Indian Journal of Chemistry
Vol. 59A, April 2020, pp. 526-532

VO(IV) complexes of N_2O_2 tetradentate ligands with flexible alkyl spacer: synthesis, characterization and antibacterial activities

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Received 23 October 2019; revised and accepted 12 March 2020

Three Schiff base ligands which contain N_2O_2 donors and their oxo-vanadium(IV) complexes have been synthesized. The ligand $C_{14}H_{16}N_2O_2$ has obtained as a result of the reaction of 1,4-diaminobutane with 2-furan-carboxyaldehyde within the framework of Schiff base condensation method. The same reaction path is followed replacing 1,4-diaminobutane by 1,6-diaminohexane and 1,8-diaminooctane in separate reactions to obtain the two other new ligands. Then, the synthesized ligands are employed to attain the oxo-vanadium(IV) complexes as results of their reactions with $VOSO_4.H_2O$. The ligands have been characterized by FTIR, ^{13}C NMR, ^{1}H NMR, and LC/ESI-MS. The VO(IV) complexes have been elucidated by FTIR, LC/ESI-MS, energy dispersive X-ray spectroscopy, thermogravimetric methods, and the conductivity and magnetic susceptibility measurements. The antibacterial activities of the ligands and their complexes have been determined on the microorganisms which are aligned as *Escherichia coli* ATCC 25922, *Salmonella typhimurium* ATCC 14028, *Staphylococcus aureus* ATCC 25923, *Listeria monocytogenes* ATCC 19115 and *Bacillus cereus* ATCC 11778. The complexes, in general, appeared to be more active than their parent ligands. All the activities can be classified as moderate in comparison with the corresponding antibiotic effect on the same bacteria.

Keywords: Schiff base, Antibacterial activity, Oxo-vanadium(IV) complexes, Furan

The Schiff base ligand and their generally stable metal complexes have wide application fields in industrial and clinical research. Some of these metal complexes are employed in dye and textile industries, polymer technology and electronic industry[1-7] as well as in medicinal and agricultural research due to their high biological activity[8,9]. As a sub-class of the Schiff base molecules, the furan-derived ligand complexes with metals have been subjected to studies such as their optical properties and the usage of them as sensors in biomedical research[10,11]. Research has shown that vanadium complexes have potential of applications such as their antitumor, antibacterial, antiviral and antiparasitic effects[12-16], while they also show antidiabetic properties which are similar to that of insulin. Therefore, they attract attention in clinic, in vivo and in vitro studies which are carried out to explore alternative chemicals to insulin in the treatment of diabetes. Also, the furan-derived Schiff base ligands and oxovanadium(IV) complexes have a special importance in the search of antidiabetics[17]. The three ligands containing N_2O_2 donors were synthesized by Schiff base condensation of the aromatic aldehyde 2-furan-carboxyaldehyde with three different diamines which are 1,4-diaminobutane, 1,6-diaminohexane and 1,8-diaminooctane, respectively. 1,4-diaminobutane was studied and used to build ruthenium complexes, earlier[18]. The other two, i.e., 1,6-diaminohexane and 1,8-diaminooctane are newly synthesized to the best of our knowledge. These ligands were used to obtain three different tetra dentate vanadium complexes. The structures of synthesized ligands were identified by FTIR, ^{13}C-NMR, ^{1}H-NMR, LC/ESI-MS as those of oxo-vanadium(IV) complexes were elucidated by FTIR, energy dispersive x-ray spectra (EDX), thermogravimetric (TG) analysis, differential thermal analysis (DTA), conductivity and magnetic measurements. Also, the antibacterial activities of the ligands and complexes were studied in detail.

