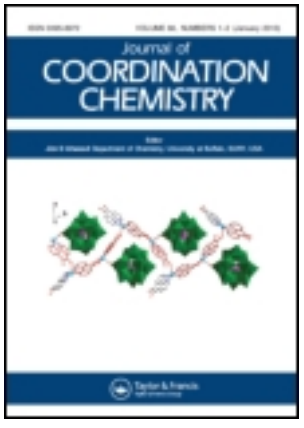

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Synthesis, characterization, reactivity, and antifungal activity of chlorobis(2,4-dinitrophenoxo) monooxovanadium(V)

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Synthesis, characterization, reactivity, and antifungal activity of chlorobis(2,4-dinitrophenoxo) monooxovanadium(V)

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[$VOCl(OC_6H_3(NO_2)_2$-2,4)$_2$] (**1**) has been synthesized by the reaction of $VOCl_3$ with bimolar amounts of $Me_3SiOC_6H_3(NO_2)_2$-2,4 in toluene and characterized by elemental analyses, molar conductance, infrared (IR), ^1H and ^{13}C NMR and mass spectral, and thermal studies. Molecular modeling dynamics of the complex suggests tetrahedral geometry around vanadium. The reaction of **1** with sodium alkoxides, NaOR (OR = OMe (methoxy); OEt (ethoxy), OBu^n(n-butoxy); OPr^i (isopropoxy); and OAm^i(isoamyloxy)) afforded mixed alkoxo–phenoxo complexes, [$VO(OR)(OC_6H_3(NO_2)_2$-2,4)$_2$] authenticated by physicochemical and IR spectral studies. The antifungal activities of the ligand and complexes against three fungi, namely *Aspergillus niger*, *Byssachlamys fulva,* and *Mucor circinelloides* have been assayed by the minimum inhibitory concentration method. The complexes have improved antifungal activity compared to free ligand.

Keywords: 2,4-Dinitrophenol; Monooxovanadium(V) complexes; Sodium alkoxides; Spectroscopic studies; Antifungal activity

1. Introduction

Interest in the broad domain of vanadium chemistry stems from the potential of vanadium complexes as catalysts in industry [1], organic synthesis [2], and material sciences [3]. The coordination chemistry of vanadium has drawn considerable attention since the discovery of vanadium-dependent enzymes – haloperoxidase, nitrogenase [4–6], and nitrate reductase [7]. An upsurge of coordination chemistry of vanadium arose from insulin–mimetic behavior [8] and a number of therapeutic effects [9] of vanadium complexes. Literature survey on vanadium chemistry reveals that vanadium exhibits rich chemistry with oxygen and nitrogen donors. Oxygen donors such as glycolate [10, 11], phosphate [12], catecholate [13], hydroxamate [14], phenolate [15], and substituted phenols constitute an important class of ligands with potential for tuning both steric and electronic influences to afford structural variety of complexes. The coordination chemistry of oxovanadium(V) complexes of aminebis(phenolate)

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ligands has been reported [16]. The vanadium phenolates have also been reported to display capabilities of dinitrogen fixation [17–19] and considerable significance for polymerization [20], oxidation [16], and potential shape-selective transformations [21]. The literature reveals that vanadium aryloxides and vanadium nitrophenolates [22–26] are less studied. Continuing our efforts on the phenolate chemistry of vanadium [27–29], we report herein the synthesis and characterization of chlorobis(2,4-dinitrophenoxo)monooxovanadium(V) [$VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2$)] derived from 2,4-dinitrophenol (figure 1). The mixed alkoxo–phenoxo complexes of composition [$VO(OR)(OC_6H_3(NO_2)_2\text{-}2,4)_2$] have been obtained by the reactions of [$VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2$)] with sodium alkoxides NaOR (OR = OMe, OEt, OBu^n, OPr^i, OAm^i). The newly synthesized complexes have been assayed for their antifungal activities against three fungi, namely *Aspergillus niger*, *Byssachlamys fulva,* and *Mucor circinelloides* by the minimum inhibitory concentration (MIC) method.

