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Synthesis, Characterization and Antibacterial Studies of Oxovanadium Complexes of Tetradentate Schiff Base Derived from 4-Aminoantipyrine, *o*-Phenylene diamine and Vanillin/Furfural

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Two new vanadyl complexes were synthesized from tetradentate Schiff bases having four nitrogens act as donor atoms using 4-aminoantipyrine, *o*-phenylenediamine and vanillin/furfural. These complexes were characterized by elemental analysis, FTIR, UV-visible, ESR spectroscopic methods, magnetic susceptibility and molar conductivity measurements and thermal analysis. These complexes have the general molecular formula $[VOL]SO_4$, where L = tetradentate Schiff base. The higher molar conductivity values support the 1:1 electrolytic nature of the complexes. The infrared spectra reveals the involvement of azomethine nitrogens (-C=N-) coordinated to the metal resulting in MN_4 chromophores. The electronic spectra suggested that they were square pyramidal in shape, and the complexes are paramagnetic in nature. The thermal decomposition of both the complexes yield V_2O_5 as the stable residue in static air atmosphere and decomposition is seen taking place in two stages. The eight line hyperfine splitting in ESR spectra indicates that a single vanadium is present in the molecule. The antibacterial properties against *E. coli*, *S. aureus*, *Serratia* sp, *P. aeruginosa*, *B. cereus* were performed with the Schiff base and the metal complexes. The MIC values indicates that the complexes exhibit greater antibacterial activity than the ligands.

Keywords: Schiff base, 4-Aminoantipyrine, Vanillin, Furfural, *o*-Phenylenediamine, Vanadyl complexes, Antibacterial studies.

INTRODUCTION

Schiff bases are compounds containing a –C=N– (azomethine) group formed from condensation of an aldehyde or ketone with primary amines. These compounds are versatile ligands with different denticity, coordinated to various metals resulted in to metal complexes with novel properties. The growing importance of these ligands and their metal complexes in modern chemistry is the recent observation about their antibacterial, antifungal and oxygen carrier properties. The Schiff base derived from the condensation of 4-aminoantipyrine with ketones are important class of chelating ligands and their metal complexes are of great importance due to their application in industry, extraction properties, analytical chemistry, modelling in biosystems, catalytic and oxygen carrying systems, *etc.* [1-6].

Vanadium is found to be an important element as it exhibits variety of insulin-mimetic properties [7]. The vanadyl complexes and microminerals derived from vanadium has been shown effective in insulin sensitivity. The main advantage of increased insulin sensitivity are that it could promote less fat storage as well as that it may act as an amino acid magnets to cells. Several pharmaceutical agents have been used in diabetic treatment but many side effects occurred such as hypoglycemia, weight gain etc. Therefore some new drugs were needed and vanadyl complexes had been proposed to function as potent insulin-mimetic and antidiabetic agents [7]. Vanadium possesses medicinal pharmacological and biological applications in many enzymatic reactions [8].

Most of the Schiff bases are bidentate while some of them are tetradentate with N_2O_2 chromophore. Macrocyclic tetradentate Schiff bases with four nitrogens (N_4) as donors, similar to porphyrins, heme group in hemoglobin etc and their metal complexes are very rare in coordination chemistry. As a continuation of our work [9,10], to synthesize such ligands and their metal complexes, the present paper describes two new vanadyl complexes and their characterization using physicochemical methods, molar conductance, and their antibacterial properties.

EXPERIMENTAL

Vanillin, 4-aminoantipyrine, furfural, *o*-phenylenediamine, vanadylsulphate, ethanol, methanol etc. were purchased from Merck and used as such without any further purification. The elemental analysis (CHNS) were performed using EL elemental analyzer at Central Electrochemical Research Institute (CECRI). The FT infrared spectra were recorded in the range

4000-400 cm^{-1} on a Shimadzu FTIR 8400S spectrometer using KBr pellet techniques. Electronic (UV-VIS) spectra were recorded on a Schimadzu UV- spectrophototmeter in the range 1100-200 cm^{-1} using DMSO solvent. The thermal analyses were carried out using universal V4.5A thermal analysis instrument in an atmosphere of static air with a heating rate of 10 K/min. The ESR spectra of various Schiff base complexes were recorded on a JES-X3 series in the scan range of 2300-4300 Gauss. The molar conductance was measured on ELICO-CM180 using DMSO as the solvent at room temperature. The antibacterial studies was carried out with disc diffusion method.

