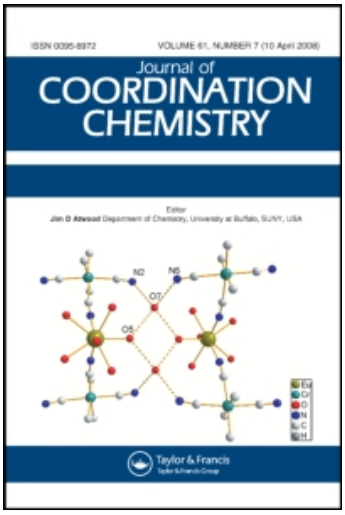

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Synthesis, characterization, and antibacterial activity of vanadium(IV) complexes of hydroxamic acids

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Synthesis, characterization, and antibacterial activity of vanadium(IV) complexes of hydroxamic acids

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Vanadium(IV) complexes of composition $[VCl_{2-n}(acac)_2(HL^{1,2})_n]$ (**1**–**4**) (where acac = $(CH_3COCHCOCH_3^-)$ $HL^1 = C_6H_5OCH_2C(O)NHO^-$; phenoxyacetohydroxamate ion; $HL^2 = C_6H_5CH=CHC(O)NHO^-$; cinnamylhydroxamate ion, $n = 1$ and 2 have been synthesized by reaction of $[VCl_2(acac)_2]$ with the potassium salt of phenoxyacetohydroxamic and cinnamylhydroxamic acids in predetermined molar ratios in THF + MeOH. The characterization of the complexes has been accomplished by elemental analyses, molar conductivity, magnetic measurements, IR, electronic, and mass spectral studies. Based upon spectral and molecular modeling dynamics, a distorted octahedral geometry around vanadium has been proposed. The thermal behavior of the complexes has been studied by TG and DTA techniques. The antibacterial activities of the newly synthesized complexes, vanadium precursor, and ligands have been assayed by the minimum inhibitory concentration method. The complexes have improved antibacterial activity over the free ligands.

Keywords: Potassium salts of phenoxyacetohydroxamic and cinnamylhydroxamic acids; Non-oxovanadium(IV) complexes; Antibacterial activity

1. Introduction

Hydroxamic acids constitute an important class of organic bioligands [1], with the hydroxamic moiety (–NHOH), a constituent of antibiotics, antifungal agents, food additives, drugs, tumor inhibitors, and growth factors [2–4]. The biological activities of several naturally occurring hydroxamic acids and some synthetic derivatives are related to their ability to chelate a variety of metals, which is also responsible for their inhibitory effect on several metal-containing enzymes [5–7]. Hydroxamic acids display diverse ligating [8, 9] behavior, wherein two hydroxamate oxygens and nitrogen offer potential binding sites. Hydroxamic and hydroximic forms exist because of tautomerism [10], but the hydroxamic acid form predominates in free acids [11] and metal hydroxamates [12]. Compared with the well-documented chemistry of transition metal

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hydroxamates [13], there are only a few examples of oxovanadium(IV), vanadium(IV), and (V) hydroxamate complexes [14–17], perhaps because of the stereochemical and structural diversity offered by both vanadium and hydroxamate ligands in their complexes. Nevertheless, there has been continuous interest in coordination chemistry of vanadium [18–20], owing to biochemical investigations of vanadium dependent haloperoxidases, nitrogenases, and other biologically active vanadium complexes. Vanadium as well as its complexes exhibit promising insulinomimetic [21], appetite suppressing, and antihypertensive effects. The role of vanadium in phospholipid oxidation, sulfur metabolism, cholesterol biosynthesis, and its complexes as effective inhibitors of human sperm mobility [22] anticancer [23], and antiamoebic agents [24, 25] has furthered vanadium chemistry. In view of the biological significance of both vanadium metal and hydroxamate ligands, in this work we report synthesis, characterization, and antibacterial screening of complexes synthesized from reaction of $VCl_2(acac)_2$ as a virtually unexplored non-oxovanadium(IV) precursor, with two hydroxamic acids.