Materials and Methods

Instruments

The FTIR spectra were acquired within the range 450−4000 cm^{-1} by a Perkin-Elmer spectrometer. The ^{1}H NMR and ^{13}C NMR spectra of the compounds were recorded on Varian 300 MHz and Varian 75.5 MHz, respectively. The mass spectra of ligands and complexes were recorded in the Agilent Technologies 6460 Triple Quad LC/ESI-MS device. The thermogravimetric measurements were made in the temperature range of 20−1200 °C with the heating rate of 10 °C min^{-1} under nitrogen atmosphere (20 mL min^{-1}) by a Seiko SII TG-DTA 6300-TG/DTA analyzer. The chemical composition has been determined by EVO LS 10 model Electron Microscope (SEM-TEM-EDX). The biological activities of the the ligands and their oxo-vanadium complexes were realized by absorbance measurements in thermoscientific multiscan Go multi-plate spectrophotometer. The solid-state magnetic susceptibility data were recorded on powdered microcrystalline samples using a Sherwood Scientific Magnetic Susceptibility Balance. The molar conductivities were measured using a Jenco 3173 Conductivity Meter.

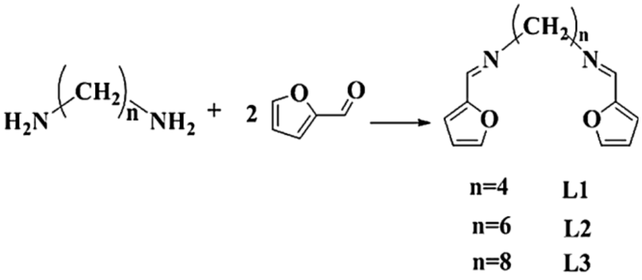
Synthesis of Furan-derived Schiff Base Ligands

The synthesis of the ligands is shown in Scheme 1. In details, 1,4-diaminobutane (0.44 g, 5 mmol) was dissolved in 20 mL of methanol to prepare $C_{14}H_{16}N_2O_2$ (L1). 2-furan-carboxaldehyde (0.96 g, 10 mmol) was weighed and dissolved by adding 25 mL methanol in a different container. The solution was heated and mixed by adding the aldehyde solution slowly within an hour. A few drops of glacial acetic acid were added to the mixture to ease the reaction. It was refluxed monitoring the reaction with thin-layer chromatography using (1:1) ethylacetate: hexane solvent. Then, the methanol was removed using a rotary evaporator. The end-product was dried in vacuum oven. The dark brown colored and viscose L1 (0.97 g, 80%) was obtained.

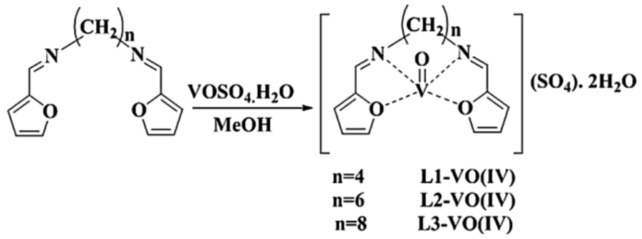
The above procedure was repeated twice using 1,6-diaminohexane (0.58 g, 5 mmol) and 1,8-diaminooctane (0.72 g, 5 mmol) instead of 1,4-diaminobutane (0.44 g, 5 mmol), respectively. The ligands $C_{16}H_{20}N_2O_2$ (L2) (1.03 g, 78%) and $C_{18}H_{24}N_2O_2$ (L3) (0.99 g, 83%) were obtained in viscous brown colored form.

Synthesis of oxo-vanadium(IV) complexes

The formation of the complexes is shown in Scheme 2. First, L1 (0.244 g, 1 mmol) was diluted in 20 mL methanol while heated at the same time. Then, $VOSO_4.H_2O$ salt (0.163 g, 1 mmol) was dissolved in 20 mL methanol and added dropwise to the L1 solution within an hour. The mixture was refluxed for 2 days and left for a few days to obtain its solid form. The L1-VO(IV) complexes were filtered and washed with methanol. Finally, it was dried in a vacuum oven.



Scheme 1



Scheme 2

The above procedure was repeated twice using L2 and L3 instead of L1. All the complexes L1-VO(IV), L2-VO(IV) and L3-VO(IV) were green in powder form.They were weighted 0.16 g, 0.17 g and 0.50 g with the yields 52%, 50% and 40%, respectively. We did not obtain the complexes in their crystalline forms.

