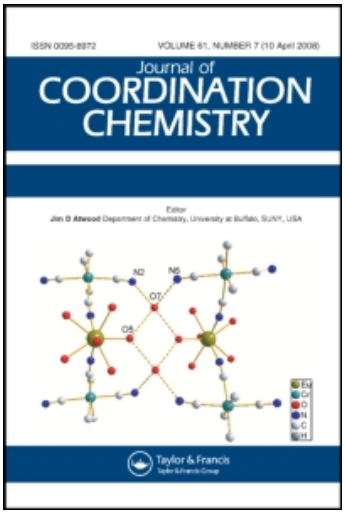

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Synthesis, characterization, electrochemical study, and antimicrobial activity of bis(benzoylacetonato) vanadium(IV) complexes of biphenylphenols

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Synthesis, characterization, electrochemical study, and antimicrobial activity of bis(benzoylacetonato) vanadium(IV) complexes of biphenylphenols

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New non-oxovanadium(IV) complexes of biphenylphenols, $[VCl_{2-n}(bzac)_2(OAr^{1,2})_n]$, have been synthesized in quantitative yields from the reaction of bis(benzoylacetonato) dichlorovanadium(IV) with the trimethylsilyl derivative of 2- and 4-phenylphenols in carbon tetrachloride. The complexes have been characterized by physicochemical, magnetic moment measurements, IR, mass spectra, and electrochemical studies. The thermal behavior of the complexes has been studied by TGA–DTA. The complexes have been screened for their antimicrobial activity against some pathogenic bacteria, *Escherichia coli* and *Staphylococcus aureus* and fungi, *Candida albicans*, *Aspergillus niger*, and *Fusarium oxysporum*, by two-fold serial dilution.

Keywords: Non-oxovanadium(IV) complexes; Biphenylphenols; Antimicrobial activity; Electrochemical study

1. Introduction

Coordination chemistry of VO^{2+} has received much attention over the years owing to its affinity toward a variety of ligands to afford complexes exhibiting diverse coordination geometries around vanadium. The well-documented applications of vanadium complexes as insulin-mimetic [1], antitumor [2], antifungal [3], antiamebic agents [4], catalysts [5–10], and in material sciences [11] have furthered phenomenal growth in its coordination chemistry.

Interest in non-oxovanadium(IV) or bare V^{4+} complexes arises from the fact that vanadium(IV) complex, amavadine, isolated from Amantia mushrooms, contained a ''non-oxo'' or ''bare'' V^{4+} center [12, 13]. Several models of amavadine have subsequently been synthesized. Utilization of oxovanadium(IV) species as precursors to non-oxovanadium(IV) complexes has provided new dimensions to exploit the chemistry of non-oxovanadium(IV) complexes and the synthesis of vanadium(IV) 4-aminoantipyrine derivatives $[L_2VCl_2]$ (L = 4-(2-pyrrolyl methylideneamino)antipyrine and 4-(2-hydroxybenzylideneamino)antipyrine) [14], dithiolenate complexes [15], and

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VCl_2(sal-N-butyl)$_2$ (sal-N-butyl = N-butylsalicylideneimine) were reported [16]. A few non-oxovanadium(IV) complexes involving oxygen ligation of 1,2-dihydroxybenzene and its derivatives are also known [17]. The formation of cationic complexes $[V(dik)_3]^+[FeCl_4]^-$ and $[V(dik)_3]^+[SbCl_6]^-$ (dik = acetylacetonate; 5,7-undecanedionate) [18], mixed ligand catechol-β-diketonate complexes $[V(cat)(acac)_2]$, $[V(cat)(bzac)_2]$ and $[V(dtbc)(bzac)_2]$ [19] [cat = catecholate, acac = 2,4-pentanedionate, bzac = 1-phenyl-1,3-butanedionate, dtbc = 3,5-di-tert-butylcatechol] and complexes of the type $[V^{IV}(dtbc)_2L]$ (L = bipy, phen), and the derivatives $[V^{V}(dtbc)_2L][SbF_6]$ have also been described [20].

