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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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First published on: 25 June 2010

To cite this Article Sharma, Neeraj , Kumari, Meena , Kumar, Vijay , Chaudhry, S. C. and Kanwar, S. S.(2010) 'Synthesis, characterization, and antimicrobial activity of oxovanadium(IV)hydroxamate complexes', *Journal of Coordination Chemistry*, 63: 11, 1940 — 1950, First published on: 25 June 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.495986

URL: <http://dx.doi.org/10.1080/00958972.2010.495986>

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Synthesis, characterization, and antimicrobial activity of oxovanadium(IV)hydroxamate complexes

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(Received 5 February 2010; in final form 17 March 2010)

Vanadium(IV) complexes, $[\text{VO}(\text{acac})(\text{HL}^{1,2})]$ and $[\text{VO}(\text{HL}^{1,2})_2]$ (I–IV) (where $\text{acac} = (\text{CH}_3\text{COCHCOCH}_3^-)$; $\text{HL}^{1,2} = \text{R}'\text{C}(\text{O})\text{NHO}^-$, $\text{R}' = -\text{CH}_2\text{OC}_6\text{H}_5$ and $-\text{CH}=\text{CHC}_6\text{H}_5$), have been synthesized by reaction of $\text{VO}(\text{acac})_2$ with the potassium salt of phenoxyacetohydroxamic and cinnamohydroxamic acids and characterized by elemental analyses, molar conductivity, magnetic measurements, molecular weight determinations, IR, electronic, mass spectral, and electrochemical studies. From the spectroscopic studies, O,O coordination of hydroxamate ligands and a square-pyramidal geometry for the complexes has been proposed. The antibacterial activities of $\text{VO}(\text{acac})_2$, the precursor, the free ligands, and the synthesized oxovanadium(IV)hydroxamate complexes against six bacteria have been assayed by the minimum inhibitory concentration method. The complexes exhibit antimicrobial activities comparable to the standard drug streptomycin.

Keywords: Oxovanadium(IV) complexes; Potassium phenoxyacetohydroxamate; Cinnamohydroxamate; Spectral studies; Antimicrobial activity

1. Introduction

Interest in the coordination chemistry of oxovanadium(IV) and (V) and dioxovanadium(V) complexes arise from their pharmacological activities [1–11] and their potential to model vanadium-containing nitrogenases [12] and haloperoxidases [13, 14]. The pronounced catalytic activity of vanadium complexes has further stimulated interest in coordination chemistry [15–17]. Amongst various classes of ligands, the biologically active hydroxamic acid ligands have diverse chelation modes affording a variety of metal complex structures [18, 19]. Hydroxamic acids possess a broad spectrum of biological activities [20–23]. Transition metal hydroxamates, in particular, find use as bioinorganic model compounds to study their enzymatic interactions [24]. Several hydroxamic acids find use in 12-metallacrown-4 synthesis [25] and their complexes with various metals including oxovanadium(IV) have been

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reported [26–29]. A literature survey, however, reveals that only a few scattered reports are available on hydroxamates of vanadium(IV) and (V) [19], despite the fact that vanadium hydroxamate interactions stem from well-established biological functions of these complexes. The amino acid monohydroxamates of vanadium(IV) and (V) derived from vanadyl (VO^{2+}), metavanadate (VO_3^{3-}), or vanadate (VO_4^{3-}) induce normoglycemia in adiabatic patients [30]. The crystal structures of oxochlorobis(benzohydroxamate)vanadium(IV) and oxoisopropoxy(*N,N'*-dihydroxy-*N,N'*-diisopropylheptanediamido) vanadium(V) involving hydroxamate O,O coordination have been reported [31]. Oxygen abstraction reactions of *N*-substituted hydroxamic acids with molybdenum(V) and vanadium(III) and (IV) compounds have also been reported [32]. Vanadyl sulfate and ammonium vanadate have mainly been exploited as starting materials for the synthesis of vanadium–hydroxamate complexes, while $\text{VO}(\text{acac})_2$, irrespective of its well-documented coordination chemistry, remained rather unexplored for synthesizing vanadium hydroxamate complexes [33]. In the present work, therefore, we have chosen $\text{VO}(\text{acac})_2$ as the precursor to investigate its reactivity with biologically important phenoxyacetohydroxamate and cinnamohydroxamate. The ligands and newly synthesized complexes have been screened for their antibacterial activity with a view to explore their use as potential biocidal agents.

