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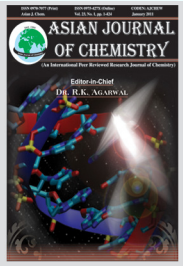

Synthesis, Characterization and Biological Activity of Vanadium(V) Complexes of 4-*n*-Hexyloxybenzoylhydrazine

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A series μ-oxo-di-vanadium(V)) complexes $[(C_6H_{13}OC_6H_4C(-O)NN=CHR)_4V_2O_3]$ (**10-17**) was prepared by the reaction of vanadyloxy(IV) sulphate pentahydrate with some Schiff's bases $[C_6H_{13}OC_6H_4C(=O)NH\text{-}N=CHR]$ (**1-9**) [where R = formaldehyde, acetaldehyde, butyraldehyde, crotonaldehyde, benzaldehyde, cinnamaldehyde, 4-N,N-dimethylaminobenzaldehyde, 4-methoxybanzaldehyde and 2-hydroxybenzaldehyde, respectively]. The Schiff's bases were characterized by physico-chemical techniques like IR, ^{1}H NMR and UV-visible spectroscopic techniques. The complexes were also characterized by using IR, ^{1}H NMR, TGA, magnetic moment and molar conductance. All the ligands coordinated with the VO_2(II) ion in a uninegative bidentate mode giving six coordinated oxobridged bimolecular complexes. The antibacterial screening of the complexes indicated that complex **10-13** and **16** showed antibacterial activity but the other complexes did not show any activity as compared to a standard drug (canamycin). Further more complex 10 showed low activity against *Bacillus sereus*, *Shigella boydii*, *Saccharromyces cerevaceae*, *Candida albicans* and *Aspergillus niger* and complex **13** showed low activity against *Bacillius subtilis*, *Escherichia coli*, *Sarcina lutea* and *Shigella boydii* bacteria. In contrast, complex **11** and **12** showed low activity whereas complex **16** showed moderate activity against all the bacteria.

Key Words: Aroyl hydrazones, VO_2(II) complexes, Antibacterial activities.

INTRODUCTION

Considerable attention has been paid to the chemistry of transition metal complexes of Schiff bases containing nitrogen and other donor atoms[1-4]. The ligands derived by the condensation of a primary amine and an active carbonyl group, contain the azomithine group[5,6]. Schiff bases are a class of important compounds in medicinal and pharmaceutical field. They show biological activities including antibacterial[7-10], antifungal[11,12], anticancer[13-15] and herbicidal[16], activities. Schiff bases are also utilized as starting materials in the synthesis of industrial materials[17]. As for example, transition metal complexes of aroylhydrazones showed prominent liquid crystalline behaviour[18,19]. Recently scientists gave special attention to the synthesis of oxovanadium complexes owing to their catalytic[20], structural[21,22], DNA binding[21] and DNA cleavage[21,24] activities. Moreover, vanadium has been shown to decrease the occurrence of cancers, by intercepting alkylating toxins before DNA damage can occur. As for example scientists revealed that dioxovanadium(V) compounds of the salicylidene hydrazide ligand provide an excellent entry into alkylation studies of oxovanadium compounds[25]. They showed that introduction of electron donating groups into the aromatic ring increase electron density on the O and N ligand donor atoms and thereby increase the electronegativity on the central metal ion which then increases nucleophilicity of the terminal oxygen ligands. As a consequence reactivity towards alkylating agents can be enhanced[25]. The present work deals with the biological activities of a series of μ-oxo-di-vanadium(V) complexes of aroylhydrazones containing various aliphatic and aromatic aldehyde moieties.

EXPERIMENTAL

General procedure: IR spectra (4000-400 cm^{-1}) were taken as KBr disc using a NICOLET 380 FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a Brucker Ultra-Shield™ 400 spectrometer in $CDCl_3$ and DMSO-d_6 using tetra methyl silane as standard solvent. Magnetic measurements were carried out on a magnetic susceptibility balance (Sherwood Scientific). Conductance was determined on a heavy-duty conductivity/temperature meter, Extech Instruments (USA), model No. 407303. The UV-visible spectra were run on a T60U spectrophotometer (200-800 nm) using 10^{-5} M

solution (DMSO). Thermogravimetric analysis were recorded on a TGA Q50 V6.4 Instrument (Belgium).

Ethyl-4-hydroxybenzoate, hydrazine hydrate (99.99 %) and aldehydes were obtained from BDH chemicals (England), vanadyloxy(II) sulphate pentahydrate was obtained from Fluka Chemica (Switzerland). The solvents were purified by standard method[26]. The starting material (ethyl-4-hexyloxyethyl-be-nzoate) and the ligand precursor (4-hexyloxybenzoyl hydrazine) were prepared by known procedure[27].