2. Experimental

2.1. *Materials and methods*

All solvents used were of A.R. grade and dried by standard methods. Vanadyl trichloride ($VOCl_3$) (Aldrich) was used as procured. 2,4-Dinitrophenol (Merck) was recrystallized from chloroform and then warmed to 100°C. The purity of the phenol was checked by melting point 112–114°C (obs.) (lit. m.p. 112–115°C).

Carbon, hydrogen, and nitrogen analyses were performed on a Carlo-Erba 1108 Elemental Analyzer. Vanadium was determined gravimetrically as V_2O_5. Conductivity measurements in methanol were made using a Harco digital conductivity bridge. FTIR spectra of the complexes were collected on a Nicolet-5700 FTIR spectrophotometer (4000–200 cm^{-1}) as KBr pellets and nujol mull in CsI optics. ^1H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE II 400 spectrometer using TMS as an internal standard and $(CD_3)_2SO$ as solvent. The FAB mass spectrum was 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-nitrobenzylalcohol (NBA) was used as the matrix. The molecular model calculations using Hyper-Chem.7.5 (student version) have been performed to visualize the probable geometry acquired by the complexes by applying the MM^+ force field with Polak Ribiere algorithm and RMS gradient 0.01 kcal mol^{-1}. The molecular dynamic simulation was done up to 1000 K (relaxation time ps). Thermograms (TGA and DTA curves) of complexes were recorded on a SHIMADZU DT-60 thermal analyzer.

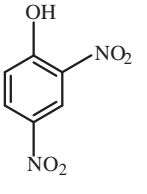


Figure 1. Structure of 2,4-dinitrophenol.

The thermal studies were carried out by heating the sample in a platinum crucible in air with a heating rate of 20°C min^{-1}. The thermocouple used was Pt/Pt–Rh 10% with a temperature range of 20–1200°C.

2.2. *Synthesis*

2.2.1. Preparation of [$Me_3Si(OC_6H_3(NO_2)_2$-2,4)]. To a solution of 2,4-dinitrophenol (2.0 g, 10.8 mmol) in toluene (20 mL) was added a solution of Me_3SiCl (1.37 mL, ($d = 0.86$ g mL^{-1}) 1.18 g, 10.8 mmol) taken in the same solvent (20 mL). The reaction mixture was refluxed for 20 h when a light yellow viscous liquid was obtained. This solution was used for carrying out the reaction with $VOCl_3$ for the synthesis of **1**.

2.2.2. Preparation of [$VOCl(OC_6H_3(NO_2)_2$-2,4)$_2$]. To a solution of $VOCl_3$ (1.0296 mL, 1.88 g, 10.84 mmol) in toluene, two equivalents of $Me_3Si(OC_6H_3(NO_2)_2$-2,4) (21.68 mmol) in toluene were added. The reaction mixture was refluxed for 20 h to ensure completion of the reaction. The Me_3SiCl formed during the reaction as a byproduct and the excess solvent were distilled off and the concentrate was then repeatedly treated with petroleum ether, whereupon brownish black solid was obtained. It was recrystallized from absolute alcohol and dried *in vacuo*. (Yield: 4.16 g, 85%). Anal. Calcd for $VClC_{12}H_6N_4O_{11}$ (468.5) (%): C, 30.7; H, 1.28; N, 12.0; Cl, 8.00; V, 10.8. Found: C, 30.50; H, 1.31; N, 11.8; Cl, 7.79; V, 10.6. Λ_m, (CH_3OH): 4.21 Scm^2 mol^{-1}.

FTIR (cm^{-1}); [$VOCl(OC_6H_3(NO_2)_2$-2,4)$_2$] – 2926m, 2855m, 1627s, 1600s, 1541s, 1480s, 1433s, 1347s, 1335s, 1256s, 1186s, 1138m, 1110s, 1066m, 989s, 851m, 837s, 768m, 738s, 716s, 686m, 639s, 581m, 526m, 424m, 366s.