2. Experimental

2.1. Materials and methods

Reagent-grade solvents were dried and distilled prior to use. All other chemicals were reagent grade. $[\text{VO}(\text{acac})_2]$ was prepared by the reported method [34] and its formation and purity were checked by C, H, N, and V microanalysis and IR spectral data. The potassium phenoxyacetohydroxamate and cinnamohydroxamate were synthesized by reported methods [35]. The vanadium content was determined as V_2O_5 . Carbon, hydrogen, and nitrogen analyses were obtained on an Eager 300 NCH System Elemental Analyzer. The molar conductances (10^{-3} mol L^{-1} solutions in nitrobenzene) were obtained at $25 \pm 0.1^\circ\text{C}$ on an Elico Conductivity Bridge Type CM-82T. Room temperature magnetic susceptibilities were measured by Guoy's method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant. IR spectra of the complexes were recorded as KBr pellets on a Nicolet-5700 FT-IR 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. The FAB-mass spectra were recorded on a Jeol SX $10^2/\text{DA}-6000$ Mass Spectrometer/Data system using Argon/Xenon (6 KV, 10 mA). The accelerating voltage was 10 KV, *m*-nitrobenzylalcohol (NBA) was used as the matrix. Cyclic voltammetry was carried out on a CH instrument electrochemical analyzer. All voltammetric experiments were performed in a single compartmental cell of volume 10–15 mL containing a three-electrode system comprising a Pt-disc working electrode, Pt-wire auxiliary electrode, and Ag/AgCl electrode as reference electrode. The supporting electrolyte was 0.4 mol L^{-1} KNO_3 in milli-Q water. De-aerated solutions were obtained by purging N_2 gas for 15 min prior to measurements.

2.2. Synthesis

2.2.1. $[\text{VO}(\text{acac})_{2-n}(\text{HL}^{1,2})_n]$. In a typical reaction, to a solution of $\text{VO}(\text{acac})_2$ (1 g, 3.77 mmol) in THF (20 mL), a solution of potassium phenoxyacetohydroxamate (0.77 g, 3.77 mmol; 1.54 g, 7.5 mmol)/potassium cinnamohydroxamate (0.76 g, 3.77 mmol; 1.52 g, 7.5 mmol) in methanol (20 mL) was added in separate experiments. The reaction mixture was stirred for 1 h and then refluxed for 18–20 h. The white solid formed during the course of reaction was removed by filtration and identified as Kacac . The filtrate was distilled to remove excess solvent. The concentrate was then dried under vacuum by repeatedly treating with petroleum ether, whereupon green solids were obtained. These were recrystallized from dichloromethane.

Anal. Calcd for $\text{VC}_{13}\text{H}_{15}\text{O}_6\text{N}$ (332) (%): C, 46.98; H, 4.51; N, 4.21; V, 15.36. Found (%): C, 46.50; H, 4.09; N, 4.03; V, 15.18. $\Lambda_m(\text{PhNO}_2)$: $4.02 \text{ S cm}^2 \text{ mol}^{-1}$; μ_{eff} (293 K): 1.70 B.M. (Yield: 1.03 g, 83%).

Anal. Calcd for $\text{VC}_{16}\text{H}_{16}\text{O}_7\text{N}_2$ (399) (%): C, 48.12; H, 4.01; N, 7.01; V, 12.78. Found (%): C, 47.88; H, 3.79; N, 6.83; V, 12.36. $\Lambda_m(\text{PhNO}_2)$: $5.17 \text{ S cm}^2 \text{ mol}^{-1}$; μ_{eff} (293 K): 1.72 B.M. (Yield: 1.27 g, 85%).