Antibacterial activities

The Broth Micro dilution method by Clinic Laboratory Standards Institute (CLSI) was used to determine antibacterial efficiency of the ligands and the complexes. The bacteria tested were *Escherichia coli* ATCC 25922, *Staphylococcus aureus* ATCC 25923, *Listeria monocytogenes* ATCC 19115, *Salmonella typhimurium* ATCC 14028, and *Bacillus cereus* ATCC 11778. These microorganisms were incubated in Tryptic Soy Broth (TSB) at 37 °C for 24 and 48 h. The McFarland scale was fixed to 0.5 in determination of the cell concentrations. The antibiotic control was provided by the commercially available ampicillin. All the solutions were filtered through 0.45 µm sterile filters. The substance concentrations were 200, 100, 50, 25, 12.5 and 6.25 in the units of µg/mL. Starting from 200 µg/mL stock solutions, the concentrations were obtained diluting each concentration in half. All the microplates were incubated at 37 °C for 24 and 48 h. The sterility and the growth controls were realized by the pure chemical substance embedded wells for each concentration and the pure bacteria planted wells, respectively. The percentage viabilities were determined by measuring the absorbance values at 600 nm[19,20].

Result and discussion

The ligands

The ligands L1, L2 and L3 which were synthesized by using Schiff base condensation method were enlightened by FTIR, ^{13}C NMR, ^{1}H NMR, and LC/ESI-MS analysis.

FTIR results

The selected FTIR features for the synthesized ligands were L1- ν_{max} (cm^{-1}): 2966−2923 (C-H), 1660 (C=N), 1250 (C-O); L2- ν_{max} (cm^{-1}): 2929−2854 (C-H), 1643 (C=N), 1238 (C-O), L3- ν_{max} (cm^{-1}): 3043−2924 (C-H), 1624 (C=N), 1260 (C-O).

The C-H vibrations at 3000±45 cm^{-1}, C=N vibrations at 1642±48 cm^{-1} and C-O vibrations at 1249±19 cm^{-1} for L1, L2, and L3 ligands, respectively are in agreement with the previous measurements[21]. The typical starting material signals represented by N-H vibrations of primary amines (3500−3300 cm^{-1}) and C=O vibration of aldehyde (1750 cm^{-1}) have been absent in all the three spectra. This indicates that H-N-H and C=O groups in the starting chemicals ended up as C=N groups in the final products, as expected.

NMR results

The ^{1}H NMR and ^{13}C NMR spectra results for the ligands are as follows: L1-δ_H (300 MHz; $CDCl_3$): 1.65−1.71 (2H, m, CH_2), 3.52 (2H, t, CH_2), 6.37 (1H, t, CH), 6.63 (1H, d, CH), 7.41 (1H, d, CH), 7.98 (1H, s, CHN), L2-δ_H (300 MHz; $CDCl_3$): 1.35−1.38 (2H, m, CH_2), 1.69−1.70 (2H, m, CH_2), 3.56 (2H, t, CH_2), 6.43 (1H, t, CH), 6.67 (1H, d, CH), 7.47 (1H, d, CH), 8.04 (1H, s, CHN), L3-δ_H (300 MHz; $CDCl_3$): 1.170−1.173 (4H, m, CH_2), 1.53−1.56 (2H, m, CH_2), 3.92 (2H, t, CH_2), 6.28 (1H, t, CH), 6.55 (1H, d, CH), 7.32 (1H, d, CH), 7.89 (1H, s, CHN), L1-δ_C (75.5 MHz; $CDCl_3$): 28.62 (CH_2), 61.68 (CH_2), 111.74, 114.08, 144.80 (CH), 149.88 (C), 151.62 (CHN), L2-δ_C (75.5 MHz; $CDCl_3$): 27.34 (CH2), 30.99 (CH_2), 62.04 (CH_2), 111.75, 113.94, 144.80 (CH), 149.65 (C), 151.76 (CHN), L3-δ_C (75.5 MHz; $CDCl_3$): 27.32 (CH_2), 29.40 (CH_2), 30.87 (CH_2), 61.88 (CH_2), 111.64, 113.79, 144.59 (CH), 149.49 (C), 151.59 (CHN).