Qualitative antimicrobial assay: Sixteen pathogenic bacteria *viz*., *Bacillus sereus*, *Bacillius megaterium*, *Bacillius subtilis*, *Salmonella paratyphi*, *Salmonella typhi*, *Vibrio parahemolyticus*, *Vibrio mimicus*, *Staphylococcus aureus*, *Escherichia coli*, *Shigella dysenteriae*, *Pseudomonas aureus*, *Sarcina lutea*, *Shigella boydii*, *Saccharromyces cerevaceae*, *Candida albicans* and *Aspergillus niger* were used to test the biological potential of the complexes. Antimicrobial activity was determined by modified disc diffusion method[28].

A lawn of microorganisms was prepared by pipetting and evenly spreading 10 µL of inoculum, adjusted turbidometrically to 10^5-10^6 CFU/cm^3 (CFU = colony forming units) onto agar set in petri dishes, using nutrient agar (NA) for the bacteria. Whatman No. 1 filter paper discs of 5 mm diameter were impregnated with dimethyl sulphoxide stock solutions of the complexes (8 mg dissolved in 200 µL, 10 µL/disc, 400 µg/disc) and dried under sterile conditions. Dried dishes were then placed on previously inoculated agar surfaces. The plates were inverted and incubated for 24 h at 35 ± 2 ºC for the bacteria. Antimicrobial activity was indicated by the presence of clear inhibition zones as diameter (mm) around the discs. Canamycin (30 µg/disc) was used as standard drug.

Synthesis

Preparation of the Schiff's bases (1-9) N-(formalidene)-4-hexyloxybenzoylhydrazone, 1: Formaldehyde solution (37 %) (0.16 g, 2 mmol) was added to a solution of 4-hexyloxybenzoylhydrazine (0.57 g, 2 mmol, 20 mL ethanol) and the resulting mixture was stirred for 1 h (checked by TLC). The ligand was isolated with the evaporation of solvent in vacuum line as it is highly soluble in ethanol and purified by column chromatography in dichloromethane and pet-ether (2:1; v/v) as eluent. The ligand **2** was also obtained by the same procedure. The ligand **3** was obtained after reduction of volume into one-third. The ligands **4-9**, were prepared by stirring for 15-30 min without further treatment, separated by filtration and washed with ethanol successively.

Preparation of vanadium(V) complexes (10-17): To a solution of N-(formalidene)-4-*n*-hexyloxybenzoylhydrazone (0.248 g, 1 mmol, 20 mL ethanol) vanadyloxy(IV) sulphate pentahydrate (0.126 g, 0.5 mmol in 20 mL ethanol) was added and the mixture was refluxed for 2 h. The resultant solution was allowed to cool overnight. A dark blue precipitate was obtained, which was separated and washed successively with ethanol and chloroform and consequently dried *in vacuo* over anhydrous $CaCl_2$.

Complex **11**, was also prepared by the same manner, but complexes **12-17**, were obtained without cooling the resultant solution with the exception that complexes **15** and **16** were obtained in the presence of a solution alcoholic KOH.