Anal. Calcd for $\text{VC}_{14}\text{H}_{15}\text{O}_5\text{N}$ (328) (%): C, 51.21; H, 4.57; N, 4.26; V, 15.54. Found (%): C, 51.05; H, 4.31; N, 4.11; V, 15.22. $\Lambda_m(\text{PhNO}_2)$: $4.13 \text{ S cm}^2 \text{ mol}^{-1}$; μ_{eff} (293 K): 1.71 B.M. (Yield: 1.01 g, 82%).

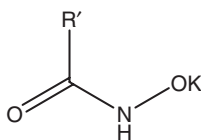
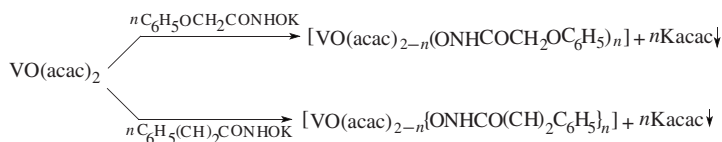
Anal. Calcd for $\text{VC}_{18}\text{H}_{16}\text{O}_5\text{N}_2$ (391) (%): C, 55.24; H, 4.09; N, 7.16; V, 13.04. Found (%): C, 55.12; H, 3.86; N, 7.09; V, 12.74. $\Lambda_m(\text{PhNO}_2)$: $4.06 \text{ S cm}^2 \text{ mol}^{-1}$; μ_{eff} (293 K): 1.74 B.M. (Yield: 1.15 g, 78%).

2.3. Antibacterial activity test

The precursor $\text{VO}(\text{acac})_2$, potassium phenoxyacetohydroxamate (KHL^1), and potassium cinnamohydroxamate (KHL^2) as well as vanadium(IV) complexes derived from these ligands of composition $[\text{VO}(\text{acac})_{2-n}(\text{HL}^{1,2})_n]$ were screened *in vitro* for their antibacterial activity on *Escherichia coli*, *Staphylococcus aureus*, *Proteus mirabilis*, *Pseudomonas aeruginosa*, *Staphylococcus epidermidis*, and *Shigella flexneri* using the minimum inhibitory concentration (MIC) method [36]. For evaluating antibacterial activity, streptomycin was used as the standard drug. All samples were tested in triplicate with error limit ± 1 .

2.4. MIC determination by two-fold serial dilution

The MIC assay was performed in a 96-well micro-titre plate. For MIC assay of each drug; a stock solution of 1 mg mL^{-1} was prepared in DMSO and 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 $100 \mu\text{L}$ of the Muller–Hinton broth, except the first well, which received $200 \mu\text{L}$ of broth containing $500 \mu\text{g mL}^{-1}$ concentration of the test drug. From the first well, $100 \mu\text{L}$ broth (containing test drug) was withdrawn with a sterile tip and added to $100 \mu\text{L}$ of the broth in the second well. The contents were mixed four times. Then $100 \mu\text{L}$ was withdrawn from the second well and was added to the third well.

Figure 1. Structure of potassium hydroxamate (KHL^{1,2}).

Scheme 1. Schematic view of the preparation of oxovanadium(IV) complexes.

This way a range of two-fold serial dilutions were prepared (500–0.98 $\mu\text{g mL}^{-1}$). The broth in each of the wells was inoculated with 2 μL of the bacterial culture and the contents were mixed by 10 clockwise, and thereafter by 10 anticlockwise rotations on a flat surface, and the plate was incubated at 35°C. The observations for the growth of bacteria were recorded after 24 h. To evaluate the role of solvent in biological screening, if any, separate studies were carried out with DMSO. The solvent did not show any activity against bacteria.

3. Results and discussion

Reaction of $\text{VO}(\text{acac})_2$ with potassium phenoxyacetohydroxamate and potassium cinnamohydroxamate (figure 1) in THF/methanol solvent afforded $[\text{VO}(\text{acac})(\text{HL}^1)]$, {acetylacetonato(phenoxyacetohydroxamato)oxovanadium(IV); $[\text{VO}(\text{HL}^1)_2]$, bis(phenoxyacetohydroxamato)oxovanadium(IV); $[\text{VO}(\text{acac})(\text{HL}^2)]$, acetylacetonato(cinnamohydroxamato)oxovanadium(IV) and $[\text{VO}(\text{HL}^2)_2]$, bis(cinnamohydroxamato)oxovanadium(IV)} in quantitative yields according to scheme 1.