2. Experimental

2.1. *Materials and methods*

Reagent-grade solvents were dried and distilled prior to use. All other chemicals were reagent grade. $[VCl_2(acac)_2]$ was prepared from $[VO(acac)_2]$ by the reported methods [26, 27] under nitrogen and its formation and purity checked by C, H, Cl, and V microanalyses, and IR spectral data. The potassium phenoxyacetohydroxamate and cinnamylhydroxamate were synthesized by the method reported earlier [28]. The vanadium content in complexes was determined as V_2O_5 while chlorine was determined by Volhard's method. Carbon, hydrogen, and nitrogen analyses were obtained on an Eager 300 NCH System Elemental Analyzer. The molar conductances (10^{-3} M solutions in nitrobenzene) were obtained at $25.0 \pm 0.1^{\circ}C$ 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. IR spectra of the complexes were recorded as KBr pellets on a Nicolet-5700 FTIR spectrophotometer. The pellets were prepared in a dry box to avoid moisture. Electronic spectra of complexes were recorded on a Varian Cary-100 Bio UV-Vis spectrophotometer using acetonitrile as solvent. FAB-mass spectra were recorded on a Jeol SX 10^2/DA-6000 Mass Spectrometer/Data system using Argon/Xenon (6 KV, 10 mA). The accelerating voltage was 10 KV and m-nitrobenzylalcohol (NBA) was used as the matrix. Thermograms of powdered samples were recorded on a simultaneous TG-DTA SHIMADZU DT-60 thermal analyzer in air at a heating rate of $20^{\circ}C\ min^{-1}$ using a platinum crucible.

2.2. *Synthesis*

2.2.1. $[VCl_{2-n}(acac)_2(HL^1)_n]$. To a solution of potassium phenoxyacetohydroxamate (0.64 g, 3 mmol/1.28 g, 6 mmol) in methanol (20 mL), a solution of $VCl_2(acac)_2$ (1 g, 3 mmol) in THF (20 mL) was added. The reaction mixture was stirred for 1 h and then

refluxed for 4–6 h. The white residue obtained during the course of the reaction was removed by filtration and identified as KCl. The filtrate was distilled to remove excess solvent. The concentrate was then dried under vacuum by repeatedly treating with petroleum ether, whereupon light-green and violet-blue solids were obtained. These were recrystallized from dichloromethane (Yield: 1.20 g, 85%/1.49 g, 82%). Anal. Calcd for $VClC_{18}H_{22}O_7N$ (450.5) (%): C, 47.95; H, 4.88; N, 3.10; Cl, 7.88; V, 11.32. Found: C, 47.40; H, 4.65; N, 2.98; Cl, 7.55; V, 11.28. Λ_m, ($PhNO_2$): 4.12 S $cm^2 mol^{-1}$; μ_{eff} (293 K): 1.72 B.M. Anal. Calcd for $VC_{26}H_{30}O_{10}N_2$ (581) (%): C, 53.70; H, 5.16; N, 4.81; V, 8.78. Found: C, 53.14; H, 5.08; N, 4.32; V, 8.52. Λ_m ($PhNO_2$): 5.07 S $cm^2 mol^{-1}$; μ_{eff} (293 K): 1.76 B.M.