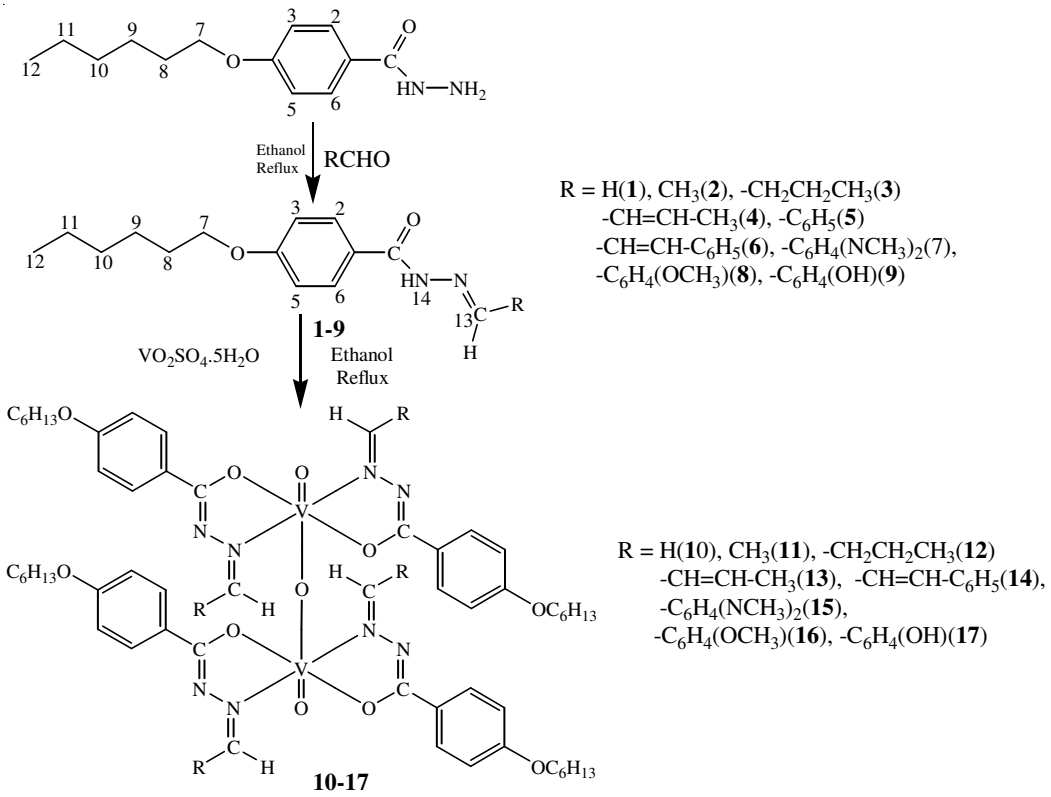
RESULTS AND DISCUSSION

Synthesis: The Schiff base ligands **1-9**, of the type [$C_6H_{13}OC_6H_4C(=O)NHN=CHR$] were prepared by the condensation of 4-*n*-hexyloxybenzoyl hydrazine, with different aliphatic and aromatic aldehydes such as formaldehyde, acetaldehyde, butyraldehyde, crotonaldehyde, benzaldehyde, cinnamaldehyde, 4-N,N'-dimethylaminobenzaldehyde, 4-methoxybenzaldehyde and 2-hydroxybenzaldehyde at room temperature. The oxobridged divanadium(V) complexes of the type [$(C_6H_{13}OC_6H_4C(-O)NN=CHR)_4V_2O_3$], **10-17**, (**Scheme-I**) were prepared by condensation of the Schiff bases with vanadyloxy(IV) sulphate pentahydrate under reflux up to 2 h. Only the complexes **15**, **16** were obtained in the presence of potassium hydroxide. The ligand **5** did not coordinate with VO_2(II) ion even in the presence of potassium hydroxide or pyridine up to 48 h of reflux. Probably the high electron withdrawing effect of phenyl ring in the Schiff base prevents the coordination of VO_2(II) ion, whereas the presence of KOH neutralizes the electron donating effect of 4-N,N-dimethylaminobenzaldehyde and 4-methoxybenzaldehyde derivatives in deprotonation of the Schiff bases during coordination. All the complexes were insoluble in most common organic solvents except DMSO. The room temperature molar conductance values of the complexes in DMSO (Table-1) at 10^{-5} M solution was found to be in the range form 19.6-6.0 ohm^{-1} cm^2 mol^{-1}, suggested that the complexes are non-electrolytic in nature. All the complexes are diamagnetic in nature.

TABLE-1
ANALYTICAL DATA OF THE COMPOUNDS

Comp.	Formula	Colour	m.p. (ºC)	Yield (%)	Λ_m (µS)
1	$C_{14}H_{20}N_2O_2$	White	87	49	–
2	$C_{15}H_{22}N_2O_2$	White	89	47	–
3	$C_{17}H_{26}N_2O_2$	White	91	45	–
4	$C_{17}H_{24}N_2O_2$	White	160	42	–
5	$C_{20}H_{24}N_2O_2$	White	181	44	–
6	$C_{22}H_{26}N_2O_2$	White	200	66	–
7	$C_{22}H_{29}N_3O_2$	White	193	43	–
8	$C_{21}H_{26}N_2O_3$	White	142	54	–
9	$C_{20}H_{24}N_2O_3$	White	135	62	–
10	$C_{56}H_{76}N_8O_{11}V_2$	Dark blue	280	27	7.5
11	$C_{60}H_{84}N_8O_{11}V_2$	Orange	285d	25	18.5
12	$C_{68}H_{100}N_8O_{11}V_2$	Reddish brown	285d	23	19.6
13	$C_{68}H_{92}N_8O_{11}V_2$	Dark yellow	275	37	23.6
14	$C_{88}H_{100}N_8O_{11}V_2$	Dark yellow	255	38	19.6
15	$C_{88}H_{112}N_{12}O_{11}V_2$	Dark green	330d	33	6.0
16	$C_{80}H_{102}N_8O_{15}V_2$	Orange yellow	165	25	19.6
17	$C_{84}H_{100}N_8O_{15}V_2$	Orange	170	25	9.7