The complexes are green to blackish green microcrystalline solids, soluble in water, methanol, chloroform, dichloromethane, acetonitrile, etc. Molar conductance values of the complexes in methanol are between 4.02 and 5.17 $\text{S cm}^2 \text{mol}^{-1}$ suggesting nonelectrolytes. The cryoscopic molecular weight determinations of the complexes in water indicated that these complexes exist as monomers. The room temperature magnetic moment values of 1.70–1.74 B.M. correspond to the spin-only value of 1.73 B.M. indicating no intermolecular interactions. The paramagnetic nature and +4 oxidation state of vanadium is also confirmed.

3.1. IR spectra

Comparison of IR spectra of newly synthesized oxovanadium(IV) complexes with that of the free ligands, potassium phenoxyacetohydroxamate (KHL¹), and potassium

cinnamohydroxamate (KHL²) gave supporting evidence for the formation. The important frequencies of hydroxamic group are $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{N})$, $\nu(\text{N}-\text{O})$, and $\nu(\text{N}-\text{H})$, which may undergo a significant change on complexation. The $\nu(\text{C}=\text{O})$ at 1610–1585 cm^{-1} in free hydroxamate shift to lower wavenumbers by 40–60 cm^{-1} upon coordination [37, 38], which is accompanied by shift in $\nu(\text{C}-\text{N})$ (1370–1310 cm^{-1}). Bonding through hydroxylamine oxygen results in $\nu(\text{N}-\text{O})$ (945–910 cm^{-1}) remaining unaltered or shifting to higher wave numbers. Bands due to the $\nu(\text{N}-\text{H})$ and NH deformations occur at ~ 3200 , 3080–3060, and 1440–1400 cm^{-1} in uncoordinated hydroxamate [39]. Absorptions at 1680–1597 and 1650–1560 cm^{-1} have been assigned to $\nu(\text{C}=\text{O})$ in potassium phenoxyhydroxamate and potassium cinnamohydroxamate, respectively. The occurrence of sharp absorptions due to the $\nu(\text{C}=\text{O})$ at 1655–1646 and 1636–1631 cm^{-1} in complexes derived from KHL¹ and KHL², respectively, suggest bonding through carbonyl oxygen to vanadium. The absorption due to the $\nu(\text{C}-\text{N})$ at $\sim 1370 \text{ cm}^{-1}$ in free ligands appears at 1385–1378 cm^{-1} in two series of complexes. Bands at 3297 and 3229 cm^{-1} assigned to $\nu(\text{N}-\text{H})$ mode in KHL¹ and KHL², respectively, did not undergo any change (~ 3295 and $\sim 3225 \text{ cm}^{-1}$) in the complexes suggesting that $-\text{NH}$ group is retained and coordination through nitrogen does not occur. Sharp bands at 938 and 958 cm^{-1} in KHL¹ and KHL² ascribed to $\nu(\text{N}-\text{O})$ are at $\sim 973 \text{ cm}^{-1}$ in both series of complexes. Since $\nu(\text{V}=\text{O})$ is reported to occur at 1035–935 cm^{-1} in vanadyl salts and complexes, this band may be ascribed to $\nu(\text{N}-\text{O}) + \nu(\text{V}=\text{O})$ modes. The sharp bands at 485–475 cm^{-1} are assigned to $\nu(\text{V}-\text{O})$ mode. The complexes did not show a band assigned to V–O–V asymmetric at $\sim 785 \text{ cm}^{-1}$, thereby excluding association/dimerization in complexes. Although it is improbable to use unambiguously V=O stretch as a probe of complex coordination geometry, it was suggested that $\nu(\text{V}=\text{O}) \sim 950 \text{ cm}^{-1}$ indicates octahedral geometry and $\sim 980 \text{ cm}^{-1}$ square pyramidal. Based on this correlation, the coordination about vanadium is assumed to be distorted square pyramidal. A shift in $\nu(\text{C}=\text{O})$ to lower wave number and $\nu(\text{N}-\text{O})$ to higher is suggestive of bonding through carbonyl and hydroxylamine oxygens (O,O coordination), thereby establishing bidentate ligands.