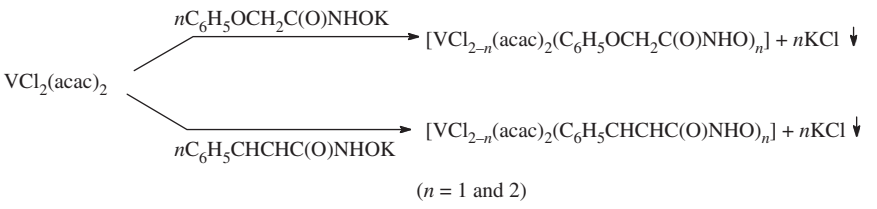
2.2.2. $[VCl_{2-n}(acac)_2(HL^2)_n]$. To a solution of potassium cinnamylhydroxamate (0.63 g, 3 mmol/1.26 g, 6 mmol) in methanol (20 mL), a solution of $VCl_2(acac)_2$ (1 g, 3 mmol) in THF (20 mL) was added. The reaction mixture was stirred for 1 h, refluxed for 4–6 h, filtered, and a white residue obtained was identified as KCl. The filtrate was then distilled to remove excess solvent. The concentrate was dried under vacuum by repeatedly treating with petroleum ether. The dark blue and bluish-violet solids obtained were recrystallized from dichloromethane (Yield: 1.22 g, 87%/1.52 g, 85%). Anal. Calcd for $VClC_{19}H_{22}O_6N$ (446.5) (%): C, 51.06; H, 4.93; N, 3.14; Cl, 7.95; V, 11.42. Found: C, 51.02; H, 4.35; N, 3.01; Cl, 7.66; V, 11.31. Λ_m ($PhNO_2$): 4.3 S $cm^2 mol^{-1}$; μ_{eff} (293 K): 1.71 B.M. Anal. Calcd for $VC_{28}H_{30}O_8N_2$ (573) (%): C, 58.63; H, 5.23; N, 4.89; V, 8.90. Found: C, 58.26; H, 5.11; N, 4.53; V, 8.66. Λ_m ($PhNO_2$): 4.6 S $cm^2 mol^{-1}$; μ_{eff} (293 K): 1.73 B.M.

2.3. *Antibacterial activity*

The precursor $[VCl_2(acac)_2]$, potassium phenoxyacetohydroxamate (KHL^1), potassium cinnamylhydroxamate (KHL^2), and vanadium(IV) complexes derived from these ligands of composition $[VCl_{2-n}(acac)_2(HL^{1,2})_n]$ were screened *in vitro* for their antibacterial activity on selected bacteria gram(+) *Staphylococcus aureus* and gram(−) *Escherichia coli* using the minimum inhibitory concentration (MIC) method. MIC is the lowest concentration of the antimicrobial agents that prevents development of visible growth after overnight incubation [29]. All samples were tested in triplicate.

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

The MIC assay [30] was performed in a 96-well microtitre plate. For MIC assay of each test drug, a row of 12 wells was used out of which the last two wells were taken as control (no drug added). Each of the 10 wells received 100 µL of the Muller-Hinton 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 (containing test drug), 100 µL broth was withdrawn with a sterile tip and added to the 100 µL of the broth in the second well; 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}). The broth in each well was inoculated with 2 µL of the bacterial culture (*S. aureus*/*E. coli*) and the contents were mixed by 10 clockwise and



Scheme 1. Reaction scheme of the preparation of vanadium (IV) complexes.

10 anticlockwise rotations on a flat surface. The plate was incubated at 35°C thereafter and observations for growth of bacteria were recorded after 24 h.

3. Results and discussion

Complexes of composition $[VCl_{2-n}(acac)_2(HL^{1,2})_n]$ have been synthesized in quantitative yields by reaction of $[VCl_2(acac)_2]$ with equi- and bi-molar amounts of potassium phenoxyacetohydroxamate and potassium cinnamylhydroxamate in THF/methanol according to scheme 1.

The complexes are green, blue, and bluish-violet microcrystallines and soluble in water and common organic solvents, such as methanol, chloroform, dichloromethane, and acetonitrile, reflecting their monomeric nature. The molar conductance values of the complexes in methanol were 4.12–5.07 S cm^2 mol^{-1}, suggesting non-electrolytes. The cryoscopic molecular weight determinations in water indicated monomers. The room temperature magnetic moment values of the complexes are 1.71–1.76 B.M., consistent with +4 oxidation state for vanadium.