NMR (δ, ppm); ^{1}H, 8.72(d, 1H, $J_{m-m'} = 2.12$ Hz), 8.32, 8.34(dd, 1H, $J_{m'-m} = 2.0$ Hz, $J_{m'-o} = 9.08$ Hz), 7.33 (d, 1H, $J_{m'-o} = 9.16$ Hz); ^{13}C, 158.25 C-1, 136.11 C-2, 122.15 C-3, 138.87 C-4, 129.64 C-5, 120.41 C-6.

2.2.3. Reactions of [$VOCl(OC_6H_3(NO_2)_2$-2,4)$_2$] with sodium alkoxides NaOR (OR = OMe, OEt, OBu^n, OPr^i, OAm^i) [30]. In a typical reaction, to [$VOCl(OC_6H_3(NO_2)_2$-2,4)$_2$] in methanol, methanolic solution of sodium methoxide (in excess of 1 : 2 molar ratio) was added. The reaction mixture was then refluxed for 6–7 h to ensure completion of the reaction during which a marked color change was observed. It was then filtered to remove the solid formed (sodium chloride) during the reaction. The filtrate was concentrated under vacuum. The solid thus obtained was treated with petroleum ether and dried under vacuum, whereupon a dark yellow solid was obtained.

Similar synthetic procedure was employed using solutions of sodium alkoxides in respective alcohols. The complexes of composition [$VO(OMe)(OC_6H_3(NO_2)_2$-2,4)$_2$], [$VO(OEt)(OC_6H_3(NO_2)_2$-2,4)$_2$], [$VO(Am^i)(OC_6H_3(NO_2)_2$-2,4)$_2$], and $VO(OBu^n)(OC_6H_3(NO_2)_2$-2,4)$_2$] were obtained as dark yellow solids while [$VO(Pr^i)(OC_6H_3(NO_2)_2$-2,4)$_2$] was brick red. The complexes are soluble in common organic solvents.

Anal. Calcd for $VC_{13}H_9N_4O_{12}$ (464) (%): C, 33.6; H, 1.93; N, 12.0; V, 10.99. Found: C, 33.54; H, 1.86; N, 12.21; V, 10.78. (Yield: 0.84 g, 84.8%) Λ_m, (CH_3OH): 36.13 Scm^2 mol^{-1}. Anal. Calcd for $VC_{14}H_{11}N_4O_{12}$ (478) (%): C, 35.14; H, 2.30; N, 12.0;

V, 10.66. Found: C, 35.01; H, 2.23; N, 12.11; V, 10.39. (Yield: 0.81 g, 81.8%) Λ_m (CH_3OH): 31.37 Scm^2mol^{-1}. Anal. Calcd for $VC_{15}H_{13}N_4O_{12}$ (492) (%): C, 36.58; H, 2.64; N, 12.0; V, 10.36. Found: C, 36.43; H, 2.44; N, 12.08; V, 10.28. (Yield: 0.88 g, 83.8%) Λ_m (CH_3OH): 13.58 Scm^2mol^{-1}. Anal. Calcd for $VC_{16}H_{15}N_4O_{12}$ (506) (%): C, 37.94; H, 2.16; N, 11.06; V, 10.07. Found: C, 37.84; H, 2.10; N, 11.23; V, 10.17. (Yield: 0.91 g, 84.2%) Λ_m (CH_3OH): 12.06 Scm^2mol^{-1}. Anal. Calcd for $VC_{17}H_{17}N_4O_{12}$ (520) (%): C, 39.23; H, 3.26; N, 11.0; V, 9.80. Found: C, 39.02; H, 3.21; N, 11.06; V, 9.72. (Yield: 0.94 g, 85.4%) Λ_m (CH_3OH): 21.07 Scm^2mol^1.

2.3. *Antifungal activity test*

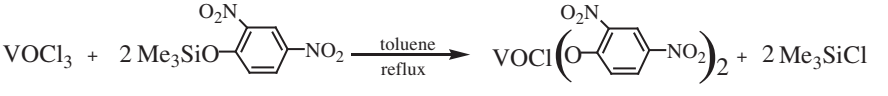
The ligand 2,4-dinitrophenol, $[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ and mixed alkoxo-phenoxo complexes of composition $[VO(OR)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ were screened *in vitro* for their antifungal activity on selected fungi *A. niger*, *B. fulva*, and *M. circinelloides* using the MIC method. MIC is the lowest concentration of the antimicrobial agents that prevents development of visible growth after 5 days incubation [31].