3.2. Electronic spectra

UV-Vis spectra of the ligands and newly synthesized oxovanadium(IV) complexes have been recorded in methanol. The interpretation of electronic spectra of oxovanadium(IV) complexes has been a subject of extensive investigation. Most oxovanadium(IV) complexes are reported to display three prominent bands at 800–625 ($b_2 \rightarrow e_\pi^*$), 690–520 ($b_2 \rightarrow b_1^*$), and 470–330 nm ($b_2 \rightarrow a_1^*$) (ϵ 10–100, 5–50, and 5–100 $\text{M}^{-1} \text{ cm}^{-1}$), respectively, attributed to $d \rightarrow d^*$ transitions. The highest energy band is generally obscured by the tail of strong transitions in the ultraviolet, which is a peculiar feature of vanadyl complexes [40, 41]. Electronic spectra of free potassium phenoxyacetohydroxamate (KHL¹) and potassium cinnamohydroxamate (KHL²) displayed absorption bands at 226 and 251 nm, 221 and 257 nm, respectively. Electronic spectra of $[\text{VO}(\text{acac})(\text{HL}^{1,2})]$ and $[\text{VO}(\text{HL}^{1,2})_2]$ exhibited two bands at 800–700 and 560–400 nm. These bands may be assigned to LMCT transition from a p orbital of acetylacetonato or the hydroxamate oxygen to vanadium and $d-d$ transition, respectively [42, 43], as the coordinated hydroxamate ions are known to induce strong charge transfer. The high energy bands lying below 350 nm are attributed

to intraligand transitions. These spectral observations are consistent with those reported for square-pyramidal oxovanadium(IV) complexes [44–46].

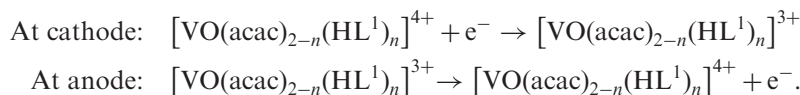
3.3. Mass spectra

The major FAB–MS peaks observed for [VO(acac)₂] and its derivatives with hydroxamate ligands are given in table 1. Mass spectra of [VO(acac)₂], [VO(HL¹)₂] (II), [VO(acac)(HL²)] (III), and [VO(HL²)₂] (IV) clearly showed the molecular ion peaks at *m/z* 265, 399, 327, and 391, respectively. The most intense peaks occurring at *m/z* 147, 136, 147, and 148 corresponded to [V(acac)–3H]⁺, [C₆H₅OCH₂CHO]⁺, [V(acac)–3H]⁺/[HL²–NH]⁺, and [HL²–NH + H]⁺, respectively. Mass spectra of [VO(acac)₂] and [VO(acac)(HL²)] exhibited some common fragment ions at 147, 207, 249 / 251, 265, and 281, characteristic of metal – β-diketonates, wherein β-diketonate ion undergoes aggregation [47, 48]. The absence of these fragments in [VO(HL¹)₂] and [VO(HL²)₂] suggest replacement of acetylacetonate by hydroxamate.

Based upon physicochemical and FT-IR, UV-Vis, and mass spectral data coupled with magnetic moment measurements, a distorted square-pyramidal geometry around vanadium may be proposed (figures 2 and 3).

3.4. Electrochemical studies

The results of cyclic voltammetric studies of [VO(acac)(HL¹)] and [VO(HL¹)₂] in methanol are given in table 2. The complexes display a single cathodic and anodic peak. The voltammograms of these complexes reveal one-electron change. The V^{III}/V^{IV} couple is quasi-irreversible as the peak current ratios are not unity [49]. The peak-to-peak separations also indicate their quasi-irreversible behavior. The following reaction pathways may be suggested to explain the electrochemical data:



From the electrochemical data, it is evident that vanadium(IV) is relatively stable to oxidation, but is easily reduced to vanadium(III), which is stable to further reduction. The vanadium(III) state is however easily oxidized to vanadium(IV).