Recently, the formation of eight-coordinate non-oxovanadium(IV) complexes VL_2 where H_2L is a tetradentate ONNO donor [21], the isolation, and characterization of non-oxovanadium(IV) complexes containing disulfide and thioether groups have been reported [22]. The preparation, redox, and spectroscopic properties of the first monomeric non-oxovanadium(IV) complex with concomitant vicinal carboxylate and hydroxylate coordination, $[V(salen)(benzilate)] \cdot 1.5CH_2Cl_2$, has been reported [23]. Four-coordinate vanadium(IV) neopentylidene complexes containing short vanadium–carbon bonds have been reported [24].

Synthetic chemistry of non-oxovanadium(IV) center, V^{4+}, is much less developed than that of the VO^{2+}. Hence, in continuation of our work to expand the range of known non-oxovanadium(IV) complexes [25, 26], in particular, by using substituted phenols, we report herein a facile synthetic route to non-oxovanadium(IV) complexes of 2- and 4-phenylphenols using $VCl_2(bzac)_2$ as the vanadium precursor.

2. Experimental

2.1. *Materials and methods*

All solvents were of A.R. grade and dried by standard methods. 2-Phenylphenol (Merck) (m.p. 57°C) and 4-phenylphenol (Merck) (m.p. 168°C) were recrystallized from benzene. $[VCl_2(bzac)_2]$ was prepared from $[VO(bzac)_2]$ by reported method [27, 28] under nitrogen; its formation and purity were checked by C, H, Cl, and V microanalysis and IR spectral data. Vanadium was determined gravimetrically as V_2O_5 while chlorine was determined by Volhard's method. C and H analyses were performed on a Carlo-Erba 1108 Elemental Analyzer. Conductivity measurements in nitrobenzene were made on an Elico Conductivity Bridge type CM-82T. Room temperature magnetic susceptibilities were measured by Guoy's method using $Hg[Co(NCS)_4]$ as calibrant. FT-IR spectra of complexes were collected on a Nicolet-5700 spectrophotometer (4000–200 cm^{-1}) as KBr pellets and nujol mulls in CsI optics. Cyclic voltammetry were carried out with a CH instrument electrochemical analyzer. Voltammetric experiments were performed in a single 5–10 mL compartment cell containing a three electrode system, a Pt-working electrode, Pt-wire auxiliary electrode, and Ag/AgCl as reference electrode. The supporting electrolyte was 0.4 M KNO_3 in milli-Q water; deaerated solutions were obtained by purging N_2 gas for 15 min prior to measurements. Redox behavior was studied in DMSO 5 : 95 H_2O : electrolyte system by means of cyclic voltammetry. UV-Vis spectra were recorded on a Varian CARY 100 BIO UV-Vis spectrophotometer. FAB mass spectra were recorded at room temperature on a

JEOL SX 102/DA-600 mass spectrometer/data system using Ar/Xe (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV. The *m*-nitrobenzyl alcohol (NBA) was used as the matrix. Molecular model calculations using Hyper-Chem 7.5 (student version) have been performed to visualize the probable geometry acquired by the complexes by applying MM^+ force field with Polka–Ribiere algorithm and RMS gradient 0.01 kcal mol^{-1}. The molecular dynamic simulation was done up to 1000 K (relaxation time 1 ps).

2.2. *Synthesis*

2.2.1. General method for preparation of $Me_3SiOC_6H_4$–X (X = C_6H_5-2 and C_6H_5-4). To a solution of 2-/4-phenylphenol (2.0 g, 0.011 mol) in THF, a solution of trimethylsilyl chloride (1.277 g, 1.48 mL, 0.011 mol) in tetrahydrofuran was added. The reaction mixture was refluxed for 24 h and the excess solvent was removed by distillation that gave a colorless viscous liquid. This liquid was used for carrying out the reactions with $VCl_2(bzac)_2$ for the synthesis of complexes.