FTIR Spectra: The IR spectra (Table-2) of the Schiff bases showed a sharp medium intensity band in the region between 3286-3157, a very strong band in between 1649-1630 and a strong band in the region between 1610-1607 cm^{-1} corresponding to the ν(N-H), ν(C=O) and ν(C=N) stretching vibrations, respectively[21]. The ligands also exhibited a strong band at *ca.* 1261-1251 cm^{-1} assignable to the ν(C-O) (phenolate) stretching vibration[23]. The ligands also showed a medium to strong band at 1055-1022 cm^{-1} region for the ν(N-N) vibration of the azine moiety. The complexes **10-17**, exhibited a medium



R = H(**1**), CH_3(**2**), -$CH_2CH_2CH_3$(**3**)
-CH=CH-CH_3(**4**), -C_6H_5(**5**)
-CH=CH-C_6H_5(**6**), -$C_6H_4(NCH_3)_2$(7),
-$C_6H_4(OCH_3)$(**8**), -$C_6H_4(OH)$(**9**)

R = H(**10**), CH_3(**11**), -$CH_2CH_2CH_3$(**12**)
-CH=CH-CH_3(**13**), -CH=CH-C_6H_5(**14**),
-$C_6H_4(NCH_3)_2$(**15**),
-$C_6H_4(OCH_3)$(**16**), -$C_6H_4(OH)$(**17**)

Scheme-I

TABLE-2
IR SPECTRA OF THE LIGANDS AND THEIR VANADIUM COMPLEXES

Compound	ν(V-O-V)	ν(N-H)	ν(C=O)	ν(C=N)	ν(C=C) ring	ν(V=O)	ν(V-O-V)	ν(V-O)	ν(V-N)
1	–	3276 m	1647 vs	1610 s	1586 ms 1506 s	–	–	–	–
2	–	3270 m	1642 vs	1609 s	1575 s 1508 s	–	–	–	–
3	–	3262 m	1638 s	1609 s	1576 m 1505 m	–	–	–	–
4	–	3280 m	1637 s	1608 s	1582 m 1506 s	–	–	–	–
5	–	3270 m	1645 s	1610 s	1586 m 1508 s	–	–	–	–
6	–	3157 br	1630 s	1609 s	1508 s	–	–	–	–
7	–	3211 m	1631 s	1609 vs	1597 s 1508 s	–	–	–	–
8	–	3246 m	1647 vs	1607 s	1541 m 1506 s	–	–	–	–
9	–	3286 m	1649 vs	1607 s	1546 m 1506 s	–	–	–	–
10	3441 br	–	–	1607 vs	1577 m	980 m	843 m	467 w	420 w
11	3180 br	–	–	1608 vs	1506 s	981 m	843 m	661 m	603 m
12	3424 br	–	–	1608 vs	1505 s	979 m	843 m	659 m	588 m
13	3393 br	–	–	1607 vs	1508 ms	991 ms	842 m	662 m	607 w
14	3417 br	–	–	1607 vs	1567 s	989 m	680 w	600 w	4022
15	3436 br	–	–	1608 s	1508 m	968 m	619 ms	618 m	400 w
16	3448 br	–	–	1609 vs	1506 m	981 m	840 s	619 w	400 w
17	3483 br	–	–	1607 vs	1545 m	887 m	–	619 s	441 w

intensity broad band in the region between 3483- 3417 cm^{-1}, along with a medium to strong band at 843-840 cm^{-1}, assigned for the ν(V-O-V) stretching vibration, which suggested the formation of μ-oxo bridged vanadium(V) complexes[23]. The complexes contained a medium intensity band at 991-987 cm^{-1} region due to the ν(V=O) stretching mode of VO_2(II) ion[23]. The complexes showed prominent strong bands at *ca.* 1607 cm^{-1} for the ν(C=N) stretching mode of the azomithine moiety. This band has shifted to the lower frequency due to coordination through the nitrogen atom. The absence of ν(N-H) and ν(C=O) band in the complexes indicated that coordination had taken place through the deprotonation of the ligands *via* the

enol form during complexation, *i.e.*, through the transformation of $[C_6H_{13}OC_6H_4C(=O)NHN=CHR] \rightarrow [C_6H_{13}OC_6H_4C(O) = NN=CHR]$ mode. The complexes showed a strong to medium band for the ν(C-O) (phenolate) stretching mode[23], at 1262-1256 cm^{-1}. The stretching was shifted to the higher frequency region (*ca.* 5 cm^{-1}) than the corresponding ligands. In the complexes the ν(N-N) stretching vibration was shifted to the lower frequency (1033-1002 cm^{-1}) because of coordination through azomithine nitrogen atom.