Synthesis of tetradentate Schiff bases

From 4-aminoantipyrine, vanillin and *o*-phenylenediamine (AVOP) [9]: The synthesis of Schiff bases can be carried out in two different steps. An ethanolic solution of 4-aminoantipyrine (2.03 g, 0.01 mol, 20 mL) was added to an ethanolic solution of vanillin (1.52 g, 0.01 mol, 20 mL). This mixture was refluxed for 5 h and allowed to cool. The resulting solution was poured into crushed ice, a yellow coloured crystals were formed, filtered and recrystallized from ethanol. The solid intermediate (3.373 g, 0.01 mol in ethanol) was added to an ethanolic solution (20 mL) of *o*-phenylene diamine (0.541 g, 0.005 mol) and refluxed for about 30 h. The contents were poured into crushed ice. The brown solid was separated out, filtered and recrystallized from hot ethanol [11-13]. The Scheme of preparation is shown in Fig. 1.

From 4-aminoantipyrine, furfural and *o*-phenylenediamine (AFOP) [10]: The same method was adopted for this in which furfural (1.52 g, 0.01 mol) in 20 mL alcohol was used instead of vanillin in the first step. Its scheme is represented in Fig. 2.

Synthesis of vanadyl complexes: A solution of the Schiff base was prepared by dissolving 1.493 g (0.002 mol) in 50 mL ethanol. To this solution add an ethanolic solution of $VOSO_4$ (2.53 g, 0.01 mol) and refluxed on a water bath for about 5 h. Its volume was reduced to one third on a waterbath and cooled. The dark green coloured complex was precipitated out, separated, filtered and washed several times with distilled water and hot ethanol [9]. The same method was used for other complex with a solution containing 1.268 g (0.002 mol) of the ligand AFOP in 20 mL ethanol [10].

RESULTS AND DISCUSSION

Elemental analysis and molar conductance studies: The analytical data (Table-1) suggests 1:1 metal ligand stoichiometry in both the cases with SO_4^{2-} as counter ion. The synthesized complexes have the molecular formula [VO(AVOP)] SO_4 and [VO(AFOP)]SO_4 where AVOP and AFOP are the new tetradentate Schiff bases. These complexes are stable, non-hygroscopic and dark green colour. These complexes have molar conductance in the range of 92.5-95.0 S cm^2 mol^{-1} indicating that they are 1:1 electrolytes . The physical analytical and conductivity data are presented in Table-1.