3.5. Antibacterial activity

Transition metal complexes, in particular biometals containing biologically important ligands, have significance as potential biologically relevant agents [50–54]. The precursor VO(acac)₂, potassium phenoxyacetohydroxamate, potassium cinnamohydroxamate, and the synthesized complexes were tested *in vitro* for their antibacterial activity against *E. coli*, *S. aureus*, *P. mirabilis*, *P. aeruginosa*, *S. epidermidis* and *S. flexneri* (table 3, figure 4). The results were compared with positive control, containing both broth and bacteria and the control containing only broth. The data indicate that VO(acac)₂ inhibits in concentration range 125–250 μg mL⁻¹, while both the ligands inhibit the bacterial growth in concentration range 62.5–250 μg mL⁻¹.

Table 1. FAB-mass spectrum of oxovanadium(IV) complexes.

Complex [VO(acac) ₂]	<i>m/z</i> (%)	Complex [VO(HL ¹) ₂] (II)	<i>m/z</i> (%)	Complex [VO(acac)(HL ²)] (III)	<i>m/z</i> (%)	Complex [VO(HL ²) ₂] (IV)	<i>m/z</i> (%)
[VO(acac) ₂ + CH ₃ + H] ⁺	281(66.66)	[VO(HL ¹) ₂ + NBA ₁] ⁺	535(16.8)	[VO(acac)(HL ²) + CONHO - 2H] ⁺	385(44.4)	[VO(HL ²) ₂] ⁺	391(56)
[VO(acac) ₂] ⁺	265(86.11)	[VO(HL ¹) ₂ + 2NHO] ⁺	461(36.4)	[VO(acac)(HL ²) - H] ⁺	327(50)	[VO(HL ²) ₂ - NHO + H] ⁺	369(66.6)
[V(acac) ₂] ⁺	249(80.55)	[VO(HL ¹) ₂ + 2NHO] ⁺	430(33.6)	[V(acac)(HL ²) - H] ⁺	311(66.60)	[VO(HL ²) ₂ - NHO + Na] ⁺	345(30.8)
[VO(acac) ₂ - 3CH ₃ + H] ⁺	221(61.11)	[VO(HL ¹) ₂ + 2H] ⁺	401(30.8)	[VO(acac) ₂ + CH ₃ + H] ⁺	281(77.7)	[VO(HL ²) ₂ - 2NHO] ⁺	329(22.4)
[V(acac) ₂ - CH ₃ CO + H] ⁺	207(88.88)	[VO(HL ¹) ₂ - 3H] ⁺	396(28)	[VO(acac) ₂] ⁺	265(38.8)	[VO(HL ²) + V] ⁺	279(22.4)
[V(acac) + CH ₃ CO] ⁺	193(27.77)	[VO(HL ¹) ₂ + NHO - 2H] ⁺	370(33.6)	[V(acac) ₂ + 2H] ⁺	251(30.8)	[VO(HL ²) + NHO + H] ⁺	261(25.2)
[VO(acac)] ⁺	166(41.66)	[(HL ¹) ₂ + Na + H] ⁺	356(58.8)	[V(acac) ₂ - CH ₃ CO + H] ⁺	207(88.88)	[VO(HL ²) - 3H] ⁺	226(28)
[V(acac) - 3H] ⁺	147(100)	[VO(HL ¹) + OC ₆ H ₅ + H] ⁺	327(58.8)	[(HL ²) + NHO - 2H] ⁺	191(44.44)	[(HL ²) + NHO - H] ⁺	192(84)
[V(acac) - 2CH ₃] ⁺	120(19.44)	[VO(HL ¹) + NHO + H] ⁺	249(61.6)	[(HL ²) + CH ₃] ⁺	177(16.66)	[(HL ²) + NH - H] ⁺	176(39.2)
		[VO(HL ¹) - 4H] ⁺	229(86.8)	[V(acac) - 3H] ⁺ / [(HL ²) - NH] ⁺	147(100)	[(HL ²) - NH + H] ⁺	148(100)
		[(HL ¹) ₂ + Na + 3H] ⁺	192(28)	[(HL ²) - NHO] ⁺	131(51)	[(HL ²) - NHO] ⁺	131(84)
		[C ₆ H ₅ OCH ₂ CHO] ⁺	136(100)				

NBA₁ = 136; NBA₂ = 137; NBA₃ = 154.