2.4. *MIC determination by two-fold serial dilution*

The MIC assay [32] was performed in a 96-well micro-titre plate. For MIC assay of each test drug, a row of 12 wells was used out of which, last two wells were taken as control (no drug added). Each of the 10 wells received 100 µL of Potato-Dextrose broth, except the first well that received 200 µL of broth containing 500 µg ml^{-1} concentration of the test drug. From the first well, 100 µL broth (containing test drug) was withdrawn with a sterile tip, and same was added to 100 µL of the broth in the second well. The contents were mixed four times. Then 100 µL was withdrawn from the second well and was added to the third well. This way a range of two-fold serial dilutions were prepared (500–0.98 µg mL^{-1}) by performing two-fold serial dilution. The broth in each of the wells was inoculated with 5 µL of the fungal culture and the contents were mixed by 10 clockwise and thereafter 10 anticlockwise rotations on a flat surface and the plate was incubated at 30°C. The observations for growth of fungi were recorded after 5 days. The results were compared with standard antifungal drug fluconazole (treated control), untreated control containing both broth and fungi, and the control containing only broth (blank).

3. Results and discussion

The reaction of $VOCl_3$ with trimethylsilyl derivative of 2,4-dinitrophenol in toluene afforded quantitative formation of $[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ according to the following equation:



The complex is brownish black, soluble in most common organic solvents as well as in methanol and DMSO. The molar conductance value of the millimolar solution of the complex in methanol (4.21 $Scm^2 mol^{-1}$) suggested its non-electrolytic nature.

3.1. *Infrared spectra*

A comparison of infrared (IR) spectra of **1** with that of free 2,4-dinitrophenol showed the absence of an absorption due to phenolic υ(OH) at 3200 cm^{-1} in 2,4-dinitrophenol. The band due to υ(C–O) is at 1256 cm^{-1} in **1** suggesting bonding of phenolic oxygen to vanadium. The bonding from phenolic oxygen to vanadium has further been indicated by bands at 580–520 cm^{-1} ascribed to υ(V–O). Bands at 1541 cm^{-1}, 1347 cm^{-1}, and 1333 cm^{-1} in **1** have been attributed to υ_{asym} (NO_2) and υ_{sym} (NO_2) in line with previous reports on nitro compounds [33–36]. A band at 989 cm^{-1} in [$VOCl(OC_6H_3(NO_2)_2$-2,4)$_2$] has been ascribed to υ(V=O) related to that occurring at 1035 cm^{-1} [37] in $VOCl_3$ and 1020–960 cm^{-1} region in a number of vanadyl salts and complexes [38]. A lowering in υ(V = O) mode may be attributed to a weakening of V = O bond from terminal oxo oxygen p$\pi \rightarrow$ vanadium dπ donation upon complexation with phenoxide ion. An absorption at 366 cm^{-1} has been assigned to υ(V–Cl) mode.

3.2. *^{1}H NMR spectra*

Comparison of the room temperature ^{1}H NMR spectra of **1** with that of 2,4-dinitrophenol further substantiates its formation. The ^{1}H NMR spectrum of free 2,4-dinitrophenol displays signals at δ4.65, 7.35, 9.1, and 8.5 ppm attributed to the presence of phenolic –OH group, ortho, meta proton (m) having adjacent –NO_2 groups at 2-and 4-positions of the ring and other meta proton (m′) having 4 –NO_2 substituent as its immediate neighbor, respectively. The ^{1}H NMR spectra of **1** did not display any signal at δ4.65 ppm, confirming deprotonation of phenolic proton. The resonance due to ortho proton of aromatic ring was found at δ7.33 ppm while m and m′ resonances appeared at δ8.74 ppm and δ8.33 ppm, respectively. Upfield shifts observed for different types of protons may be ascribed to shielding of o, m, and m′ protons resulting from drift of electron density from vanadyl (V=O) onto the aromatic ring through phenolic oxygen. The shielding experienced by the protons may be governed by structural features also (Supplementary material).