2.2.2. $[VCl_{2-n}(bzac)_2(OC_6H_4–X)_n]$ (X = C_6H_5-2 and C_6H_5-4; n = 1–2). In a typical reaction for the preparation of $[VCl_{2-n}(bzac)_2(OC_6H_4–X)_n]$, a solution of trimethylsilyl derivatives (1 : 1 or 1 : 2) of 2- and 4-phenylphenols was added to a solution of $VCl_2(bzac)_2$ (1.826 g, 0.010 mol) in dry carbon tetrachloride. The reaction mixture was refluxed for 28 h, excess solvent was distilled off, and the residue was treated with petroleum ether to give solid complexes. The complexes were then dried under vacuum.

$VCl(bzac)_2(OC_6H_4–C_6H_5$-2). (yield: 1.68 g, 71%), $C_{32}H_{27}ClO_5V$ (577.9): Calcd (%): C 66.50, H 4.71, Cl 6.13, V 8.91; found (%): C 65.89, H 4.34, Cl 5.99, V 9.12, Λ_m ($PhNO_2$): 0.35 $Scm^2\,mol^{-1}$, μ_{eff}: (293 K) 1.73 B.M.

$V(bzac)_2(OC_6H_4–C_6H_5$-2)$_2$. (yield: 2.04 g, 70%) $C_{44}H_{36}O_6V$ (711.69): Calcd (%): C 74.77, H 4.90, V 7.54; found (%): C 74.77, H 4.90, V 7.54, Λ_m ($PhNO_2$): 0.31 $Scm^2\,mol^{-1}$, μ_{eff}: (293 K): 1.70 B.M.

$VCl(bzac)_2(OC_6H_4–C_6H_5$-4). (yield: 2.01 g, 85%) $C_{32}H_{27}ClO_5V$ (577.94) Calcd (%): C 66.50, H 4.71, Cl 6.13, V 8.91; found (%): C 66.12, H 5.09, Cl 6.57, V 9.11 (%), Λ_m ($PhNO_2$): 0.46 $Scm^2\,mol^{-1}$, μ_{eff}: (293 K): 1.75 B.M.

$V(bzac)_2(OC_6H_4–C_6H_5$-2)$_2$. (yield: 2.24 g, 83%) $C_{44}H_{36}O_6V$ (711.69): Calcd (%): C 74.26, H 5.10, O 13.49, V 7.16; found (%): C 74.13, H 5.87, V 7.57, Λ_m ($PhNO_2$): 0.40 $Scm^2\,mol^{-1}$, μ_{eff}: (293 K): 1.73 B.M.

2.3. In vitro *antimicrobial assay*

The *in vitro* antibacterial and antifungal activity of non-oxovanadium(IV) complexes were studied against fungi *Candida albicans*, *Aspergillus niger*, and *Fusarium oxysporum* and bacteria Gram(−) *Escherichia coli* and Gram(+) *Staphylococcus aureus* by a minimum inhibitory concentration (MIC) method. MIC is the lowest concentration of the antimicrobial agents that prevents visible growth after overnight incubation [29]. All the samples were tested in triplicate. The MIC was determined by reported methods [30]. All test cultures were streaked on soyabean casein digest agar (SCDA) and

incubated overnight at 37°C. A stock solution of 4 mg mL^{-1} of each compound was prepared in DMSO and appropriately diluted to give final concentrations of 100, 50, 25, 12.5, 6.25, 3.12, 1.56, 0.78, 0.39, 0.19, and 0.09 μg mL^{-1}. Standard bactericides Tetracycline, Chloramphenicol, Kanamycin, Cefazoline sodium, and Cefotaxime and fungicides Cycloheximide, Carbendazim, and Fluconazole were also diluted in a similar manner. A volume of 320 μL of each dilution was added to 20 mL molten and cooled in Mueller Hilton agar (MHA; separate flasks were taken for each dilution). After thorough mixing, the medium was poured into sterilized Petri plates and the plates were incubated at 37 ± 1°C for 24 h for bacteria and for 7 days at 25 ± 1°C and 36 h at 37 ± 1°C for *A. niger* and *C. albicans*, respectively.