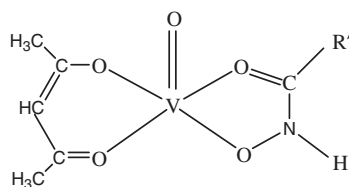
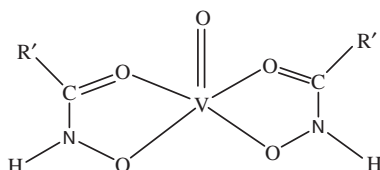
Figure 2. Proposed structure of $[\text{VO}(\text{acac})(\text{HL}^{1,2})]$.Figure 3. Proposed structure of $[\text{VO}(\text{HL}^{1,2})_2]$.

Table 2. Cyclic voltammetric data of oxovanadium(IV) complexes.

Complex	E_{pc} (V)	E_{pa} (V)	ΔE (mV)	I_{pc}	I_{pa}	I_{pa}/I_{pc}
$[\text{VO}(\text{acac})(\text{HL}^1)]$	-0.4068	-0.3104	96.4	7.144	-4.541	0.635
$[\text{VO}(\text{HL}^1)_2]$	-0.3471	-0.259	88.1	8.312	-1.411	0.169

Table 3. Antibacterial activity of ligands and oxovanadium(IV) complexes by MIC method (in $\mu\text{g mL}^{-1}$).

Compound	<i>E. coli</i>	<i>S. aureus</i>	<i>P. mirabilis</i>	<i>P. aeruginosa</i>	<i>S. epidermidis</i>	<i>S. flexneri</i>
$\text{C}_6\text{H}_5\text{OCH}_2\text{C}(\text{O})\text{NHOK} (\text{HL}^1)$	125	250	125	125	125	62.5
$\text{C}_6\text{H}_5\text{CH}=\text{CHC}(\text{O})\text{NHOK} (\text{HL}^2)$	125	250	125	62.5	125	62.5
$[\text{VO}(\text{acac})_2]$	250	250	125	125	125	125
$[\text{VO}(\text{acac})(\text{HL}^1)]$	31.25	62.5	62.5	62.5	62.5	31.25
$[\text{VO}(\text{HL}^1)_2]$	31.25	62.5	15.625	62.5	125	62.5
$[\text{VO}(\text{acac})(\text{HL}^2)]$	31.25	62.5	62.5	31.25	125	125
$[\text{VO}(\text{HL}^2)_2]$	31.25	62.5	62.5	62.5	125	125
Streptomycin	31.25	62.5	62.5	31.25	62.5	31.25

Of the four complexes derived from two different hydroxamate ligands, $[\text{VO}(\text{acac})(\text{HL}^1)]$ exhibits significant activity toward all bacteria under study with MIC of $31.25\text{--}62.5\ \mu\text{g mL}^{-1}$. $[\text{VO}(\text{HL}^1)_2]$ has most activity against *Pr. mirabilis* at concentration $15.62\ \mu\text{g mL}^{-1}$, but least activity against *S. epidermidis* at MIC value $125\ \mu\text{g mL}^{-1}$. Significant activity has also been displayed against *E. coli*, *S. aureus*, *P. aeruginosa*, and *S. flexneri* at MIC values $31.25\text{--}62.5\ \mu\text{g mL}^{-1}$ by $[\text{VO}(\text{HL}^1)_2]$. *Staphylococcus epidermidis* and *S. flexneri* are the least effected organisms by $[\text{VO}(\text{acac})(\text{HL}^2)]$ at MIC $125\ \mu\text{g mL}^{-1}$, while *E. coli* and *S. aureus* are most effective