3.3. *^{13}C NMR spectra*

The information obtained from ^{1}H NMR spectra of **1** was further supported from its ^{13}C NMR spectra. The ^{13}C NMR spectrum of 2,4-dinitrophenol exhibits six distinct resonances due to aromatic carbons of the phenolic ring from δ117.5 to 158.5 ppm. Less intense signals due to C-1, C-2, and C-4 bearing –OH and –NO_2 substituents occur at δ158.5, 136.5, and 141.9 ppm, respectively, while intense signals due to C-3, C-5, and C-6 occur at δ120.1, 131.1, and 117.5 ppm, respectively. The spectrum of [$VOCl(OC_6H_3(NO_2)_2$-2,4)$_2$] also shows six distinct signals indicating their non-equivalent nature. Moderate to significant upfield shifts have been observed for C-1, C-2, C-4, and C-5, ascribed to hyperconjugation. Downfield shifts observed for C-3 and

C-6 of $-\Delta = \delta 2.05$ ppm and $\delta 2.91$ ppm, respectively, may be attributed to the substituents (–OH and NO_2 groups) showing an influence beyond the carbon to which the substituent is directly attached; hence, these carbons are deshielded. Nevertheless, the role of vanadyl (V=O) cannot be excluded as the cause of such behavior (Supplementary material).

3.4. *Mass spectra*

The FAB-mass spectrum (table 1) of $[VOCl\{(OC_6H_3(NO_2)_2\}_2]$ (M) displayed molecular ion peak at m/z 469 corresponding to $[M+H]^+$ and base peak at m/z 243 (100%) ascribed to $[VOCl(OC_6H_4(NO_2))+3H]^+$ resulting from the removal of one 2,4-dinitrophenoxide ion and one nitro substituent. The other intense fragment ions appeared at m/z 403, 357, 341, 316, 289, 227, 197, 102, 88, and 71 corresponding to vanadyl and vanadium species $[VO(OC_6H_3(NO_2)_2)(OC_6H_3(NO)_2+2H]^+$, $[VO(OC_6H_4NO_2)(OC_6H_3(NO)_2+H]^+$, $[V(OC_6H_4NO_2)(OC_6H_3(NO)_2+H]^+$, $[VOCl(OC_6H_5)(OC_6H_4(NO)-H]^+$, $[VOCl(OC_6H_5)_2+H]^+$, $[VCl(OC_6H_4NO_2)+3H]^+$, $[VOCl(OC_6H_5)+2H]^+$, $[VOCl]^+$, $[VCl+2H]^+$, and $[VOH+3H]^+$, respectively. The fragment ion at m/z 181 $[HOC_6H_3(NO_2)_2-3H]^+$ corresponded to that of the coordinated phenolic ligand.

3.5. *Thermal studies*

The TGA curve of $[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ (Supplementary material) shows that it is thermally stable to 130°C after which it undergoes decomposition in two steps. An initial weight loss of 48.20% in 130–224°C temperature range agrees well with the formation of $[VO_2(OC_6H_3(NO_2)_2)]$ as the possible intermediate by the removal of Cl^- and phenolate. The intermediate formed is unstable with no plateau in the TG curve, undergoing continuous decomposition with a slight inflexion in the TG. The weight loss amounting to 35.11% in 224–738°C in the second stage accounted for the formation of V_2O_5 as the final residue. The observed modes of decomposition can be represented as

$$\left[VOCL(OC_6H_3(NO_2)_2)_2\right] \xrightarrow[-Cl]{-OC_6H_3(NO_2)_2} \left[VO_2(OC_6H_3(NO_2)_2\right] + \text{Organic matter}$$

$$2\left[VO_2(OC_6H_3(NO_2)_2\right] \xrightarrow[-35.11\ \%]{} V_2O_5 + \text{Organic matter.}$$

Table 1. Mass spectral data of **1**.

