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Synthesis And Characterization Of Oxovanadium(IV) Complexes Having Diacetyl As Precursor Molecule

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Abstract: Oxovanadium(IV) complexes were synthesised with ligands derived from condensation of Diacetyl with amino acids such as glycine, alanine, serine, cysteine and valine, in which significant kinetic template effect of VO^{+2} cation is observed. The synthesised oxovanadium(IV) complexes were characterized by elemental analysis, electrical conductance, magnetic moment measurements and spectral (infrared, electronic and electron spin resonance) data. The spectral data of the complexes indicate that ligands act as tetradentate chelating agent and complexes are five coordinate. All the complexes showed significant antifungal activity against the fungi *Aspergillus flavus* and *Candida glaberata*.
Keywords: amino acids, condensation, template effect, chelating agents and tetradentate ligand.

Introduction

The versatile nature of vanadium is due to its possible oxidation states from -1 to +5 which is exist in both cationic and anionic forms [1-3]. Vanadium is a biometal in the first transition series which is important for animals, plants and microorganisms. The oxovanadium(IV) complexes act as catalyst in some biological processes[4] as well as industrial processes[5-7]. Oxovanadium(IV) complexes have been found to show insulin memetic activity [8] and potent anti-diabetic agents[9]**.** Vanadium compounds have well established potential in the oral treatment of both types of diabetes. Vanadium catalysed oxygen- transfer reactions have attracted considerable interest due to their relevance in biological processes. Due to their catalytic properties and biological activities, coordination chemistry of oxovanadium(IV) is an interesting area of current research. Diacetyl is versatile molecule having two reactive carbonyl groups capable of undergoing condensation reaction with a variety of diamines. In order to explore the pharmaceutical importance of vanadyl ion in biological systems, a series of oxovanadium(IV) complexes with ligands derived by reaction of diacetyl with amino acids such as glycine, alanine, serine, cysteine and valine are synthesised where VO^{+2} cation appears to act as kinetic template.

Experimental

Materials and Methods

All the chemicals and solvent, used were Analytical grade Reagent and used without further purification. Diacetyl used was Aldrich product. Oxovanadium(IV) complexes were prepared by standard method using hydrated salt of vanadyl sulphate.

Analytical Methods and Physical Measurements

The analysis of carbon, nitrogen and hydrogen were carried out at Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Bombay by using CHN analyser

(Model : FLASH EA 1112 series) with the help of "Dumas method". Infrared spectra of the complexes were recorded in KBr medium in the range 4000 – 667 cm^{-1} on a Perkin-Elmer Paragon 1000 Fourier-transform spectrometer and collected data were plotted in X-Y axis using Spectrum software. ESR spectra were recorded at liquid nitrogen temperature by using Electron Spin Resonance Spectrometer, VARIAN,USA, Model : E-112 ESR Spectrometer, Specification : X- band microwave frequency 9.5 GHz.

In-situ preparation of oxovanadium(IV) complexes with ligands derived by condensation of Diacetyl with glycine

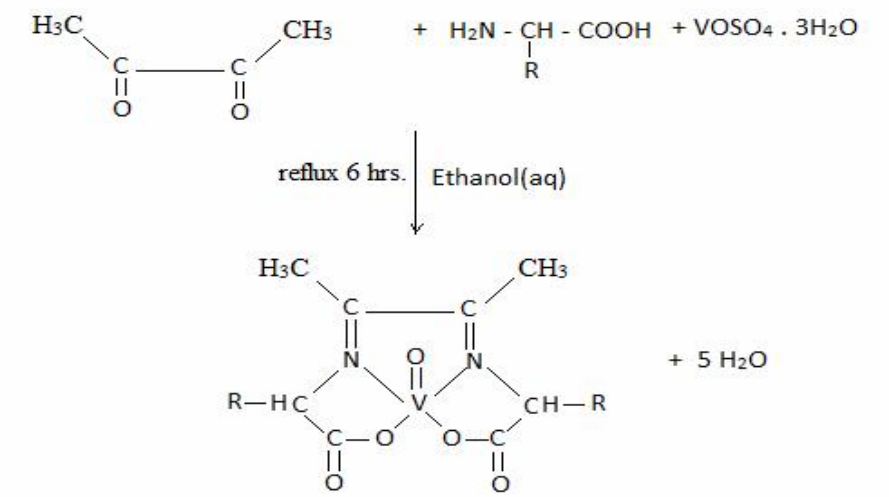
Vanadium sulphate (2 mmol) dissolved in ethanol (25 mL) was added to refluxing solution mixture(1 : 1) of diacetyl (2 mmol) and glycine (4 mmol) in ethanol (25 mL). The mixture was refluxed for 6 hours, when the colour of the solution turned green. The solvent was removed under vacuo at room temperature and the dark green colour product was isolated. The complex was thoroughly washed with ethanol.