^{1}H NMR spectra: The ^{1}H NMR spectra of the Schiff bases (Table-3) showed multiplet bands at δ *ca.* 0.90 (H_{12}), 1.33 (H_{11+10}), 1.45 (H_9), 1.78 (H_8), respectively for the hexyl moiety[27]. The ligands also showed a triplet at δ 4.0-3.95 ppm for the CH_2O protons (H_7) of the hexyl moiety moiety[27]. The ligands contained doublets at δ 7.98-7.68 and 6.93-6.81 ppm for the H_{2+6} and H_{3+5} protons of -C_6H_4- aromatic ring[27]. Both the H_{2+6} and H_{3+5} protons were shielded in case of saturated aldehydes due to the inductive effect of the alkyl group where as these protons were deshielded in the ligands in case of aromatic and conjugated aldehydes. The ligands exhibited two singlets at δ 8.41-7.52 and 9.92-8.99 corresponding to the azomithine (H_{13}) and amide (H_{14}) protons of [-C(=O)NH-N=CHR] moiety[27]. In ligand **3**, the shift for the -$CH_2CH_2CH_3$ group was overlapped with the hexyl moiety. In ligand **4**, a doublet at δ 1.84, a multiplet at 6.06 and a triplet at 6.29 was observed for the protons of -CH=CH-CH_3 moiety[27]. The ligand **5**, showed two doublets at δ 7.84, 7.64 for the $H_{2'+6'}$ and $H_{3'+5'}$ protons and a triplet at δ 7.35 for the $H_{4'}$ proton of phenyl ring in N=CHR moiety[27]. The ligand **6**, exhibited a triplet at δ 7.07 for the -C<u>H</u>=CH-Ph, a doublet at δ 6.74 for the -CH=C<u>H</u>-Ph and a multiplet at 7.37-7.30 for the -CH=CH-<u>Ph</u> protons, respectively[27]. The ligand **7**, displayed a singlet at δ 2.99 for the -N(C<u>H</u>$_3$)$_2$ and two doublets at δ 7.59 and 6.65 for the $H_{2'+6'}$ and $H_{3'+5'}$ protons of the -$C_{6'}H_{4'}N(CH_3)_2$ moiety. Similarly ligand **8**, contained a singlet at δ 3.78 and two doublets δ 7.60 and 6.87 for the -OCH_3, $H_{2'+6'}$ and $H_{3'+5'}$ protons, respectively of the -$C_{6'}H_{4'}(OCH_3)$ moiety. The ligand **9**, showed a multiplet band at δ 7.67-7.28 and a singlet at 11.16 for the phenyl (C_6<u>H</u>$_4$) and -O<u>H</u> protons, respectively of the -$C_{6'}H_{4'}$(OH) moiety.

The ^{1}H NMR spectra of complex **11**, **14** and **15** were recorded using deuterated DMSO which are as follows: The absence of amide proton (H_{14}) in the complexes indicated that condensation of VO_2(II) ion had taken place *via* the deprotonation of the ligands *i.e.*, *via* the enol form. Complex **11** showed a multiplet at δ 5.14, complex **14** showed a doublet at δ 7.73 and complex **15** showed a singlet at 7.99 ppm for the azomithine (H_{13}) proton of the ligand. This proton signal has shielded in the complexes form their corresponding ligand, suggested the coordination of the ligand had also taken place through the azomithine nitrogen atom. The shielding of the azomithine proton is due to the presence of electron rich vanadium ion. The complexes contained two doublets at δ 7.87-7.41 and 6.89-6.63 ppm for the H_{2+6} and H_{3+5} protons of the -C_6H_4- aromatic ring[27]. The H_{2+6} proton signals were deshielded but the H_{3+5} proton signals were shielded in complexes as compared to their corresponding ligands. The hexyl protons gave multiplet bands from 4.0-0.89 ppm in the complexes which remained almost same as compared to their corresponding ligands.