3.1. *IR spectra*

Formation of complexes has been inferred from a comparison of IR spectra with those of the free ligands potassium phenoxyacetohydroxamate (KHL^1) and potassium cinnamylhydroxamate (KHL^2) from 4000 to 250 cm^{-1}. Absorptions from 1680 to 1597 cm^{-1} and from 1650 to 1560 cm^{-1} in potassium phenoxyacetohydroxamate and potassium cinnamylhydroxamate, respectively, attributed to ν(C=O), appear at 1695–1580 cm^{-1} and 1657–1560 cm^{-1} in the respective vanadium(IV) complexes. No appreciable shift in ν(C=O) in complexes relative to free ligands indicates carbonyl does not participate in coordination with vanadium. Likewise, the absorption due to ν(C–N) at ~1370 cm^{-1} in free ligands is almost unaltered at ~1374 cm^{-1} and 1362 cm^{-1} in complexes. Bands at 3297 cm^{-1} and 3229 cm^{-1} assigned to ν(N–H) in KHL^1 and KHL^2, respectively, did not undergo any change appearing at ~3292 and ~3232 cm^{-1} in the respective complexes, suggesting that –NH is retained and not coordinated. Sharp bands at 938 cm^{-1} and 958 cm^{-1} in KHL^1 and KHL^2, respectively, ascribed to ν(N–O) move to higher wavenumbers at ~973 and ~992 cm^{-1} in the respective complexes, suggesting that both phenoxyacetohydroxamate and cinnamylhydroxamate coordinate via oxygen of –NHO only, contrary to reports describing O,O coordination in simple

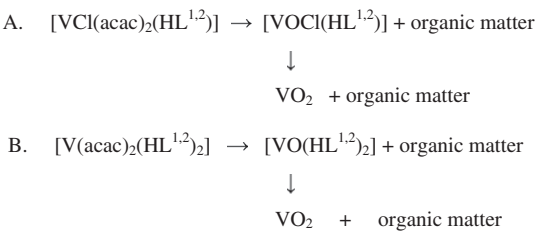
hydroxamic acids [31] and N,N and N,O coordination for many aminohydroxamic acids [32]. The two to three absorptions in the 560–465 cm^{-1} region have been assigned to ν(V–O) [33, 34]. So far IR spectra of the chlorovanadium(IV) complexes [$VCl(acac)_2(HL^{1,2})$], absorptions at ~365 cm^{-1} may be attributed to ν(V–Cl) [35] and additional sharp bands at 1575–1500 cm^{-1} and 1400–1365 cm^{-1} may be assigned to ν_{as}(C=O) and ν_s(C=O) of the coordinated acetylacetonate.

3.2. *Electronic spectra*

Electronic absorption spectra of KHL^1 and KHL^2 show sharp bands at 44,247, 38,910, and 45,248, 39,062 cm^{-1}, respectively, attributed to intraligand $\pi \rightarrow \pi^*$ transitions. The precursor $VCl_2(acac)_2$ has a low intensity band at 15,873 cm^{-1} with a shoulder at 14,285 cm^{-1} and another band at 28,985 cm^{-1} assigned to acetylacetonate (π) $\rightarrow$ vanadium (dπ) LMCT and vanadium (dπ) $\rightarrow$ acetylacetonate (π^*) MLCT transitions, respectively. Deep green solutions of [$VCl(acac)_2(HL^1)$] and [$V(acac)_2(HL^1)_2$] display four bands at 36,101, 32,362, 17,452, and 13,192 cm^{-1} and 37,174, 32,362, 17,123, and 12,048 cm^{-1}, respectively. Electronic spectra of bluish-violet solutions of [$VCl(acac)_2(HL^2)$] and [$V(acac)_2(HL^2)_2$] exhibit four bands at 36,363, 32,258, 17,006, and 12,091 cm^{-1} and 37,313, 32,362, 17,152, and 12,033 cm^{-1}, respectively, implying that these two series of complexes have similar features. The intense high energy bands at 37,313–36,101 cm^{-1} and 32,258 cm^{-1} may be assigned to intraligand and vanadium (dπ) $\rightarrow$ acetylacetonate (π^*)/hydroxamate ligand (π^*) transitions, respectively. The less intense absorptions at 17,006–17,452 cm^{-1} and 12,033–13,192 cm^{-1} may be ascribed to $^2E_g \leftarrow {}^2T_{2g}$ in octahedral geometry and ligand (π) to vanadium (π) charge transfer, respectively. For non-oxovanadium(IV) complexes VL_2 (where H_2L is a tetradentate ONNO donor), both the high intensity transitions at 17,241–18,181 cm^{-1} and 20,833–23,255 cm^{-1} have been reported to be assigned to enolate O $\rightarrow$ vanadium(IV) charge transfer transitions by analogy to previously reported non-oxovanadium(IV) complexes [36–39].