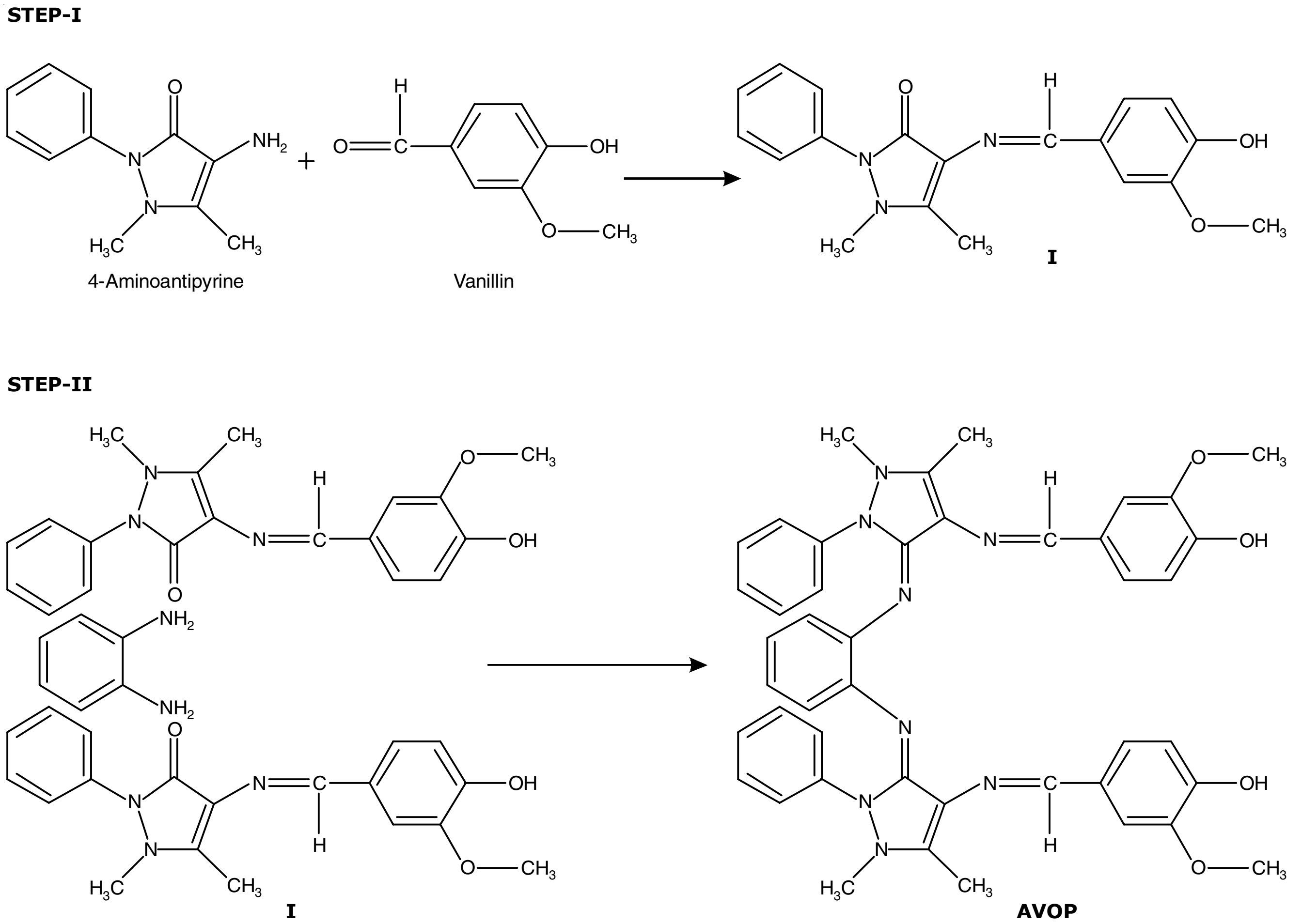

Fig. 1. Schematic representation of synthesis of tetradentate ligand 4-aminoantipyrine, vanillin and *o*-phenylenediamine (AVOP)