TABLE-3
^{1}H NMR SPECTRA, CHEMICAL SHIFT δ (ppm) IN $CDCl_3$ AND DMSO-d_6

Comp.	Chemical shift δ (ppm) in $CDCl_3$ and DMSO-d_6
1	0.90 (t, 3H, H_{12}); 1.32 (m, 4H, H_{11+10}); 1.44 (p, 2H, H_9); 1.78 (p, 2H, H_8); 3.95 (t, 2H, *J* = 6.4 Hz, H_7); 7.68 (d, 2H, *J* = 8.0 Hz, H_{2+6}); 6.81 (d, 2H, *J* = 8.0 Hz, H_{3+5}); 7.67 (s, 2H, H_{13}); 9.75 (bs, 1H, H_{14}).
2	0.90 (t, 3H, H_{12} + CH_3); 1.33 (m, 4H, H_{11+10}); 1.41 (m, 2H, H_9); 1.77 (m, 2H, H_8); 3.94 (t, 2H, *J* = 6.2 Hz, H_7); 7.82 (d, 2H, *J* = 8.8 Hz, H_{2+6}); 6.89 (d, 2H, *J* = 8.8 Hz, H_{3+5}); 7.59 (m, 1H, H_{13}); 9.80 (bs, 1H, H_{14}).
3	0.89 (t, 6H, *J* = 6.7 Hz, H_{12} + CH_3); 1.32 (m, 6H, H_{11+10} + CH_3C<u>H</u>$_2$); 1.44 (m, 4H, H_9); 1.77 (m, 2H, H_8); 4.09 (t, 2H, *J* = 6.4 Hz, H_7) 3.96 (m, 2H, CH_3CH_2C<u>H</u>$_2$); 7.69 (d, 2H, *J* = 8.7 Hz, H_{2+6}); 6.88 (d, 2H, *J* = 8.7, H_{3+5}); 7.52 (s, 1H, H_{13}); 9.73 (bs, 1H, H_{14}).
4	0.89 (t, 3H, *J* = 6.8 Hz, H_{12}); 1.34 (m, 4H, H_{11+10}); 1.45 (m, 2H, H_9); 1.77 (p, 2H, H_8); 3.95 (t, 2H, *J* = 6.4 Hz, H_7); 7.83 (d, 2H, *J* = 8.0 Hz, H_{2+6}); 6.85 (d, 2H, *J* = 8.4 Hz, H_{3+5}); 7.92 (d, 1H, *J* = 6.8 Hz, H_{13}); 9.92 (bs, 1H, H_{14}); 1.84 (d, 3H, *J* = 5.6 Hz, N=CH-CH=CH-C<u>H</u>$_3$); 6.06 (m, 1H, *J* = 6.8 Hz, N=CH-CH=C<u>H</u>-CH_3); 6.29 (t, 1H, *J* = 12.4 Hz, N=CH-C<u>H</u>=CH-CH_3).
5	0.90 (t, 3H, H_{12}); 1.32 {m, 4H, H_{11+10}); 1.44 (p, 2H, H_9); 1.76 (p, 2H, H_8); 3.97 (t, 2H, *J* = 6.4 Hz, H_7); 7.98 (d, 2H, *J* = 8.8 Hz, H_{2+6}); 6.90 (d, 2H, *J* = 8.8 Hz, H_{3+5}); 7.48 (s, 1H, H_{13}); 9.26 (bs, 1H, H_{14}). 7.85 (d, 2H, *J* = 8.4 Hz, Ph<u>H</u>$_{2'+6'}$); 7.64 (d, 2H, *J* = 8.4 Hz, Ph<u>H</u>$_{3'+5'}$); 7.35 (t, 1H, Ph<u>H</u>$_{4'}$).
6	0.90 (t, 3H, *J* = 6.8 Hz, H_{12}); 1.35 (m, 4H, H_{11+10}); 1.46 (m, 2H, H_9); 1.79 (m, 2H, H_8); 4.0 (t, 2H, *J* = 6.5 Hz, H_7); 7.45 (d, 2H, *J* = 8.0 Hz, H_{2+6}); 6.93 (d, 2H, *J* = 8.7, H_{3+5}); 7.82 (d, 1H, H_{13}); 8.99 (bs, 1H, H_{14}); 7.36 (d, 2H, *J* = 6.8 Hz, $PhH_{2'+6'}$); 7.31 (d, 2H, *J* = 6.7Hz, $PhH_{3'+5'}$); 7.28 (t, 1H, *J* = 7.6 Hz, $PhH_{4'}$); 6.87 (d, 1H, *J* = 16.0 Hz, N=CH-CH=C<u>H</u>Ph); 7.07 (t, 1H, N=CH-C<u>H</u>=CHPh).
7	0.90 (t, 3H, *J* = 6.5 Hz, H_{12}); 1.33 (m, 4H, H_{11+10}); 1.44 (m, 2H, H_9); 1.78 (m, 2H, H_8)}; 3.94 (t, 2H, H_7); 7.87 (d, 2H, *J* = 8.5Hz, H_{2+6}); 6.83 (d, 2H, *J* = 7.88 Hz, H_{3+5}); 8.28 (s, 1H, H_{13}); 9.85 (bs, 1H, H_{14}). 7.60 (d, 2H, *J* = 7.18 Hz, $H_{2'+6'}$); 6.87 (d, 2H, *J* = 7.98 Hz, $H_{3'+5'}$); 3.78 (s, 3H, Ph(OCH_3).
8	0.89 (t, 3H, H_{12}); 1.34 (m, 4H, H_{11+10}); 1.44 (m, 2H, H_9); 1.77 (m, 2H, H_8)}; 3.94 (t, 2H, H_7); 7.87 (d, 2H, *J* = 8.5Hz, H_{2+6}); 6.83 (d, 2H, *J* = 7.88 Hz, H_{3+5}); 8.28 (s, 1H, H_{13}); 9.85 (bs, 1H, H_{14}). 7.60 (d, 2H, *J* = 7.18 Hz, $H_{2'+6'}$); 6.87 (d, 2H, *J* = 7.98 Hz, $H_{3'+5'}$); 3.78 (s, 3H, Ph(OCH_3).
9	0.90 (t, 3H, *J* = 6.4 Hz, H_{12}); 1.33 (m, 4H, H_{11+10}); 1.45 (m, 2H, H_9); 1.77 (m, 2H, H_8); 3.95 (t, 2H, *J* = 6.2 Hz, H_7); 7.78 (d, 2H, *J* = 8.5Hz, H_{2+6}); 6.89 (d, 2H, *J* = 8.5 Hz, H_{3+5}); 8.41 (s, 1H, H_{13}); 9.56 (s, 1H, H_{14}); 7.67-7.28 {m, 4H, C_6<u>H</u>$_4$(OH); 11.16 (s, 1H, C_6H_4(O<u>H</u>)}.
11	0.88 (t, 3H, H_{12} + CH_3); 1.34 (m, 4H, H_{11+10}); 1.42 (p, 2H, H_9); 1.78 (p, 2H, H_8); 3.99 (t, 2H, *J* = 6.2 Hz, H_7); 7.41 (d, 2H, *J* = 8.0 Hz, H_{2+6}); 6.89 (d, 2H, *J* = 8.4 Hz, H_{3+5}); 5.14 (m, 1H, H_{13})
14	0.89 (t, 3H, H_{12}); 1.31 (m, 4H, H_{11+10}); 1.42 (m, 2H, H_9); 1.73 (m, 2H, H_8); 4.02 (t, 2H, *J* = 6.5 Hz, H_7); 7.88 (d, 2H, *J* = 8.0 Hz, H_{2+6}); 6.63 (d, 2H, *J* = 8.0 Hz, H_{3+5}); 7.73 (d, 1H, H_{13}); 7.63 (d, 2H, *J* = 7.6 Hz, $PhH_{2'+6'}$); 7.39 (d, 2H, *J* = 6.8 Hz, $PhH_{3'+5'}$); 7.34 (t, 1H, *J* = 6.4 Hz, $PhH_{4'}$); 7.03 (t, 1H, *J* = 6.0 Hz, N=CH-C<u>H</u>=CHPh); 7.47 (d, 1H, *J* = 6.0 Hz, N=CH-CH=C<u>H</u>Ph).
15	0.91 (t, 3H, H_{12}); 1.34 (m, 4H, H_{11+10}); 1.44 (m, 2H, H_9); 1.77 (m, 2H, H_8); 3.95 (t, 2H, *J* = 6.2 Hz, H_7); 7.87 (d, 2H, J = 8.0 Hz, H_{2+6}); 6.75 (d, 2H, *J* = 7.6 Hz, H_{3+5}); 7.99 (s, 1H, H_{13}); 7.65-7.07 (m, 4H, C_6<u>H</u>$_4$(OH) 11.72 {s, 1H, C_6H_4(O<u>H</u>)}.