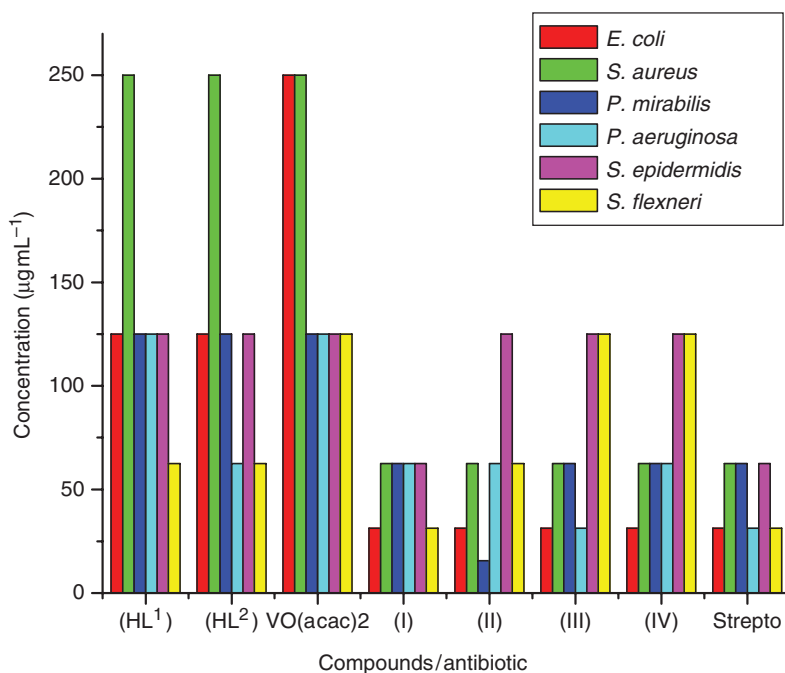


Figure 4. *In vitro* antibacterial spectrum of synthesized compounds.

at MIC $31.25 \mu\text{g mL}^{-1}$; *S. aureus* and *P. Mirabilis* are moderately affected at MIC $62.5 \mu\text{g mL}^{-1}$. [VO(HL²)] shows antibacterial activity similar to VO(acac)(HL²) toward all bacterial organisms except *P. aeruginosa*. The enhancement in the activity of the complexes in comparison to parent ligands and precursor [VO(acac)₂] may be due to the coordination of hydroxamate ligands to metal and an efficient diffusion of the metal complexes into bacterial cell [55–58].

All the complexes have similar antibacterial activity against *E. coli* and *S. aureus* while a different growth inhibition was displayed toward other bacteria. This observation may be ascribed to different liposolubility of complexes for different bacteria [59, 60]. The antibacterial activities of the complexes were compared with streptomycin. The complexes show promising antibacterial activity.

4. Conclusion

[VO(acac)₂] can be exploited as precursor toward phenoxyacetohydroxamate and cinnamohydroxamate (HL^{1,2}) to obtain stable [VO(acac)(HL^{1,2})] and [VO(HL^{1,2})₂] complexes by metathetic reaction. The hydroxamates are bidentate involving O,O coordination through hydroxylamine and carbonyl oxygen. The magnetic studies indicated oxidation state of vanadium and geometry around vanadium is suggested as distorted square pyramidal. The complexes have variable and promising antibacterial activity.

Acknowledgments

Meena Kumari is grateful to the University Grant Commission, New Delhi for providing financial support in the form of Major Research Project F. No.33-295 / 2007 (SR) dated 28.02.2008. The authors are grateful to Prof S. Tabassum, Aligarh Muslim University Aligarh for his assistance in providing electrochemical data. The authors thank the Department of Science & Technology (DST), Government of India, New Delhi for providing financial assistance for FT-IR and UV-Vis Spectrophotometer facility, Sophisticated Analytical Instrument Facility of CDRI, Lucknow, Punjab University Chandigarh for recording mass spectra, elemental analysis data and magnetic susceptibility measurements, respectively.

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