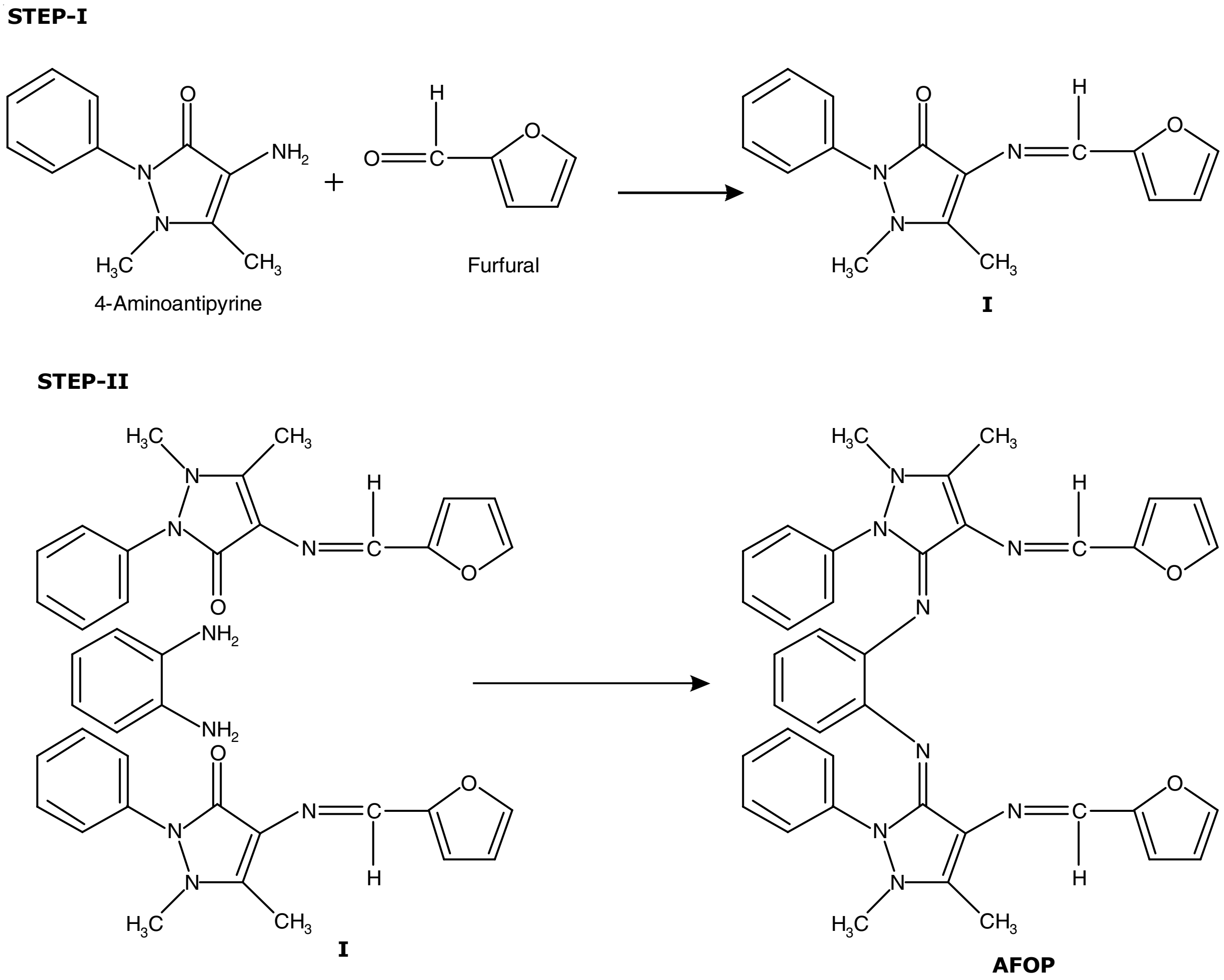

Fig. 2. Schematic representation of the synthesis of tetradentate ligand 4-aminoantipyrine, furfural and *o*-phenylenediamine (AFOP)

Infrared spectra: The absorption at 3107-2990 cm^{-1} (broad peak) is assigned to ν(OH) of phenolic group of AVOP which also appears in the vanadyl complex. This indicates that the deprotonation of –OH group does not take place and was not coordinated to the metal ion. The spectrum of the ligand 1 (AVOP) shows two ν(C=N) bands observed at 1650 and 1624 cm^{-1} was found to be shifted to lower frequencies 1607 and 1573 cm^{-1}, attributed to the coordination of N atom of azomethine group to the metal ion [14-16]. This is further substantiated by the presence of a new band around 445 cm^{-1} due to ν(V–N). Another absorption band at 949 cm^{-1} corresponds to ν(V=O) which was found to be absent in the IR spectrum of the ligand. The peaks observed at 993 cm^{-1} (ν_1), 1120 cm^{-1} (ν_3) and 619 cm^{-1} (ν_4) are due to tetrahedral non-coordinated sulphato ions indicating the presence of SO_4^{2-} ion outside the coordination sphere [17,18] .