Ionic species	m/z (relative abundance %)
$[VOCl\{(OC_6H_3(NO_2)_2\}_2+H]^+$	469 (8)
$[VO(OC_6H_3(NO_2)_2)(OC_6H_3(NO)_2+2H]^+$	403 (50)
$[VO(OC_6H_4NO_2)(OC_6H_3(NO)_2+H]^+$	357 (52)
$[V(OC_6H_4NO_2)(OC_6H_3(NO)_2+H]^+$	341 (11)
$[VOCl(OC_6H_5)(OC_6H_4(NO)-H]^+$	316 (22)
$[VOCl(OC_6H_5)_2+H]^+$	289 (84)
$[VOCl(OC_6H_4(NO_2))+3H]^+$	243 (100)
$[VCl(OC_6H_4NO_2)+3H]^+$	227 (82)
$[VOCl(OC_6H_5)+2H]^+$	197 (21)
$[HO(OC_6H_3(NO_2)_2)3H]^+$	181 (40)
$[VOCl]^+$	102 (69)
$[VCl+2H]^+$	88 (75)
$[VOH+3H]^+$	71 (85)

The decomposition in TG is accompanied by a sharp endothermic peak at 112°C corresponding to the melting point of the complex. The observance of two weak and slightly broad coupled exotherms at 235°C and 301°C and a broad exotherm at 498°C in the DTA curve of $[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ substantiated the second step decomposition.

3.6. *Molecular modeling*

Molecular mechanical adjustments for energy optimization from strained structures to the likely geometry of parent complex were made. The molecular mechanics were repeated five to six times to ensure that the structure with minimized energy has been attained. The structure with minimized energy is assumed to be closer to the stable geometry and is in conformity with physicochemical and spectral data. On the basis of molecular modeling calculations for **1**, a probable distorted tetrahedral geometry around vanadium may tentatively be proposed (figure 2).

3.7. *Reactions of $[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ with sodium alkoxides NaOR ($OR = OMe, OEt, OBu^n, OPr^i$, and OAm^i)*

Interactions of $[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ with an excess above 1 : 2 molar ratio of sodium alkoxides in respective alcohol led to the formation of mixed ligand alkoxo phenoxo complexes according to the equation:

$$\left[VOCL(OC_6H_3(NO_2)_2)_2\right] + \underset{\text{(in excess)}}{NaOR} \xrightarrow[\text{reflux}]{ROH} \left[VO(OR)(OC_6H_3(NO_2)_2)_2\right] + NaCl\downarrow$$

$$(OR = OMe, OBu^n, OPr^i, OAm^i)$$

Elemental analyses of the isolated complexes agree with their stoichiometric formulations, indicating replacement of chloride by alkoxide. Like **1**, mixed alkoxo–phenoxo oxovanadium(V) complexes are soluble in methanol. The molar conductivities

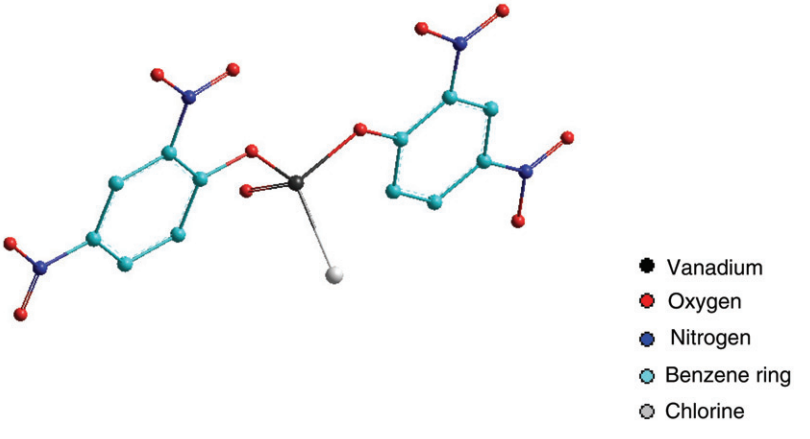


Figure 2. Tetrahedral structure of $[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$.

of the millimolar solutions of the complexes in methanol at $25 \pm 0.1^{\circ}C$ suggest their non-electrolytic nature. The formation of complexes is further ascertained from their IR spectra (4000–200 cm^{-1}). Characteristic vibrational modes of the coordinated alkoxo groups occur from 1150 to 1000 cm^{-1} in metal alkoxides [39, 40]; the number and band positions are related to terminal and bridged alkoxo groups [41, 42]. The υ(CO) shifts to higher frequencies upon complexation and a splitting of this band in the presence of bridged and terminal alkoxo groups may occur.

