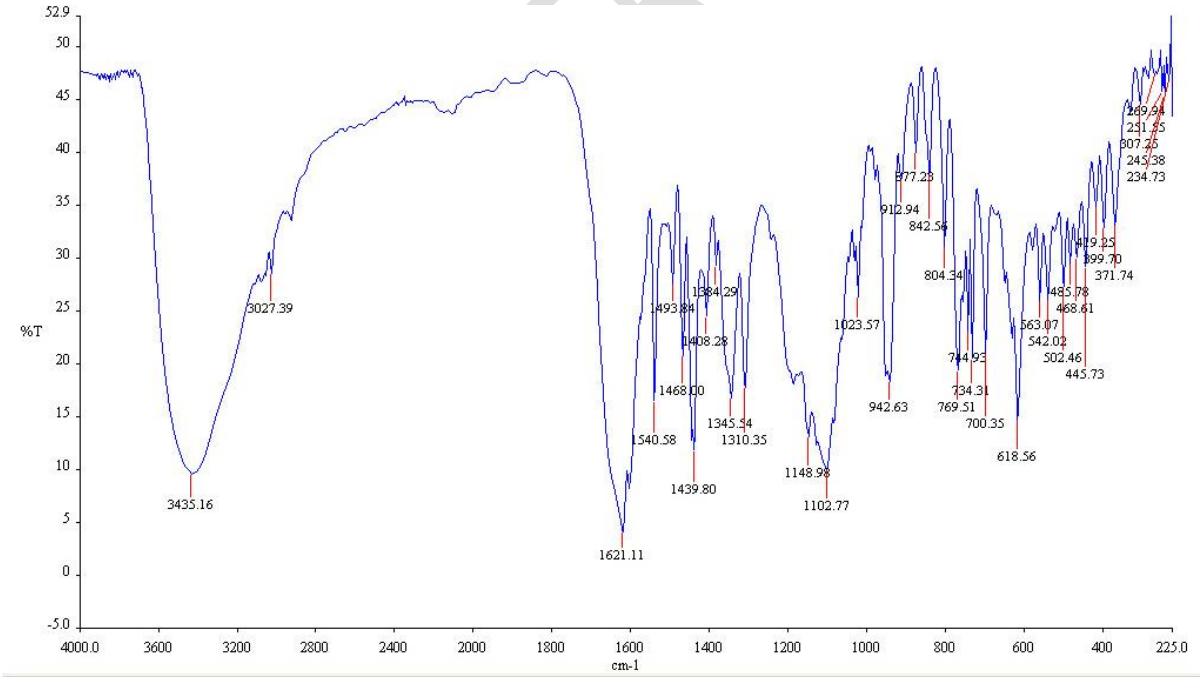

Figure 2: IR spectrum of [VO(sal-pheala)(bpy)] complex, V-2

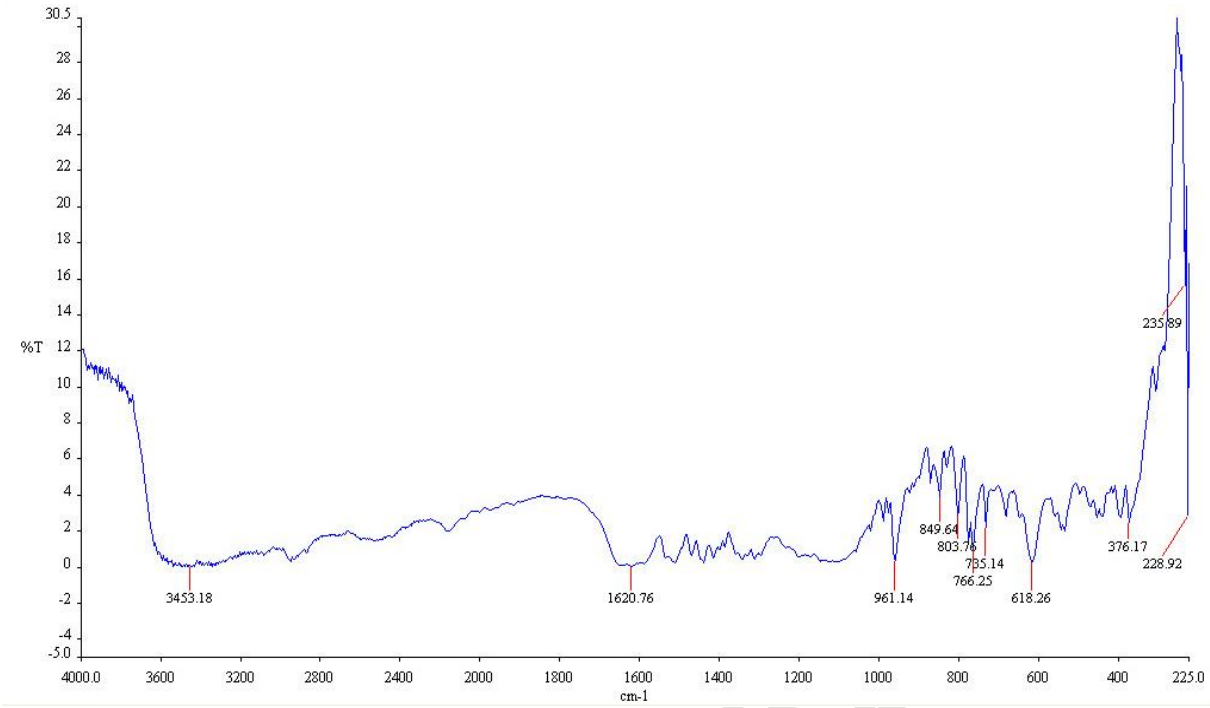

Figure 3: IR spectrum of [VO(sal-leu)(bpy)] complex, V-3

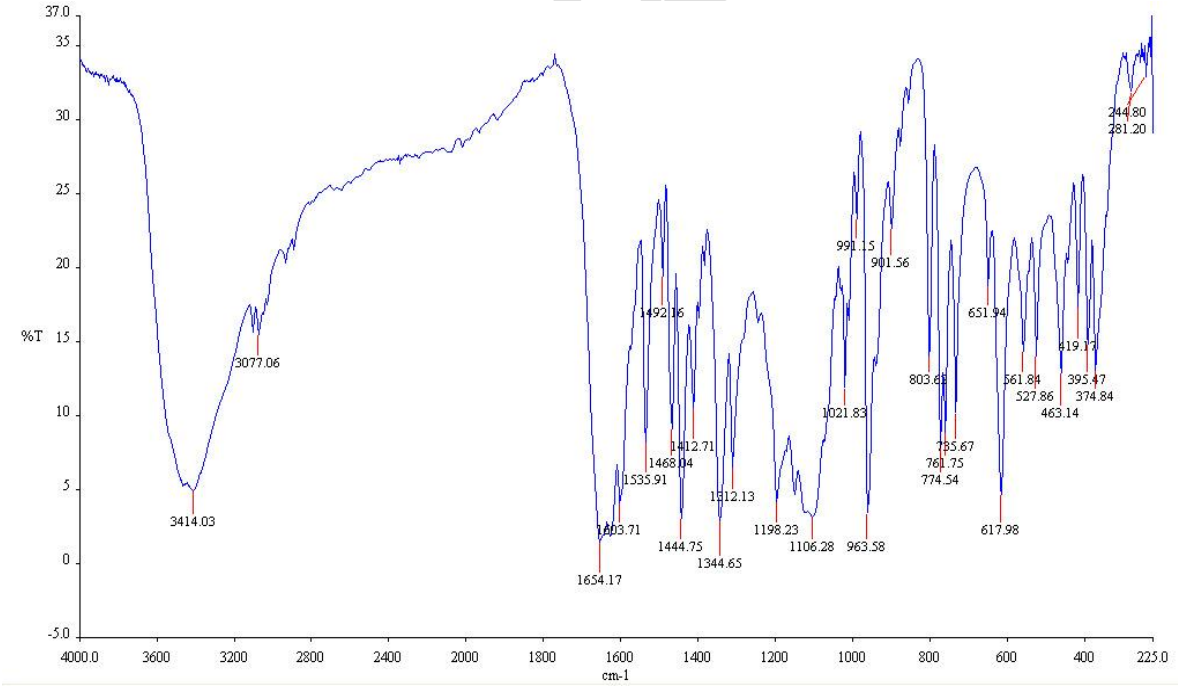

Figure 4: IR spectrum of [VO(sal-gly)(bpy)] complex, V-4

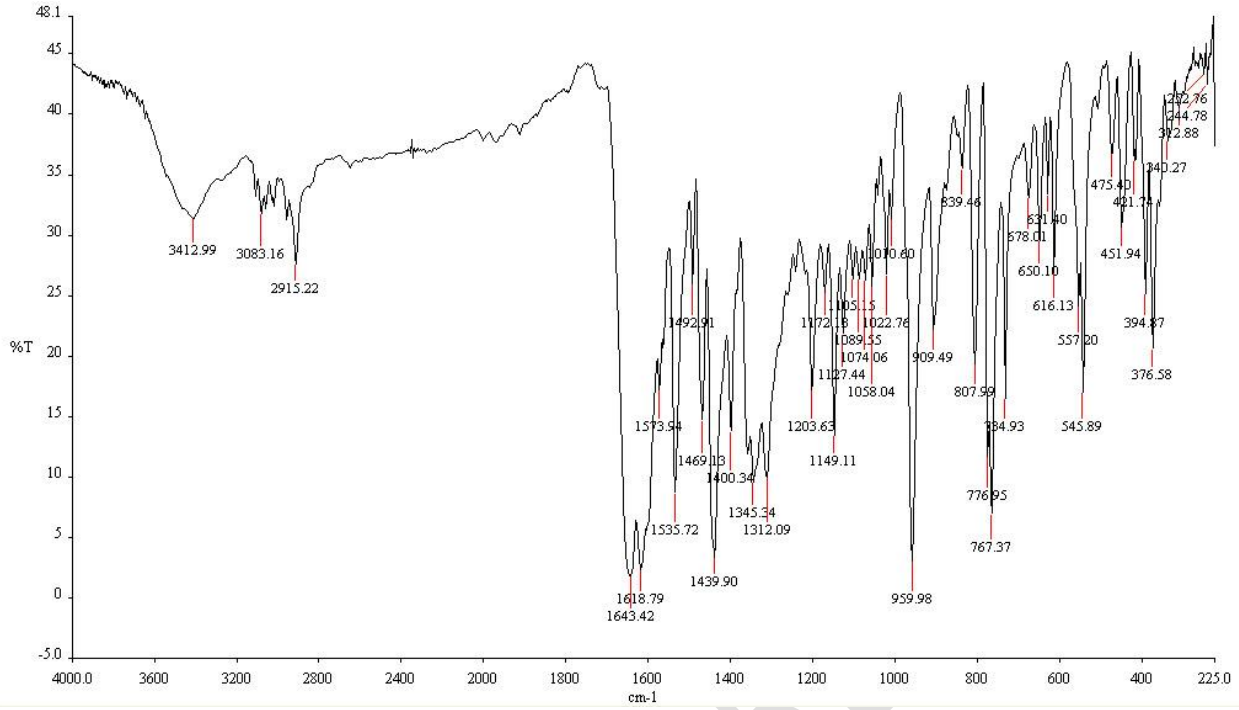

Figure 5: IR spectrum of [VO(sal-met)(bpy)] complex, V-5

3.2 UV-Visible spectral studies

The absorption spectra of the complexes were recorded in DMSO in the wavelength of 200–800 nm range. Important UV-Visible spectra of complexes **(V-1 to V-5)** are tabulated in **Table 3.**

Complexes (**V-1 to V-5)**exhibit a shoulder at ~375 nm due to ligand-to-metal charge-transfer (LMCT, $PhO^{-}\rightarrow V$) transition, and the remaining bands appearing in the UV region are assignable to the intraligand transitions.[55] All complexes display bands at 267–307 nm which are assignable to the $\pi\rightarrow\pi^*$ transition.[56]The absence of low-intensity bands for the d-d transition at around 500 nm[57]in the current complexes could be the result of not optimizing sample concentration during UV data collection.UV-Visible spectra of complexes (V-**1 to V-5**) are given in the Figures **6 –10**.