Almost the same absorption peaks were found in ligand (AFOP) and its vanadyl complex. The ν(C=N) stretching frequency observed at 1650, 1565 cm^{-1} in the free ligand was shifted to lower frequencies 1607 and 1582 cm^{-1} can be attributed to the coordination of N atom of azomethine group to the metal. The new absorption at 445 cm^{-1} was due to ν(V–N) and a new weak absorption peak at 969 corresponds to ν(V=O). The peaks observed at 987 (ν_1), 1122 (ν_3) and 653 (ν_4) are due to non-coordinated tetrahedral SO_4^{2-} ion. The decrease in the ν(C=N) is due to the lowering of CN bond order as a result of coordination of ligand to metal *via* azomethine nitrogen. The IR data are presented in Table-2.

UV-visible electronic spectra and magnetic susceptibility measurement: The free ligands show absorption maxima appearing around 34482 and 29850 cm^{-1} for AVOP and 33557 and 27777 cm^{-1} for AFOP was due to n→π* and π→π* transi-

TABLE-1
PHYSICAL, ANALYTICAL AND CONDUCTIVITY DATA OF LIGANDS AND COMPLEXES

Compound	m.w.	Colour	Yield (%)	Elemental analysis (%): Found (calcd.)					Λ_M (S cm^2 mol^{-1})
				C	H	N	S	V	
$C_{44}H_{42}N_8O_4$ (AVOP)	746.77	Brown	80	71.02 (70.76)	5.52 (5.67)	14.80 (14.99)	–	–	
$[VO(AVOP)]SO_4$	909.72	Dark green	75	59.16 (58.08)	4.53 (4.65)	13.52 (12.31)	3.42 (3.52)	7.34 (7.36)	95.0
$C_{38}H_{34}N_8O_2$ (AFOP)	634.73	Brown	75	72.00 (71.90)	5.30 (5.40)	17.55 (17.65)	–	–	
$[VO(AFOP)]SO_4$	797.67	Dark green	70	55.05 (57.21)	4.47 (4.30)	13.86 (14.05)	4.98 (4.01)	8.40 (8.39)	92.5

TABLE-2
INFRARED SPECTRAL DATA OF THE SCHIFF BASES AND ITS VANADYL COMPLEXES

Compound	ν(OH)	ν(C=N)	$ν(SO_4^{2-})$			ν(V=O)	ν(V–N)
			$ν_1$	$ν_3$	$ν_4$		
$C_{44}H_{42}N_8O_4$ (AVOP)	3107-2990 (broad)	1650, 1624	–	–	–	–	–
$[VO(AVOP)]SO_4$	3055-2998 (broad)	1607, 1573	993	1120	619	949	445
$C_{38}H_{34}N_8O_2$ (AFOP)		1650, 1565	–	–	–	–	–
$[VO(AFOP)]SO_4$		1607, 1582	987	1122	653	969	445

tion respectively. But in the complex three higher energy bands appearing around 22471, 15151 and 11904 cm^{-1} assigned to $^2B_2{\rightarrow}^2A_1$, $^2B_2{\rightarrow}^2B_1$ and $^2B_2{\rightarrow}^2E$ for complex **1** and 22471, 15822 and 11210 cm^{-1} due to $^2B_2{\rightarrow}^2A_1$, $^2B_2{\rightarrow}^2B_1$ and $^2B_2{\rightarrow}^2E$ for complexes **2**, respectively. These absorption bands are typical of square pyramidal [19-23] VO^{2+} species.

The magnetic moments of these complexes were seen to be in the range 1.98-2.0 BM which are also supporting the square pyramidal geomentry of VO^{2+} complexes, a 3d^1 system [24]. The electronic spectral details and magnetic moments were presented in Table-3.