Same method was adopted to obtain oxovanadium (IV) complexes with ligand derived by condensation of diacetyl with alanine, serine, cysteine and valine.

Results and Discussions

The oxovanadium (IV) complexes were sythesized using in-situ method by refluxing the reaction mixture of diacetyl and glycine or alanine or serine or cysteine or valine and vanadylsulphate in 1:2:1 molar ratio in aqueous ethanol and the reaction proceeds as scheme I shown in figure.

Scheme I : In-situ preparation of oxovanadium(IV) complexes E_1- E_5



Complex	Substituent GroupS(-R)
E_1	- H
E_2	- CH_3
E_3	-CH_2OH
E_4	-CH_2SH
E_5	- $CH(CH_3)_2$

Analytical and spectral data of the vanadyl complexes

Complex $\mathbf{E_1}$: Yield: 64%; m.p. 276^{0}C ; Anal. Calcd for $VO_5C_8N_2H_{10}$ (FW 264.94): C, 36.23 ; H, 3.77 ; N, 10.57; O, 30.19; V, 19.23 %. Found : C, 36.22 ; H, 3.78 ; N, 10.55 %. IR(KBr, cm^{-1}): 1620(C=N), 305(V-N), 983(V=O), 560(V-O); Magnetic moment, μ_{eff} = 1.71.

Complex **(E_2)** : Yield : 62% ; m.p. 280^{0}C; Anal. Calcd for $VO_5C_{10}N_2H_{14}$ (FW 292.94) ; C, 40.96 ; H, 4.78 ; N, 9.56; O, 27.31; V, 17.39%. Found : C, 41.00 ; H, 4.77 ; N, 9.54%. IR (KBr, cm^{-1}): 1617(C=N), 306(V-N), 305(V-N), 970(V=O), 580(V-O); Magnetic moment, μ_{eff} = 1.76.

Complex **(E_3)** : Yield : 60%; m.p. 278^{0}C; Anal. Calcd for $VO_7C_{10}N_2H_{14}$ (FW 324.94) ; C, 36.93 ; H, 4.31 ; N, 8.61; O, 34.47; V, 15.68%. Found : C, 36.95 ; H, 4.30 ; N, 8.62 %. IR (KBr, cm^{-1}): 1616(C=N), 304(V-N), 975(V=O), 591(V-O). Magnetic moment, μ_{eff} = 1.72.

Complex **(E_4)** : Yield : 64%; m.p.282^{0}C; Anal. Calcd for $VO_5C_{10}N_2H_{14}S_2$(FW 356.94) ; C, 33.61 ; H, 3.92 ; N, 7.84; O, 22.41; S, 17.93%; V, 14.27%. Found : C, 33.62 ; H, 3.94 ; N, 7.86 %. IR(KBr, cm^{-1}): 1616(C=N), 303(V-N), 981(V=O), 589(V-O) ; Magnetic moment, μ_{eff} = 1.70.

Complex **(E_5)** : Yield : 62%; m.p.284^{0}C; Anal. Calcd for $VO_5C_{14}N_2H_{22}$ (FW 348.94) ; C, 48.14 ; H, 6.30 ; N, 8.02; O, 22.92 ; V, 14.59%. Found : C, 48.12 ; H, 6.32; N, 8.04%. IR (KBr, cm^{-1}): 1618(C=N), 307(V-N), 983(V=O), 570(V-O); Magnetic moment, μ_{eff} = 1.72 .

The elemental analysis of complexes show 1 : 1 metal to ligand stoichiometry.

Antifungal Screening Test

The antifungal tests for the complexes were carried out by using well diffusion method. The antifungal results of the synthesised complexes are recorded in Table I. All the complexes showed significant antifungal activity against the fungi *Aspergillus flavus* and *Candida glaberata*.

Infrared Spectra

The ν(C = N) absorption bands of oxovanadium (IV) complexes exhibit at about 1620 – 1616 cm^{-1} which is normally observed at 1660 cm^{-1} in free ligands[10,11]. The lowering of this band in the oxovanadium(IV) complexes indicates coordination N-atoms of azomethine groups to the VO^{2+} ion[10-12]. A band at around 305 cm^{-1},further support the ν(V- N) vibration[13]. The complexation of vanadium[14] with oxygen donor ligand is also confirmed by the appearance of ν(V-O) bands in the range 591 – 560 cm^{-1}. The band at 1700 cm^{-1} indicates the presence of ν(C=N) band and the absence of ν(C=O) supporting the evidences for coordination of – NH_2 group of amino acids with the keto groups of diacetyl.