UV-Visible spectra: The UV spectra of the ligands were scanned in the region between (200-400) nm using 10^{-3} and 10^{-4} M solution in chloroform. All the ligands showed a

medium intensity broad band from 256-306 nm, due to the intraligand charge transfer transition. The UV-visible spectra of the complexes (Table-4) were recorded using 10^{-5} M solution in DMSO. The complexes showed a medium intensity broad band at 700-428 nm (Table-4) due to the ligand to metal charge transfer (LMCT) transitions[23]. As the metal was oxidized from V(IV)-V(V) state, *i.e.*, $3d^0$ configuration, d → d transitions were not observed[20], which was supported by the diamagnetic nature of the complexes[23]. The UV-visible spectra of the complexes showed strong intensity sharp bands below 400 nm corresponding to the intraligand charge transfer transitions.

TABLE-4
UV-VISIBLE SPECTRA OF THE COMPLEXES (nm) IN DMSO (10^{-5} M)

Compound	λ_{max} (log ε)		
	I	II	II
10	385 (1.22)	472 (3.25)	–
11	381.2 (9.99)	458 (3.41)	700 (0.80)
12	3.88 (9.99)	460 (3.85)	572.7 (0.83)
13	380 (9.99)	465 (3.26)	–
14	368 (9.99)	428 (3.98)	–
15	379 (9.99)	459 (3.79)	–
16	405.8 (4.80)	453 (4.50)	–
17	396 (4.91)	456 (3.49)	–