TABLE-3
UV-VISIBLE SPECTRAL DATA AND
MAGNETIC MOMENTS OF THE COMPLEXES

Compound	Absorption max (cm^{-1})	Assignments	$μ_{eff}$ (BM)
$C_{44}H_{42}N_8O_4$-AVOP	34482 29850	n→π* π→π*	
$[VO(AVOP)]SO_4$	22471 15151 11904	$^2B_2{\rightarrow}^2A_1$ $^2B_2{\rightarrow}^2B_1$ $^2B_2{\rightarrow}^2E$	1.98
$C_{38}H_{34}N_8O_2$-AFOP	33557 27777	n→π* π→π*	
$[VO(AFOP)]SO_4$	22471 15822 11210	$^2B_2{\rightarrow}^2A_1$ $^2B_2{\rightarrow}^2B_1$ $^2B_2{\rightarrow}^2E$	2.0

Thermal studies: From the thermogram of the complex $[VO(AVOP)]SO_4$ (Fig. 3) it was observed that the compound is thermally stable upto 170 °C indicating a well defined horizontal plateau. The first stage of decomposition is seen starting at 175 °C and progressing till 272.63 with a mass loss of 72.2 %. The second stage of decomposition starts immediately at 272.63 °C itself and ends at 725 °C with a mass loss of 17.8 % leaving behind a residue of 10 %. After 725 °C, the residue is seen stable in static air atmosphere.

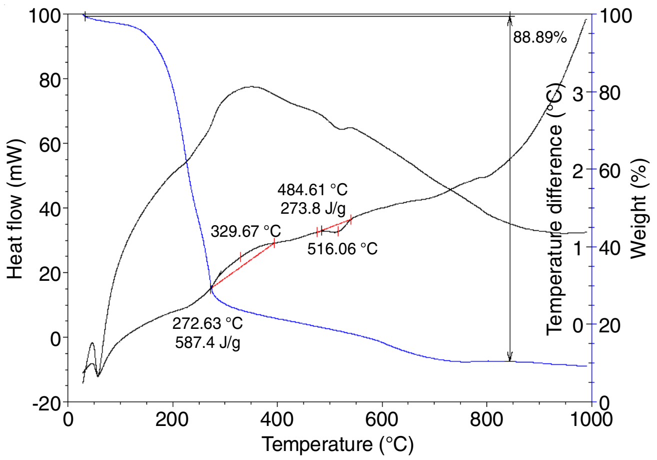

Fig. 3. TG/DTA curve of $[VO(AVOP)]SO_4$ in static air

On heating above 175 °C, the loss of bulky Schiff bases takes place from the complex with a calculated value of 82 %. But the observed value was only 72.2 % (first stage) suggested that before the complete loss of Schiff base, the second stage, decomposition of counter ion SO_4^{2-} is taking place. The observed mass percentage of the residue 10 % is in good agreement with the theoritical value of 9.99 % due to the formation of V_2O_5 [25].

$$[VO(AVOP)]SO_4 \longrightarrow \tfrac{1}{2}V_2O_5 + \text{Gaseous products}$$

The thermogram of the complex **2**, $[VO(AFOP)]SO_4$ also show the same two stage decomposition pattern (Fig. 4). This compound was thermally stable upto 150 °C and first stage of decomposition is seen in the range 150-225 °C with a mass loss of 78.5 %. The second stage starts immediately at 225 °C and ends at 625 °C with a mass loss of 11.7 % leaving behind a residue of 9.8 %. Here also decomposition pattern is similar to the first compound $[VO(AVOP)]SO_4$. At high temperature decomposition of bulky Schiff base and SO_4^{2-} takes place with a stable residue of V_2O_5 in static air atmosphere. The calculated value of the residue was 11.3 %.