Table 3 Important UV-Visible spectra of complexes (**1**–**5**)

SI No.	**Complex**	**λ**, nm (**ε**, M^{-1} cm^{-1})		
V-1	[VO(sal-ala)(bpy)]	268−301 (3436−3462)	364 (2572)	377sh (2312)
V-2	[VO(sal-pheala)(bpy)]	267−302 (3676−3524)	364 (2181)	376sh (2161)
V-3	[VO(sal-leu)(bpy)]	268−301 (3662−3325)	364 (2027)	374sh (2008)
V-4	[VO(sal-gly)(bpy)]	270−303 (3462−3311)	364 (2459)	375sh (2364)
V-5	[VO(sal-met)(bpy)]	269−307 (3263−3325)	363 (3175)	388sh (2709)

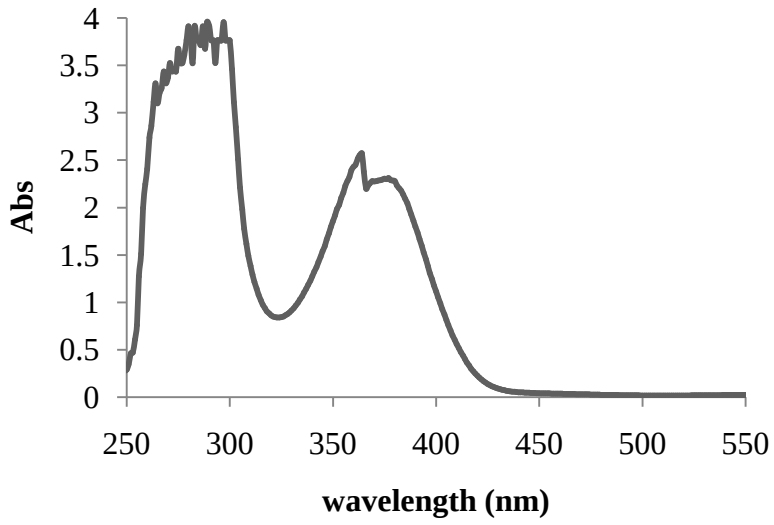

Figure 6 UV-Visible spectrum of [VO(sal-ala)(bpy)] complex, V-1

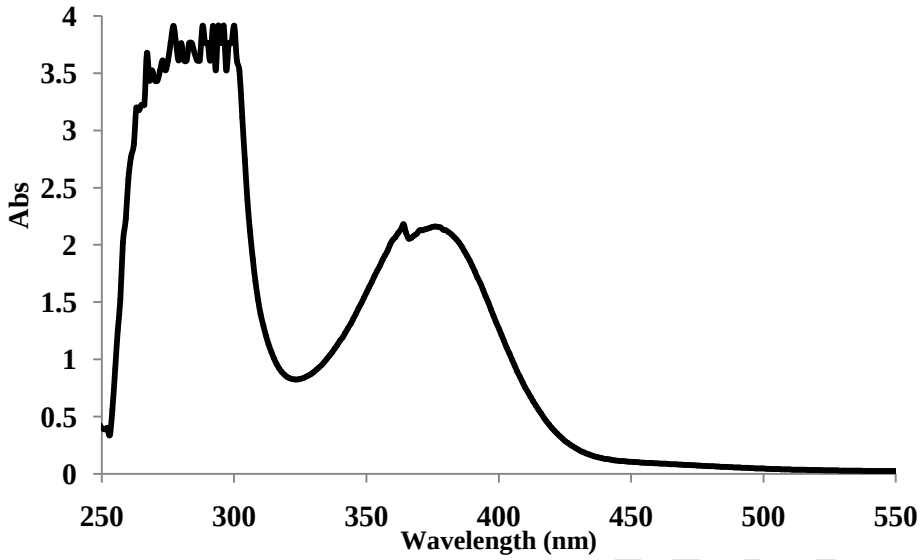

Figure 7 UV-Visible spectrum of [VO(sal-pheala)(bpy)] complex, V-2

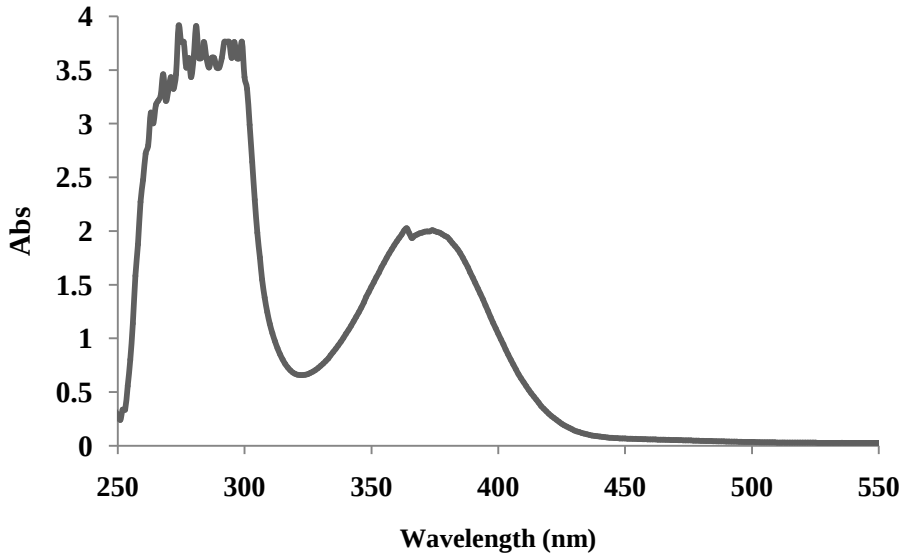

Figure 8: UV-Visible spectrum of [VO(sal-leu)(bpy)] complex, V-3

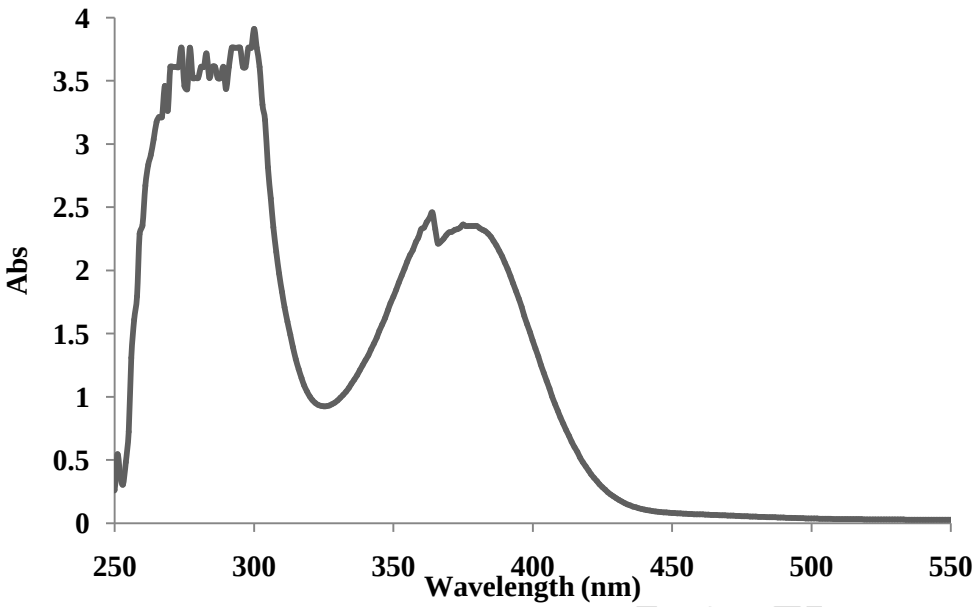

Figure 9: UV-Visible spectrum of [VO(sal-gly)(bpy)] complex, V-4

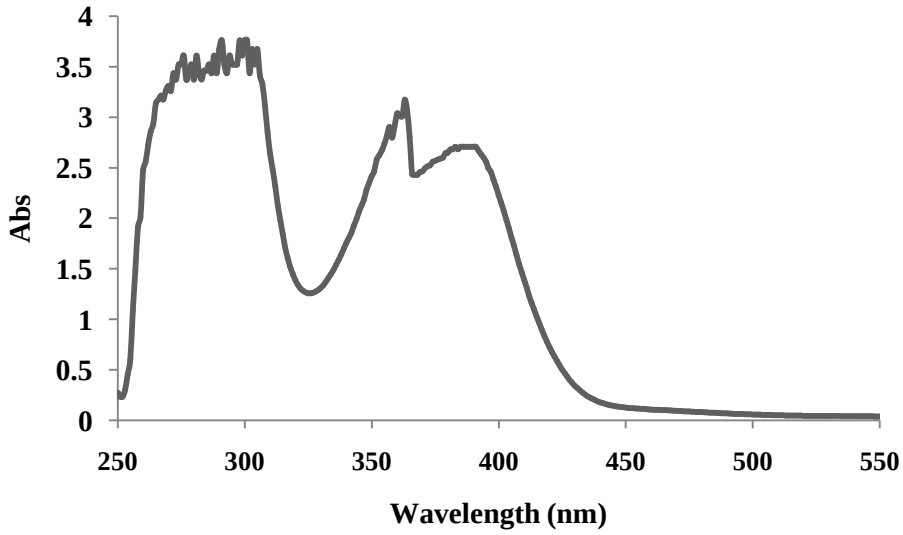

Figure 10: UV-Visible spectrum of [VO(sal-met)(bpy)] complex, V-5

On the basis of the above physical and spectroscopic data, the structure of the complexes may be proposed as distorted octahedral geometry with VO_3N_3 coordination environment. The proposed structure of the oxovanadium(IV) complexes is given below.