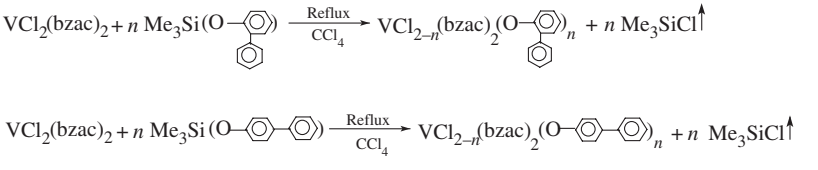
3. Results and discussion

The new vanadium(IV) complexes of composition $[VCl_{2-n}(bzac)_2(OC_6H_4-X)_n]$ were obtained in good yield (70–85%) by direct reaction of $VCl_2(bzac)_2$ with trimethylsilyl derivatives of 2- and 4-phenylphenols in separate experiments in appropriate molar ratios in carbon tetrachloride. The analytical data of the complexes confirm proposed formulations (scheme 1).

The complexes are green solids and soluble in common organic solvents. Millimolar solutions of the complexes in nitrobenzene (0.31–0.46 Scm^2 mol^{-1}) indicate their non-ionic nature. The room temperature magnetic moments of the complexes are 1.70–1.75 B.M. confirming their paramagnetic nature and +4 oxidation state for vanadium.

3.1. *IR spectra*

A comparison of IR spectra of $[VCl_{2-n}(bzac)_2(OAr^{1,2})_n]$ with those of $VCl_2(bzac)_2$ and 2- and 4-phenylphenols has been useful in providing information regarding the formation of mixed-ligand complexes. Particular attention has been focussed on the characteristic absorption bands due to γ(C–O) mode of the substituted phenols and γ_{as}(C–O) and γ_s(C–O) modes of benzoylacetonate. The absorptions due to γ(C–O) occurring at 1327–1269 cm^{-1} and 1335–1199 cm^{-1} [31–33] in uncoordinated 2-phenyl and 4-phenylphenol, respectively, are at 1215–1180 cm^{-1} and 1260–1200 cm^{-1} in the vanadium(IV) complexes. The observed shift of γ(C–O) is suggestive of bonding through phenolic oxygen. Bands at 1590–1490 cm^{-1} and 1380–1310 cm^{-1} ascribed



(where n = 1–2)

Scheme 1. Synthesis of non-oxovanadium(IV) complexes.

to γ_{as}(C–O) and γ_s(C–O) of benzoylacetonate in $VCl_2(bzac)_2$ appeared at 1592–1490 cm^{-1}, 1365–1310 cm^{-1}, and 1597–1485 cm^{-1}, 1375–1310 cm^{-1} in complexes derived from 2- and 4-phenylphenols, respectively, indicating that benzoylacetonate has not been replaced by aryloxo group. Absorptions at 590–485 cm^{-1} in both the series of complexes have been ascribed to γ(V–O) [34, 35]. Bands of $[VCl(bzac)_2(OAr^{1,2})]$ at 370–350 cm^{-1} have been assigned to γ(V–Cl) [18].

3.2. *Electronic spectra*

The electronic spectra of $[VCl_{2-n}(bzac)_2(OAr^{1,2})_n]$ were recorded in methanol from 200 to 900 nm. Spectra of all the complexes exhibited two less-intense, low-energy bands at 750–700 nm and 600–550 nm, attributed to benzoylacetonate (π) → vanadium (d) and vanadium (d) → benzoylacetonate (π^*) LMCT and MLCT transitions in consonance with previous reports on non-oxovanadium(IV) complexes [18]. In addition, intense high-energy bands at 348 and 390 nm are due to intraligand transitions. The electronic spectral observations substantiate the characteristic features of non-oxovanadium(IV) complexes containing phenolate ligands, displaying charge-transfer transitions in visible region such that d–d transitions are obscured.