$$[VO(AVOP)]SO_4 \longrightarrow \tfrac{1}{2}V_2O_5 + \text{Gaseous products}$$

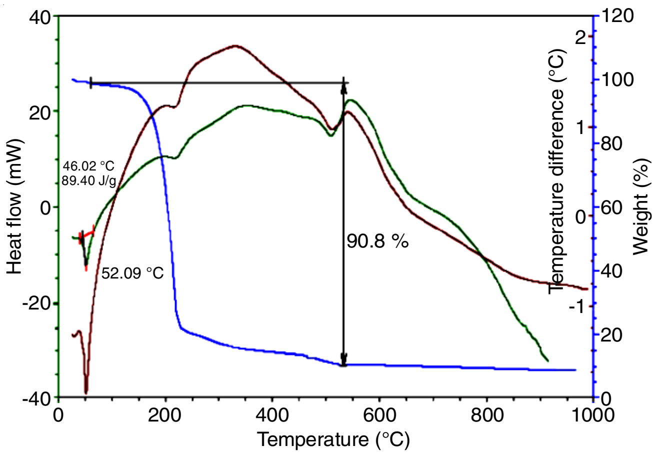

Fig. 4. TG/DTA curve of $[VO(AFOP)]SO_4$ in static air

ESR spectra: The X-band ESR spectra of the oxovanadium complexes were recorded in DMSO solution at liquid nitrogen temperature (Figs. 5 and 6). In the frozen state, the complexes gave typical eight line spectra with two sets of resonance peaks, one set due to parallel while the other set due to perpendicular components, due to the interaction between the electron and the vanadium nuclear spin (I = 7/2). The two set of eight line patterns show that single vanadium is present in the molecule [26,27]. The various parameters calculated from

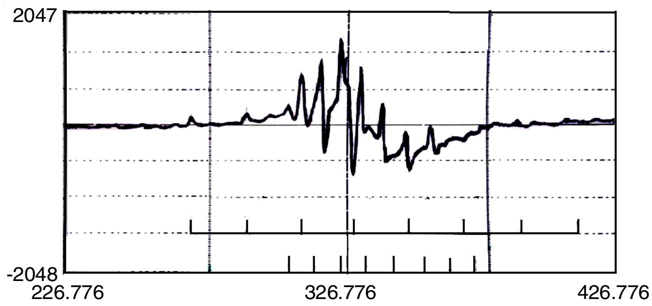

Fig. 5. ESR spectrum of [VO(AVOP)]SO_4 at LNT

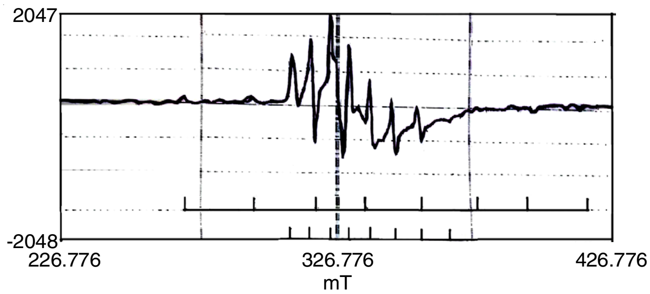

Fig. 6. ESR spectrum of [VO(AFOP)]SO_4 at LNT

the spectra are given below. The $g_{(av)}$ and $A_{(av)}$ can be calculated using:

$$g\beta H = h\nu \tag{1}$$

$$g_{(av)} = 1/3(g_{\parallel} + 2\ g_{\perp}) \tag{2}$$

$$A_{(av)} = 1/3\ (A_{\parallel} + 2\ A_{\perp}) \tag{3}$$

The various spin Hamiltonian parameters evaluated are given below:

[VO(AVOP)]SO_4 $g_{\parallel} = 1.945$, $g_{\perp} = 1.951$, $g_{(av)} = 1.949$
$A_{\parallel} = 199.13$ G, $A_{\perp} = 95.23$ G, $A_{(av)} = 129.86$ G

[VO(AFOP)]SO_4 $g_{\parallel} = 1.922$, $g_{\perp} = 1.955$, $g_{(av)} = 1.944$
$A_{\parallel} = 209.95$ G, $A_{\perp} = 83.32$ G, $A_{(av)} = 125.53$ G

The $g_{\parallel}$, $g_{\perp}$, $g_{(av)}$, $A_{\parallel}$, $A_{\perp}$, $A_{(av)}$ values are in good agreement with the square pyramidal shape.