The integration of CH_2 multiplet of L1 in 1.65−1.71 ppm interval gives two hydrogens. The two multiplets which belong to L2 in 1.35−1.38 ppm and 1.69−1.70 ppm intervals content four hydrogens. Also, the two multiplets of L3 in 1.170−1.173 ppm and 1.53−1.56 ppm intervals contain six hydrogens. This increase in the hydrogen numbers from L1 to L3 is due to the increase of CH_2 number in the bridge between two furans. The NMR signals of the other symmetrical CH_2 protons and aromatic protons and CHN protons have granted the common properties of the three ligands as the measurements of these signals are self-consistent. The different and common properties of the ligands determined by ^{1}H NMR spectra repeated by the ^{13}C NMR spectra as the number of carbons are identified as expected for each ligand. Additionally, the CH_2 carbons, aromatic carbons and CHN carbons have consistent NMR signals.

Mass spectra results

The mass spectra of L1, L2 and L3 are given in Supplementary Data, Figs S1a, S1b and S1c, respectively. LC/ESI-MS data for the ligands L1 (*m/z*) $[M+H]^+$: 245.1000, L2 (*m/z*) $[M+H]^+$: 273.2000 and L3 (*m/z*) $[M+H]^+$: 301.2000 were in agreement with the calculated molecular weights.

The oxo-vanadium(IV) complexes

The complexes L1-VO(IV), L2-VO(IV) and L3-VO(IV) were synthesized by the reaction of Schiff base ligands with $VOSO_4.H_2O$[21,11]. The structures of the obtained oxo-vanadium(IV) complexes are clarified by FTIR, LC/ESI-MS, EDX spectra, thermal analysis, conductivity and magnetic moment measurements.

FTIR results

The FTIR spectrum of L1-VO(IV) presents specific C=N stretching at 1622 cm^{-1}. Almost identically, L2-VO(IV) and L3-VO(IV) show the same stretchings at 1624 cm^{-1} and 1622 cm^{-1}. The other characteristic vibrations supporting their proposed structures of the complexes L1-VO(IV), L2-VO(IV) and L3-VO(IV) are ν(V=O) stretchings at 962, 956 and 968 cm^{-1}, respectively. Also, the ν(V-N) stretchings at 595, 611 and 598 cm^{-1} and ν(V-O) vibrations at 485, 477 and 480 cm^{-1} for L1-VO(IV), L2-VO(IV) and L3-VO(IV) supports the constitution of the complexes[22,23].

LC/ESI-MS results

The LC/ESI-MS data of L1-VO(IV) in Supplementary Data, Fig. S2a showed a molecular ion peak at (*m/z*) $[M^{\bullet+}]$: 311.2000 as radical cation, while this figure is 311.2 as its calculated molecular weight. The mass spectra of L2-VO(IV) shows in Supplementary Data, Fig. S2b gives (*m/z*) $[M^{\bullet+}]$: 339.1000 (calculated 339.3) while that of L3-VO(IV) gives (*m/z*) $[M^{\bullet+}]$: 366.9000 (calculated 367.3) in Supplementary Data, Fig. S2c. All the mass spectra results have been in agreement with the predicted molecular weights.

EDX results

The EDX elemental analysis results by percentage weight were as follows: L1-VO(IV): (w%) C 41.81(6.10), N 7.69(2.35), O 32.86(4.91), S 5.58(0.27), V 12.06(0.30), L2-VO(IV): (w%) C 41.90(5.90), N 8.06(2.33), O 30.49(4.56), S 6.99(0.32), V 12.56(0.30), L3-VO(IV): (w%) C 46.06(6.30), N 7.13(1.74), O 31.59(3.67), S 5.30(0.19), V 9.92(0.27). These experimental results are in agreement with the calculated percentage weights of the complexes. Their EDX spectra are shown in Figs 1(a, b and c) for L1-VO(IV), L2-VO(IV) and L3-VO(IV), respectively. The peaks corresponding to V, C, S, N and O elements observed in the energy dispersive spectra were in accord with the previous measurements on the similar materials[24,25]. The presences of vanadium peaks in the spectra support the formation of the complexes. The quantitative existence of the sulfur and oxygen in the EDX spectra shows that $SO_4.2H_2O$ is in the structure as the counter ion of the vanadium oxide-ligand complex.