3.3. *Cyclic voltammetric studies*

The results of cyclic voltammetric studies of four complexes in DMSO 5:95 H_2O-electrolyte system are presented in table 1 and figure 1. The cyclic voltammetry (CV) of all complexes displays a single cathodic and anodic peak, revealing one-electron change. Large peak-to-peak separations (283–848 mV) indicate quasireversible behavior. The reactions are given in scheme 2.

Comparison of the CV of complexes derived form 2- and 4-phenylphenols indicates that the cathodic potential E_c for $[VCl_{2-n}(bzac)_2(OC_6H_4{-}C_6H_5{-}4)_n]$ is more negative than those for $[VCl_{2-n}(bzac)_2(OC_6H_4{-}C_6H_5{-}2)_n]$. This indicates that 4-phenylphenoxides are more difficult to reduce, attributed to increased electron density on vanadium. Also, the tendency of 4-phenylphenoxo derivatives to get oxidized is higher than 2-phenylphenoxide analogues. For complexes containing two phenoxo groups relative to those containing one chloro and one phenoxo, the cathodic potential becomes more negative. This is again in line with the better electron-donating ability of phenoxo group. The electron-donating ability of the phenoxo makes it easier to reduce the vanadium(IV) to vanadium(III). Vanadium(III) is oxidized back to vanadium(IV), indicated by the presence of cathodic as well as anodic peaks in all complexes. The above observations point toward the exceptional stability of V^{4+} in these complexes.

Table 1. Cyclic voltammetric data of vanadium(IV) complexes.

S. No.	Complex	Epc (V)	Epa (V)	$\Delta E = Epc - Epa$ (mV)
1	$VCl(bzac)_2(OC_6H_4{-}C_6H_5\text{-}2)$	−0.5757	−0.2922	283
2	$V(bzac)_2(OC_6H_4{-}C_6H_5\text{-}2)_2$	−0.7242	−0.1508	573
3	$VCl(bzac)_2(OC_6H_4{-}C_6H_5\text{-}4)$	−0.8234	−0.0735	749
4	$V(bzac)_2(OC_6H_4{-}C_6H_5\text{-}4)_2$	−0.8782	−0.0298	848

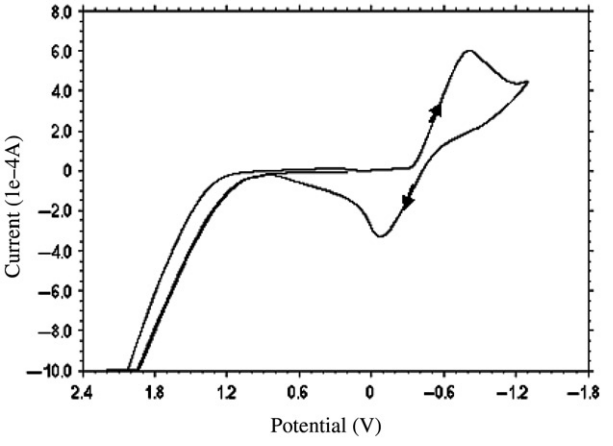


Figure 1. CV of $VCl(bzac)_2(OC_6H_4\text{-}C_6H_5\text{-}4)]$ at scan rate $0.3\,Vs^{-1}$.

At cathode: $[VCl_{2-n}(bzac)_2(OC_6H_4\text{–}X)_n]^{+4} + e^- \rightarrow [VCl_{2-n}(bzac)_2(OC_6H_4\text{–}X)_n]^{+3}$

At anode: $[VCl_{2-n}(bzac)_2(OC_6H_4\text{–}X)_n]^{+3} \rightarrow [VCl_{2-n}(bzac)_2(OC_6H_4\text{–}X)_n]^{+4} + e^-$

(where X = C_6H_5–2 and C_6H_5–4)

Scheme 2. Electrochemical reactions of non-oxovanadium(IV) complexes.