Antibacterial studies: The ligands and the vanadyl complexes were assayed for their antimicrobial activities against *E. coli*, *S. aureus*, *P. aeruginosa*, *Serratia* (sp) and *Bacillus cereus* by the disc diffusion method [28,29]. It was found that the complexes have better activity than the ligands explained by the theory of Tweedy. This is probably due to the greater lipophilicity nature of the complexes. Such increased activity of metal chelates can be explained on the basis of overtones concept and chelation theory. According to overtone's concept of cell permeability the lipid membrane that surrounds the cell favours the passage of lipid soluble materials. On chelation, the polarity of metal ion will be reduced to a greater extent due to overlap of the ligand orbitals and partial sharing of positive charge of the metal ion with donor groups. Therefore the delocalisation of π electrons in the chelate ring increases and enhances the penetration of the complexes into lipid membranes. The antibacterial data are presented in Table-4.

Conclusion

Two square pyramidal vanadyl complexes were synthesized from tetradentate Schiff bases with four nitrogen atoms as donar atoms (with two azomethine entity). The metal complexes formed were 1:1 electrolytic in nature. The synthesized systems were characterized by microanalysis, molar conductance values, FTIR, ESR, UV-visible spectroscopy and TG analyses.

The analytical and spectral data suggests that azomethine N atoms coordinated to the metal ions generating a square pyramidal VN_4O systems. The antibacterial screening tests were also performed against certain bacteria which indicate that the vanadium complexes exhibit good antibacterial activity than the ligands. Based on the above results the structure of coordination compounds were represented in Fig. 7.

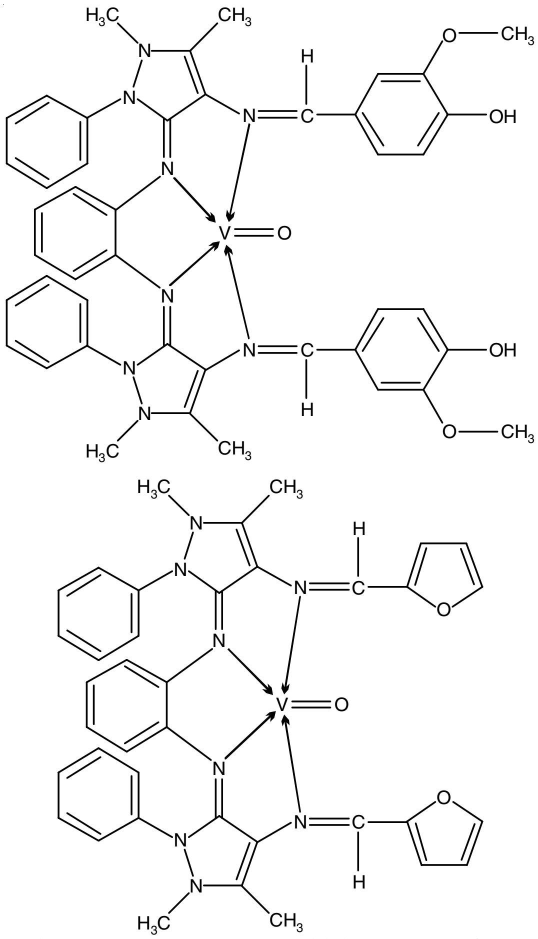

Fig. 7. The proposed square pyramidal structure of complexes [VO(AVOP)]SO_4 and [VO(AFOP)]SO_4

TABLE-4
ANTIBACTERIAL ACTIVITY DATA OF THE LIGAND AND ITS COMPLEXES

Compound	*Escherichia coli*	*Staphylococcus aureus*	*Pseudomonas aeruginosa*	*Serratia* sp	*Bacillus cereus*	Inference
$C_{44}H_{42}N_8O_4$(AVOP)	11	10	7	9	12	++
[VO(AVOP)]SO_4	12	13	12	12	12	+++
$C_{38}H_{34}N_8O_2$(AFOP)	9	10	8	11	9	++
[VO(AFOP)]SO_4	11	11	11	11	8	+++

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