The ν_{asym} (COO^-) and ν_{sym} (COO^-) starching vibration of – COOH group in free amino acids are observed at ca. 1530 cm^{-1} and 1415 cm^{-1} respectively, giving Δ(COO^-) value of the order of 114 cm^{-1}. The respective ν_{asym} (COO^-) and ν_{sym}(COO^-) in case of oxovanadium(IV) complexes occurs at ca. 1560 cm^{-1} and 1425cm^{-1}, giving Δ(COO^-) value at 135 cm^{-1}, which is higher than the free amino acids. Such increased in the Δ(COO^-) values support the monodentate coordination of the amino acids to carboxyl group[15]. Thus, these observations indicate that the monovalent anionic species of the amino acids are coordinated vanadium centre. Oxovanadium(IV) show an intense band at around 970 – 985 cm^{-1}, which assigned to the ν(V= O) vibration[16].

TABLE I : Antifungal Activity of oxovanadium(IV) complexes (E_1 – E_5)

Complex	Zone of inhibition in %		
	Aspergillus flavus	Candida glaberata	Conc./ (μgmL^{-1}
$\mathbf{E_1}$	49	59	100
$\mathbf{E_2}$	62	58	100
$\mathbf{E_3}$	56	47	100
$\mathbf{E_4}$	70	71	100
$\mathbf{E_5}$	48	53	100
Standard[a]	100	-	100
Standard[b]	-	100	100

Amphoterici B[a], Miconazole[b]

Magnetic moment

The magnetic moment values were in the range 1.70 – 1.76 B.M. for the oxovandium (IV) complexes which are in good agreement with the reported values of oxovanadium(IV) complexes with unpaired electron at vanadium centre..

Electronic spectra

The five coordinated oxovanadium(IV) complexes with tetradentate ligands show electronic spectral bands in the region 11450 – 11800 cm^{-1}, 15100 – 15850 cm^{-1} and 21200 – 2250 cm^{-1}. These bands correspond to the electronic transitions $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$ as reported in the literature[17]. Due to electronic transition of azomethine linkage[18], one more band is observed in the region 35200 – 35700 cm^{-1}.

ESR spectra

The X- band electron spin resonance spectra at room temperature and at liquid nitrogen temperature in DMSO for oxovanadium(IV) complexes show eight lines which are due to hyperfine splitting arising from the interaction of the unpaired electron with a ^{51}V nucleus having I = 7/2 being the nuclear spin number[19,20] . Due to the rapid motion of molecules in solution, the anisotropy is not observed and only g- average values were worked out at room temperature. Anisotropy is clearly visible at liquid nitrogen temperature spectra and eight bands due to $g_{\parallel}$ and $g_{\perp}$ are observed. The $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, $A_{\perp}$ values are measured from the spectra and given in table II which are in good agreement for oxovanadium(IV) complexes indicating single electron in d-orbital of oxocation, VO^{2+}.

Conclusion

The spectral data show that the Schiff base condensation of diacetyl, a versatile molecule with amino acids is achieved by virtue of kinetic template effect of oxovanadium(IV) cation in aqueous ethanol medium. The tetradentate ligands are bonded with vanadyl ion through the azomethine nitrogen atoms and o-donor atoms of carboxylate group of the amino acids. The analytical data show the presence of one metal ion per ligand molecule which suggest a mononuclear structure for the complexes. All the oxovanadium (IV) complexes are square pyramidal in geometry and show potential antifungal activity.

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TABLE II : g average value at room temperature and g and A values at frozen temperature of the oxovanadium(IV) complexes ($E_1 – E_5$)

Complex	liquid nitrogen temperature					Room temperature	
	$g_{\parallel}$	$g_{\perp}$	$\lvert g \rvert$	$A_{\parallel}$	$A_{\perp}$	$\lvert A \rvert$	$\lvert g \rvert$
E_1	1.931	1.971	1.957	190.70	66.42	107.84	1.974
E_2	1.933	1.973	1.959	190.71	66.39	107.83	1.974
E_3	1.932	1.974	1.960	189.72	66.40	107.50	1.976
E_4	1.930	1.970	1.956	190.56	65.98	107.55	1.972
E_5	1.934	1.972	1.959	189.71	66.24	107.39	1.975

The above analytical and spectral data support the tentative structures of oxovanadium (IV) complexes as shown in the scheme I.

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