3.4. *Mass spectra*

The essential features of FAB-MS spectra of $[V(bzac)_2(OAr^{1,2})_2]$ are summarized in the "Supplementary material" where relative abundances relative to 100 as the maximum are compared. Both complexes display weak molecular ion peaks (<5% relative abundance), in accordance with the SIMS of neutral β-diketonate complexes, where $VO(acac)_2$ is known to exhibit the molecular ion peak of low intensity. The base peaks at m/e 147 in both complexes are due to $[V(OC_6H_5) + 3H]^+$. The spectra displayed well-defined fragment ions corresponding to 2-/4-phenylphenolic ligand (m/e 170, 16/70%). The other high abundant fragments $[C_6H_5CO]^+$ (m/e 105, 75/82%), $[VO(OAr\text{–}Ph\text{-}2/4)(OC_6H_5) - 2H/4H]^+$ (m/e 325, 327, 55–57%), $[VO(OC_6H_4\text{–}C_6H_5) + CO + 3H]^+$ (m/e 267, 55/40%) also appear in both the complexes. For $[V(bzac)_2(OAr\text{–}Ph\text{-}2)_2]$, other structurally informative high abundant ions $[V(HOAr)]^+$ (m/e 221, 65%)/ $[VO + NBA_2]^+$, $[V(bzac) - 5H]^+$ (m/e 207, 82%) were observed. The presence of intense $[VO(bzac)]^+$ (m/e 228, 45%) and $[V(OC_6H_5\text{-}Ph\text{-}4) + CO + 3H]^+$ (m/e 251, 45%) are characteristic of $[V(bzac)_2(OAr\text{–}Ph\text{-}4)_2]$. A few fragment ions assignable to vanadyl and $[V(bzac)_3]^+$ species have been observed for these complexes [19]. For (catecholato) bis(β-diketonato) vanadium(IV) complexes, reaction in the gas phase produces $[V(acac)_3]^+$ and $[V(bzac)_3]^+$ fragments as a result of cluster formation by molecule–ion reactions characteristic of metal β-diketonates [36–38].

3.5. *Thermal studies*

Thermal behaviors of $[V(bzac)_2(OAr–Ph\text{-}2)_2]$ and $[VCl(bzac)_2(OAr–Ph\text{-}4)]$ have been studied by TG–DTA. The complexes show initial decomposition at 120°C and 100°C, respectively, after which the complexes undergo decomposition in a single step. The percentage weight loss accounts for the formation of VO_2 as the final residue in both complexes. The complexes did not display any endothermic or exothermic peaks in DTA curves.

3.6. *Molecular modeling*

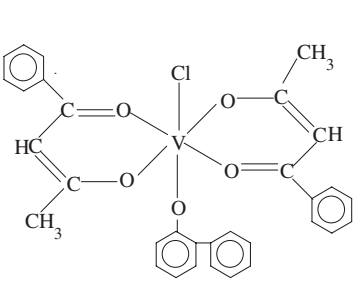
Molecular mechanical adjustments for energy optimization for the strained structure to the likely geometry of each of the complex were made. The calculations of molecular mechanics were repeated five to six times to ensure that the true energy minimum has been attained. The structure with minimum energy is assumed to be closer to the stable geometry. The probable structures exhibit molecular properties in conformity with the experimentally determined data.

On the basis of analytical and IR, UV-Vis, and mass spectral data combined with the molecular modeling calculations, a distorted octahedral geometry for the non-oxovanadium(IV) complexes has been proposed and representative structures for the complexes are given in scheme 3.