3.3. *Mass spectra*

FAB-MS peaks observed for the three vanadium(IV) complexes are given in Supplementary material. [$VCl(acac)_2(HL^1)$] (**1**) did not show a molecular ion, but structurally important fragment ions, such as $[VO(acac)_2(HL^1)]^+$, $[VO(acac)_2]^+$, $[V(acac)_2]^+$, $[(HL^1)]^+$, $[V(acac) - 3H]^+$, and $[VCl(acac) - 2H]^+$, including the most intense fragment corresponding to $[V(acac)(HL^1) + H]^+$ clearly support its formation. The FAB–mass spectra of [$V(acac)_2(HL^1)_2$] (**2**) and [$V(acac)_2(HL^2)_2$] (**4**) display molecular ion $[M]^+$ peaks. The most abundant peaks at m/z 147 and 313 correspond to $[V(acac) - H]^+$ and $[V(acac)(HL^2) + H]^+$ in **2** and **4**. A striking feature of the mass spectra of complexes is that a few fragment ions assignable to vanadyl and $[V(acac)_3]^+$ have been observed [40]. In the case of (catecholato) bis(β-diketonato) vanadium(IV) complexes, reaction in the gas phase produce $[V(acac)_3]^+$ and $[V(bzac)_3]^+$ fragments as a result of cluster formation by molecule–ion reactions characteristic of metal β-diketonates [41–43].



Scheme 2. Thermal decomposition scheme of vanadium(IV) complexes.

3.4. *Thermal studies*

The thermal decomposition behavior of complexes has been studied by thermogravimetric and differential thermal analysis in air and the data obtained from the TG and DTA curves are summarized in "Supplementary material". All the complexes have two-step decomposition. On the basis of % weight loss, the formation of $[VOCl(HL^{1,2})_2]$ and $[VO(HL^{1,2})_2]$ as probable intermediates has been proposed. The final product of decomposition has been identified as VO_2 in each complex from % weight loss in second step and physical characteristics. The decomposition may be represented as given in scheme 2.

The DTA curve of **2** exhibited endothermic peaks compared with exothermic peaks in **1**, **3**, and **4**.

3.5. *Molecular modeling*

Molecular mechanical energy optimization from strained structures to the likely geometry of complexes was attempted. 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 in consonance with physicochemical and spectral data.

On the basis of analytical and IR, electronic and mass spectral data combined with molecular modeling calculations, a distorted octahedral geometry for the complexes has been proposed. The structures for perspective complexes are presented in figures 1 and 2, and "Supplementary material".

3.6. *Antibacterial activity*

Several reports are available concerning antimicrobial activity of ligands and their complexes against pathogenic bacteria and plant pathogenic fungi [44–57]. Of these, the antibacterial activity of numerous complexes against *E. coli* and *S. aureus*, in particular, have been reported. In this work, $[VCl_2(acac)_2]$, ligands, and newly synthesized complexes were tested *in vitro* for their antibacterial activity against *E. coli* and *S. aureus* (table 1) and compared with control. The results show that both the ligands inhibit the bacterial growth at $125\,\mu g\,mL^{-1}$ for *E. coli* and $250\,\mu g\,mL^{-1}$ for *S. aureus*. $[VCl_2(acac)_2]$ inhibits bacterial growth at $250\,\mu g\,mL^{-1}$ for both bacteria. The newly synthesized complexes inhibit at $31.25\,\mu g\,mL^{-1}$ for *E. coli* and $62.5\,\mu g\,mL^{-1}$ for *S. aureus*. This enhancement in activity is due to coordination of hydroxamate to metal