Oxovanadium(IV)complexes (V-1 to V-5)

3.3 Antimicrobial Screening Result

The antibacterial activities of the fiveoxovanadium(IV) complexes were screened at the concentration of 10 µg/disc against four pathogenic bacteria viz. *Escherichia coli*, *Proteus vulgaris*, *Bacillus subtilis*and*Staphylococcus aureus*. The results obtained were compared with the inhibition of the standard antibiotic, streptomycin (10 µg/disc). The results are shown in the **Table 4.** The complexes (**V-1** to **V-5**) were found to be active against all the test bacteria, with the complexes **V-2** and **V-3** being even more potent than the standard against all the bacteria except for *Escherichia coli*. The activity of the complexes **V-2** against *Escherichia coli* and the activity of the complex **V-5** against all pathogens are comparable with the standard.

The antimicrobial activity of the complexes may be described on the basis of their effective interaction with the microbes which cause discrete and distinct types of injuries to microbial cells as a result of oxidative stress, protein dysfunction or membrane damage.

Table 4: Antibacterial activities of the oxovanadium(IV) complexes andstreptomycin.

Bacterial strains		**Zone if inhibition, diameter in mm**					
		V-1 10 µg/disc	**V-2 10 µg/disc**	**V-3 10 µg/disc**	**V-4 10 µg/disc**	**V-5 10 µg/disc**	**Streptomycin 10 µg/disc**
Gram	***Bacillus subtilis***	**10**	**24**	**25**	**5**	**19**	**19**

	Staphylococcus aureus	**13**	**26**	**33**	**9**	**15**	**19**
Gram negative	***Escherichia coli***	**8**	**12**	**16**	**6**	**12**	**19**
	Proteus vulgaris	**12**	**23**	**27**	**6**	**18**	**19**

4 Conclusions

The VO^{2+} complexes of *O*,*N*,*O*-donor α-amino acid Schiff bases and 2,2´-bipyridine have been synthesized and characterized. The analytical data reveal that the complexes are non-electrolytic and paramagnetic in nature. The magnetic moment values of the complexes are in accordance with the d^1 electronic configuration of the $V^{IV}O^{2+}$ moiety. IR spectral data indicates the coordination of tridentate amino acid Schiff base ligands to the vanadyl (VO^{2+}) ion.Further research is required before the V-3 complex may be considered a prominent/potent medication in the field of medicinal chemistry.

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