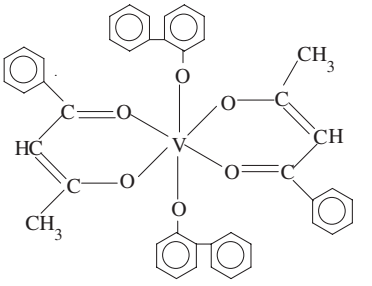
3.7. *Antimicrobial activity*

Antimicrobial activity of various ligands and their transition metal complexes has been reported [39–43]. Preliminary *in vitro* antimicrobial screening of 2-and 4-phenylphenols as well as three vanadium(IV) complexes were performed against some pathogenic fungi and bacteria by the MIC method; the results are presented in table 2 and figure 2. Vanadium(IV) 2- and 4-phenylphenoxides display pronounced antimicrobial activity compared to the free ligand under identical experimental conditions. The complexes of composition $V(bzac)_2(OAr–Ph\text{-}2)_2$ and $V(bzac)_2(OAr–Ph\text{-}4)_2$ are effective antimicrobial agents in their respective series whereas $V(bzac)_2(OAr–Ph\text{-}2)_2$ is a stronger antifungal agent than its counterpart, $V(bzac)_2(OAr–Ph\text{-}4)_2$. The MIC of the complexes lie in the range of 3.12–25 $\mu g\,mL^{-1}$ which suggests their behavior as promising antimicrobial agents. The antimicrobial activities were compared with the conventional bactericides and fungicides. Compared to the MIC of standard drugs selected for antibacterial activity (Tetracycline, Chloramphenicol, Kanamycin, Cefazoline sodium, and Cefotaxime) and antifungal activity (Cycloheximide, Carbendazim, and Fluconazole) (MIC $< 3.12\,\mu g\,mL^{-1}$), the complexes exhibit appreciable activity.

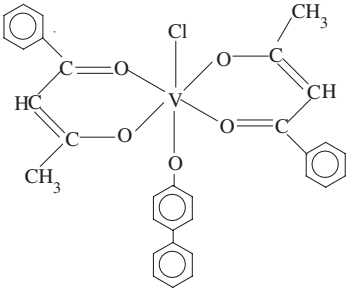
The MIC values of transition metal complexes against *E. coli* and *S. aureus* have been reported to lie in the range between 0.781 and $>128\,\mu g\,mL^{-1}$. The newly synthesized non-oxovanadium(IV) complexes show values between 3.12 and 25 $\mu g\,mL^{-1}$ range for the same microorganisms, revealing potential of vanadium complexes as antimicrobial agents; vanadium hydroxamates have been found to exhibit MIC in the 15.625–62.5 $\mu g\,mL^{-1}$ range [43].



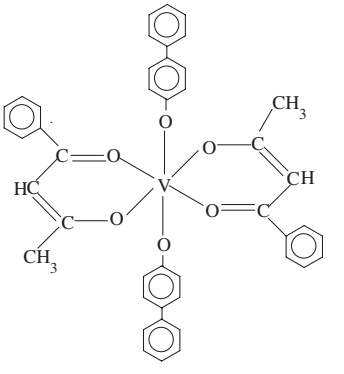
$VCl(bzac)_2(OAr–Ph–2)$



$V(bzac)_2(OAr–Ph–2)_2$



$VCl(bzac)_2(OAr–Ph–4)$



$V(bzac)_2(OAr–Ph–4)_2$

Scheme 3. Graphical representations of new complexes.

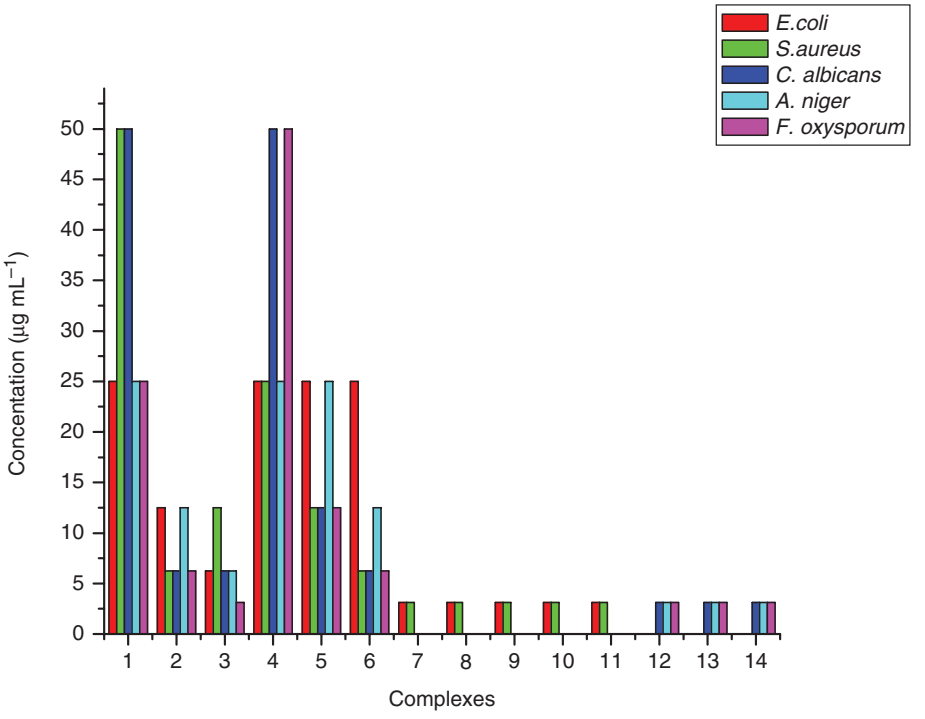
Table 2. The *in vitro* antimicrobial activity of non-oxovanadium(IV) complexes (MIC in $\mu g\,mL^{-1}$).