TG analysis

The TG and DTA plots for L1-VO(IV), L2-VO(IV) and L3-VO(IV) are shown in Figs 2(a, b and c), respectively. The decomposition processes can be described as presenting three stage occurrences in the all complexes. For the L1-VO(IV), the first stage decomposition takes place in the temperature range of 25−150 °C. It reflects a mass loss of 10.0% (calculated 8.1%) which corresponds to the two moles of water. The second and third stages of the decomposition observed in the temperature range 150−550 °C in where the organic parts and the SO_4 removed from the structure with a mass loss of 72.0% (calculated 73.2%). The remaining residue was 18.0% (calculated 18.7%) vanadium dioxide. The water loss of the L2-VO(IV) and L3-VO(IV) are 9.0% (calculated 7.6%) and 7.0% (calculated 7.2%), respectively in 25-150 °C range. These decomposition rates are similar to that of the L1-VO(IV). The decomposition of sulfate ion and the organic parts in L2-VO(IV) were 72.0% (calculated 74.9%) in the 150−600 °C against that of L3-VO(IV) 76.0% (calculated 76.2%) in the temperature range of 150−530 °C. The second and third decomposition of the complexes under nitrogen were symbolized by the exothermic peaks in the DTA for the all complexes are shown in Figs 2a–2c. The vanadium dioxide residues of L2-VO(IV) and L3-VO(IV) were 19.0% (calculated 17.5%) and 17.0% (calculated 16.5%), respectively. The TG–DTA curves of the VO(IV) complexes are very similar to each other supporting

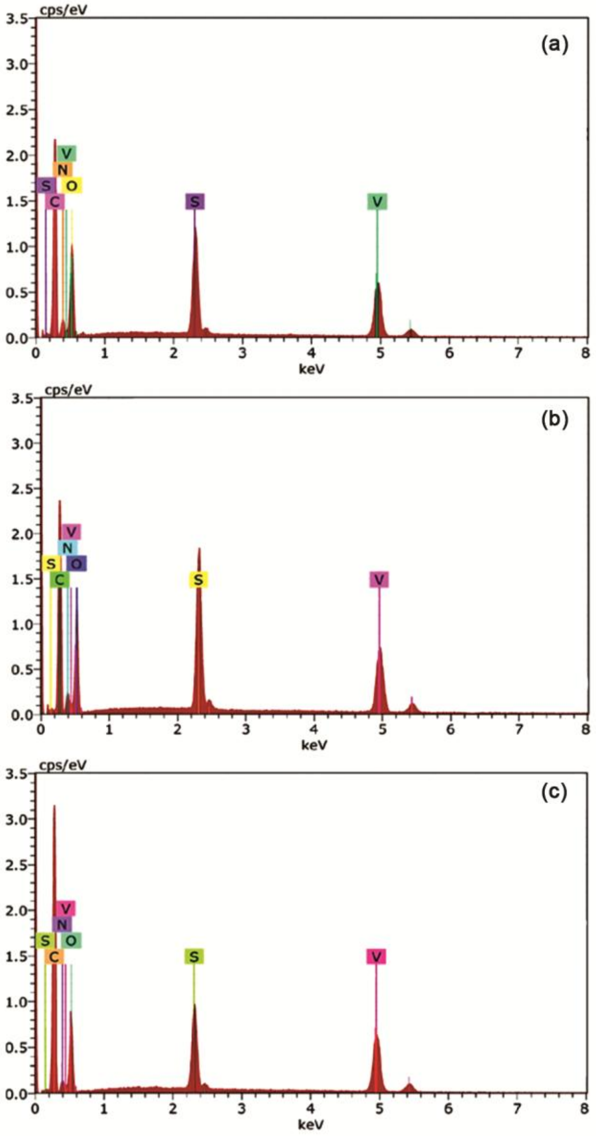


Fig. 1 — EDX spectra of the complexes (a) L1-VO(IV), (b) L2-VO(IV) and (c) L3-VO(IV).