Close examination of the IR spectra of the complexes shows additional absorptions in 1140–1020 cm^{-1} region relative to **1** which may be attributed to υ(CO) of terminal alkoxo groups. A larger number of absorptions are observed in the C–O stretching region for complexes containing an ethoxide over methoxide in line with previous reports [43]. Absorptions characteristic of alkoxo groups at ~2900 cm^{-1} and ~1450 cm^{-1} due to υ(CH) and δ(C–H) have been observed. Absorptions due to phenoxide undergo slight changes in band position and intensity. The absence of bands at 366 cm^{-1} due to υ(V–Cl) confirm the substitution of chloride by alkoxides.

3.8. *Antifungal activity*

The 2,4-dinitrophenol ligand, $[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ and mixed alkoxo-phenoxo complexes $[VO(OR)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ were screened *in vitro* for their antifungal activity on *A. niger*, *B. fulva,* and *M. circinelloides* using the MIC method (table 2).

The ligand inhibits fungal growth at 125 $\mu g\,mL^{-1}$ and **1** at 62.5 $\mu g\,mL^{-1}$. All the mixed alkoxo-phenoxo oxovanadium(V) derivatives having antifungal activity similar to that of **1** against *A. niger* at MIC of 62.5 $\mu g\,mL^{-1}$. $[VO(OR)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ ($OR = OPr^i$, OBu^n, and OAm^i) exhibited enhanced activity against *B. fulva* at 31.25 $\mu g\,mL^{-1}$ while $[VO(OR)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ ($OR = OMe$, OEt) had MIC values of 62.5 $\mu g\,mL^{-1}$. The most pronounced activity toward *M. circinelloides* was shown by $[VO(OBu^n)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ at MIC of 15.63 $\mu g\,mL^{-1}$. $[VO(OPr^i)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ inhibits *M. circinelloides* at MIC of 31.25 $\mu g\,mL^{-1}$; *M. circinelloides* is inhibited by $[VO(OR)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ ($OR = OMe$, OEt, OAm^i) at MIC 62.25 $\mu g\,mL^{-1}$. The results were compared with standard antifungal drug fluconazole (treated control).

The observed effectiveness probably reflects the specificity of interaction of complexes with fungi and easier permeability toward the microbe cells. It does not

Table 2. Antifungal activity of ligand and monooxovanadium(V) complexes by the MIC method in $\mu g\,mL^{-1}$.

Compound	*A. niger*	*B. fulva*	*M. circinelloides*
Treated control (Fluconazole)	3.91	3.91	3.91
Untreated control	–	–	–
$HOC_6H_3(NO_2)_2\text{-}2,4$	125	125	125
$[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$	62.5	62.5	62.5
$[VO(OMe)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$	62.5	62.5	62.5
$[VO(OEt)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$	62.5	62.5	62.5
$[VO(OPr^i)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$	62.5	31.25	31.25
$[VO(OBu^n)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$	62.5	31.25	15.63
$[VO(OAm^i)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$	62.5	31.25	62.5

seem plausible to compare the present results for antifungal activities with earlier reports [44–46] because of different methodologies and strains assayed.

4. Conclusion

The title complex $[VOCl(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ and $[VO(OR)(OC_6H_3(NO_2)_2\text{-}2,4)_2]$ (OR = OMe, OEt, OPr^i, OBu^n and OAm^i) have been synthesized and characterized. The antifungal screening of complexes depicts moderate to significant inhibitory effect compared to free ligand. This study reveals positive attributes associated with biological potential of oxovanadium(V) phenolate complexes.

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