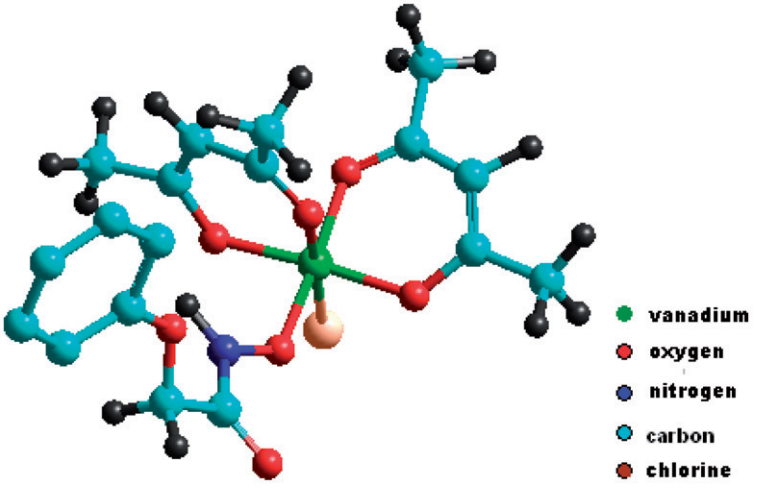


Figure 1. Octahedral structure of $[VCl(acac)_2(HL^1)]$.

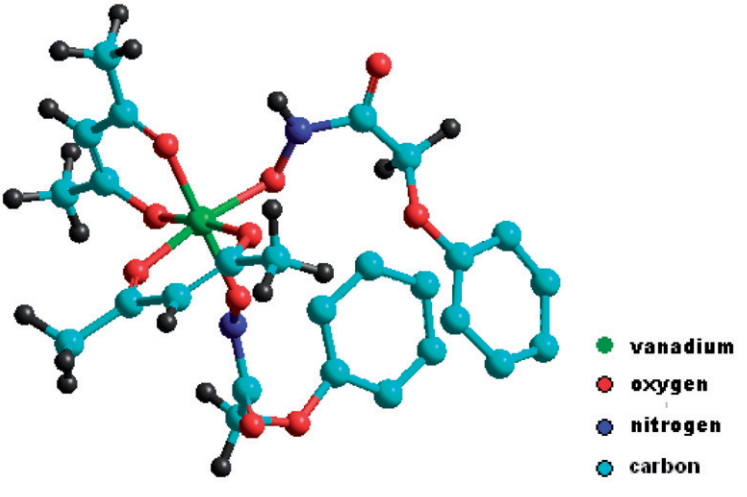


Figure 2. Octahedral structure of $[VCl(acac)_2(HL^1)]$.

Table 1. Antibacterial activity of ligands and complexes by MIC method ($\mu g\,mL^{-1}$).

Compound	*E. coli*	*S. aureus*
HL^1	125	250
HL^2	125	250
$VCl_2(acac)_2$	250	250
$VCl(acac)_2(HL^1)$	31.25	62.5
$V(acac)_2(HL^1)_2$	31.25	62.5
$VCl(acac)_2(HL^2)$	31.25	62.5
$V(acac)_2(HL^2)_2$	31.25	62.5
Streptomycin	31.25	62.5

ion and efficient diffusion of the metal complexes into bacterial cells [58, 59]. The antibacterial activity of these complexes was compared with streptomycin. It is difficult to compare this antibacterial screening with those reported earlier because of the different methodology and strains assayed, but in view of the biological significance associated with both vanadium and hydroxamate ligands, promising bioactivity has been depicted by the complexes.

4. Conclusion

In $[VCl_{2-n}(acac)_2(HL^{1,2})_n]$ ($n = 1$ and 2) the hydroxamate is monodentate, coordinating through hydroxylamine oxygen (–NHO). Complexation by hydroxamate does not change oxidation number of vanadium. Thermal decomposition of complexes afford VO_2 as the ultimate decomposition product. The complexes exhibit high-inhibitory effect compared with the parent hydroxamate ligands.

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