the constitution of the complexes. The thermal stability of complexes, based on the temperature at which the third mass loss stage ends, follows the order L3-VO(IV) < L1-VO(IV) < L2-VO(IV).

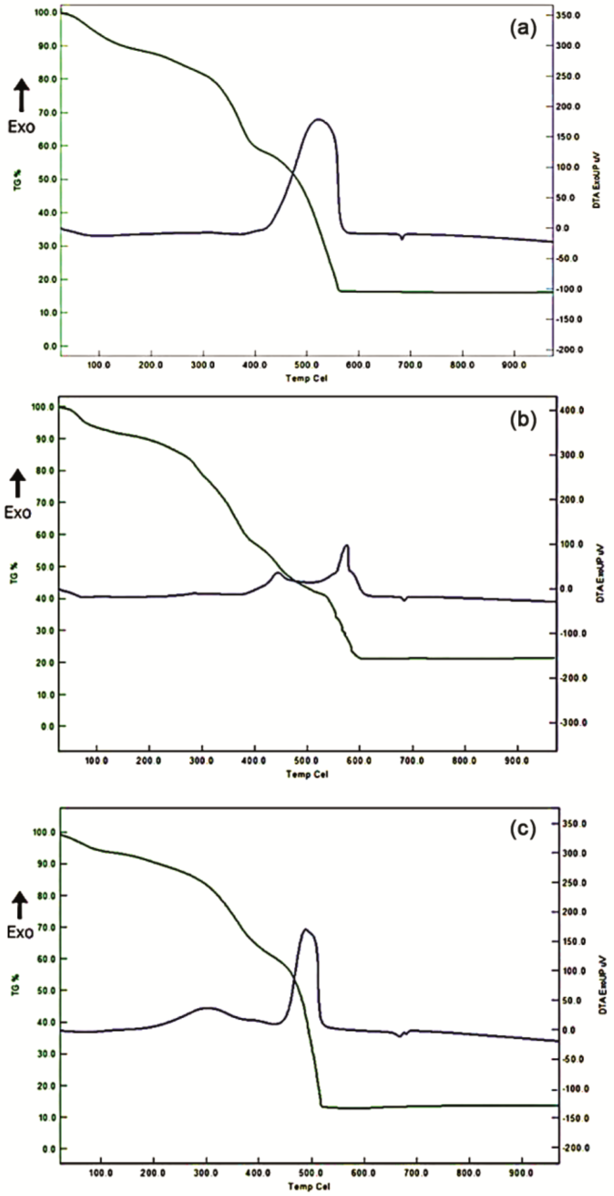


Fig. 2 — TG-DTA spectra of the complexes (a) L1-VO(IV), (b) L2-VO(IV) and (c) L3-VO(IV).

Conductivity and magnetic susceptibility

The molar conductivities and the magnetic moments of the complexes are presented in Table 1. While the magnetic moment of the coordination compound is useful in determining the valence of the metal atom and in many cases defining the geometric structure of a complex, conductivities illuminate the electrolytic nature of the complexes.

The conductance measurements were carried out for 1 mmol DMF solutions of the complexes at 25 °C. The high molar conductivity values of the complexes determined in the 78–80 Ω^{-1} cm^2 mol^{-1} range show that all three complexes were established as 1:1 electrolyte[26-28].

In determination of their geometrical structure, the magnetic susceptibilities of the solid-state complexes under discussion were measured by the Gouy balance method. The magnetic moment values measured in the range of 1.71−1.74 BM at room temperature were compatible to the reported magnetic moments for the square-pyramidal geometry. It is the fact that they are well suited for oxo-vanadium(IV) complexes having a single unpaired electron[29-31].