Thermogravimetric analyses: The thermogravimetric analyses (TGA) of the complex **10-12**, **14** and **15** at room temperature to 600 ºC (Table-5 and Fig. 1) exhibited generally three step decomposition. The first step was accompanied by the removal of one $C_6H_{13}O$- moiety in complex **10, 11** and **15**, two $C_6H_{13}O$- moiety in complex **14** and three $C_6H_{13}O$- moiety in complex **14** at 211-182 ºC, second step involved the removal of four $C_6H_{13}O$- moiety in complex **10**, **11** and **14** and three

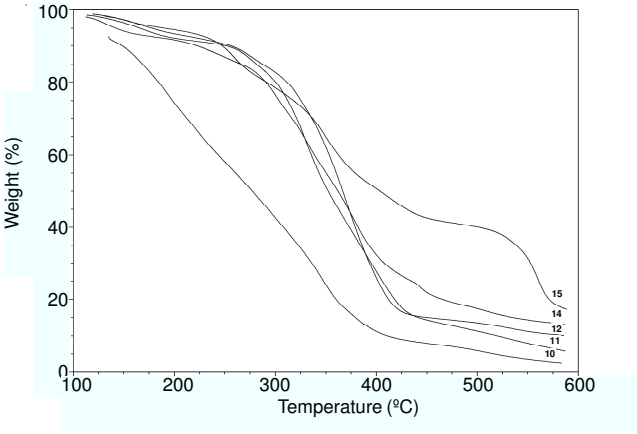


Fig. 1. TGA thermogram of complex (**10-12**), (**14**) and (**15**)

TABLE-5
THERMAL DECOMPOSITION OF METAL COMPLEXES

Compound	Step	ΔT (ºC)	Weight loss calcd. (found) (%)	Species removed	Residue V_2O_5 calcd. (found) (%)
10	1 2 3	211 398 530	8.88 (9.14) 35.52 (33.31)	$C_6H_{13}O$- $C_6H_{13}O$- × 4	15.97 (16.05)
11	1 2 3	211 398 530	8.46 (9.14) 33.86 (33.31)	$C_6H_{13}O$- $C_6H_{13}O$- × 4	15.22 (15.32)
12	1 2	245 425	12.87 (12.66)	C_4H_8- × 3	13.85 (13.91)
14	1 2 3	212 415 530	15.76 (16.25) 63.97 (63.93)	$C_6H_{13}O$ × 2 $C_6H_{13}OC_6H_4CO$ × 4	14.17 (14.21)
15	1 2 3 4	182 283 460 580	6.26 (5.83) 18.78 (17.33) 34.04 (36.15)	$C_6H_{13}O$- $C_6H_{13}O$ × 3 $C_6H_{13}O$ × 4 + $[(CH_3)_2N]$ × 4	11.25 (16.32)

TABLE-6
MICROBIOLOGICAL ANTIBIOTIC SENSITIVITY TEST OF THE COMPLEXES

Organism	Compounds (inhibition zone in mm)								
	Kanamycin	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
B. sereus	36	8	8	8	–	–	–	15	–
B. megaterium	35	–	8	8	–	–	–	12	–
B. subtilis	35	–	8	8	8	–	–	12	–
S. paratyphi	35	–	8	8	–	–	–	12	–
S. typhi	35	–	8	8	–	–	–	15	–
V. parahemolyticus	35	–	8	8	–	–	–	15	–
V. mimicus	36	–	9	9	–	–	–	15	–
S. aureus	36	–	9	9	–	–	–	15	–
E. coli	35	–	9	9	8	–	–	15	–
S. dysenteriae	36	–	10	10	–	–	–	15	–
P. aureus	35	–	9	9	–	–	–	15	–
S. lutea	35	–	9	9	8	–	–	15	–
S. boydii	36	9	9	9	8	–	–	15	–
S. cerevaceae	35	8	9	9	–	–	–	15	–
C. albicans	35	10	9	9	–	–	–	15	–
A. niger	35	10	10	9	–	–	–	15	–

$C_6H_{13}O$- moiety in complex **15**, respectively at 415-283 ºC. The third step involved in the formation of V_2O_5 (residue) for the aforesaid complexes at 460-530 ºC. All the data are in good agreement with their calculated values.

Study of antibacterial screening: The microbial screening of the test complexes was studied against sixteen pathogenic bacteria. The test results are depicted as the zone of inhibition (Table-6) in diameter (mm). The results indicated that the complexes have shown smaller zone of inhibition than the standard drug. The complexes **10-13** and **16** showed antibacterial activity but the other complexes did not show any activity as compared to a standard drug (canamycin). Further more complex **10** showed low activity against *B. sereus*, *S. boydii*, *S. cerevaceae*, *C. albicans* and *A. niger* and complex **13** showed low activity against *B. subtilis*, *E. coli*, *S. lutea* and *S. boydii* bacteria. In contrast, complex **11** and **12** showed low activity whereas complex **16** showed moderate activity against all the bacteria.

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