	Bacteria		Fungi		
Ligands/Complex	*E. coli*	*S. aureus*	*C. albicans*	*A. niger*	*F. oxysporum*
$HOC_6H_4–C_6H_5$-2	25	50	50	25	25
$VCl(bzac)_2(OC_6H_4–C_6H_5$-2)	12.5	6.25	6.25	12.5	6.25
$V(bzac)_2(OC_6H_4–C_6H_5$-2)$_2$	6.25	12.5	6.25	6.25	3.12
$HOC_6H_4–C_6H_5$-4	25	25	50	25	50
$VCl(bzac)_2(OC_6H_4–C_6H_5$-4)	25	12.5	12.5	25	12.5
$V(bzac)_2(OC_6H_4–C_6H_5$-4)$_2$	12.5	6.25	6.25	12.5	6.25
Tetracycline	<3.12	<3.12			
Chloramphenicol	<3.12	<3.12			
Kanamycin	<3.12	<3.12			
Cefazoline sodium	<3.12	<3.12			
Cefotaxime	<3.12	<3.12			
Cycloheximide	–	–	<3.12	<3.12	<3.12
Carbendazim	–	–	<3.12	<3.12	<3.12
Fluconazole		–	<3.12	<3.12	<3.12

Estimated error = 1%.

4. Conclusion

Synthesis of bis(benzoylacetonato)vanadium(IV) complexes of 2-and 4-phenylphenols by the reaction of $VCl_2(bzac)_2$ with trimethylsilyl derivatives of the respective phenols



1. $HOC_6H_4–C_6H_5–2$
2. $VCl(bzac)_2(OC_6H_4–C_6H_5–2)$
3. $V(bzac)_2(OC_6H_4–C_6H_5–2)_2$
4. $HOC_6H_4–C_6H_5–4$
5. $VCl(bzac)_2(OC_6H_4–C_6H_5–4)$
6. $V(bzac)_2(OC_6H_4–C_6H_5–4)_2$
7. Tetracycline
8. Chloramphenicol
9. Kanamycin
10. Cefazoline sodium
11. Cefotaxime
12. Cycloheximide
13. Carbendazim
14. Fluconazole

Figure 2. Bar graph showing antimicrobial activity of the free ligands, non-oxovanadium(IV) complexes and standard biocides.

give superior yield to the earlier reported sodium salt method. Distorted octahedral geometry around vanadium has been suggested from the analytical and spectral data coupled with molecular modeling. The complexes show higher antimicrobial activity ($3.12–25\,\mu g\,mL^{-1}$) than the free ligands. The present work points to the future work that $VCl_2(bzac)_2$ can be exploited as precursor for the synthesis of new complexes by metathesis using a variety of ligands and it would be fruitful to obtain complexes with promising antimicrobial activity. Further coordination chemistry needs to be explored in these chemically rich systems.

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