Antibacterial activities of ligands and complexes

The antibacterial activities for both the ligands and complexes are presented in Table 2. The viability percentages were given for the 200 µg/mL dose application including the antibiotic control on the bacteria. The incubation time allowed for each bacteria sample were 48 h.

Apparently the complexes probably due to their oxo-vanadium ion are more active than their parent ligands, and these activities can be classified moderate in terms of the antibiotic effects on the

Table 1 — Conductivity and magnetic moments of oxo-vanadium(IV) complexes

Complex	μ_{eff} (BM)	Ω_M (Ω^{-1}cm^{2}mol^{-1})
L1-VO(IV)	1.72	78
L2-VO(IV)	1.74	80
L3-VO(IV)	1.71	79

Table 2 — Antibacterial activity of the ligands and complexes in units of percentage viability for 200 µg/mL dose as compared with the activity of standard ampicillin

Viability (%)	L1/ L1VO(IV)	L2/ L2VO(IV)	L3/ L3VO(IV)	Ampicillin
Escherichia coli ATCC 25922	105 / 105	105 / 100	109 / 85	11
Salmonella typhimurium ATCC 14028	114 / 108	111 / 101	121 / 110	24
Staphylococcus aureus ATCC 25923	115 / 75	103 / 68	113 / 90	31
Listeria monocytogenes ATCC 19115	108 / 68	110/ 75	98 / 73	10
Bacillus cereus ATCC 11778	109 / 50	107 / 65	108 / 55	33

bacteria. The L1-VO(IV), L2-VO(IV) and L3-VO(IV) were active on *Bacillus cereus* ATCC 11778 with 50%, 65%, and 55% viability, respectively. These figures show quite a high efficiency of the complexes on the latter bacteria if they are compared with the antibiotic viability 33% on the same bacteria.

Conclusions

The three Schiff base ligands L1, L2 and L3 were synthesized by condensation of 2-furan-carboxaldehyde with the diamines, namely 1,4 diaminobutane, 1,6 diaminohexane and 1,8 diaminooctane, respectively. Afterwards, these ligands were separately reacted with $VO(SO_4).H_2O$ to obtain the L1-VO(IV), L2-VO(IV) and L3-VO(IV) complexes. The ^1H NMR results have shown that both the aliphatic proton resonances of the ligands and the proton resonances of their aromatic rings together with the singlets of the imine protons were found as expected and in accord with the concerning studies. The range of the aliphatic, the aromatic ring and the imine carbon resonances were also consistent with the previous studies supporting the existence of the predicted ligand structures. The structure of the ligands was also confirmed by FTIR and mass spectra. In the FTIR spectra of the ligands, the vibrations of the starting materials such as primary amine and aldehyde are not observed, and the imine vibrations occurring in their place are evidence of the robust synthesis of the ligands. Additionally, the molecular ion peaks and degradation products observed in the mass spectra have been consistent with the molecular structure of the ligands.

These syntheses of the complexes have been validated by the ν(V=O), ν(V-O) and ν(V-N) vibrations which are the characteristic peaks of the concerning bonds in their FTIR spectra. The existence of V, C, S, N and O are observed in the energy dispersive x-ray spectra. The thermal analysis results show that the ligands coordinate the vanadium ion with their nitrogens of imines and oxygens of furan. The high molar conductance of oxovanadium(IV) complexes reflects their electrolytic nature and the measured magnetic moment values of complexes suggest a square-pyramidal geometry. Finally, the oxovanadium(IV) complexes have been found to have stronger influence on the selected bacteria in comparison with those of furan-derived ligands. The activities of complexes on *Bacillus cereus* ATCC 11778 have the antibiotic equivalent effect.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at: http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(04)526-532_SupplData.pdf.

Acknowledgement

The study was supported by the Research Fund of Trakya University with the project TÜBAP-2016/22.

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