

Synthesis and characterization of tertadentate schiff base oxovanadium (IV) complexes

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Abstract : Oxovanadium(IV) complexes of tetradentate Schiff bases were synthesised in which significant kinetic template effect of vanadyl ion is observed and schiff bases were synthesised by condensation of dibenzoylmethane with amino acids such as glycine, alanine, serine, cysteine and valine. The oxovanadium(IV) complexes were characterized by elemental analysis, magnetic moment values, IR, ESR and UV-Visible electronic spectral data and antifungal activities of vanadyl complexes were screened against the fungi *Aspergillus flavus* and *Candida glaberata*.

Keywords : Oxovanadium(IV), dibenzoylmethane, Aminoacid, Schiff bases.

1. INTRODUCTION

In recent years, vanadium chemistry has attracted attention due to its interesting structural features and biological relevance. Many vanadyl complexes of oxidation states +5 and +4 have been synthesised which show catalytic activities(Gambarotta,2003) and medicinal properties like insulin mimetic, anticancer, antitumor, antifungal and antibacterial activities observed by Crans et al.(2003) and Buteler and Walker(1993).The VO²⁺ complexes are known to influence many enzymatic systems such as phosphatases, ATPases, peroxidases, ribonucleases, protein kinases and oxidoreductases. Hence, the coordination chemistry of vanadium is an interesting area of current research and according to Bracken et al(1985) and Cortizo et al.(2000), it enters into the organism by inhalation , the gastrointestinal tract and the skin which is specifically stored in certain organs mainly in the liver, kidney and bones . In order to explore the pharmaceutical importance of vanadyl ion in biological systems, a series of oxovanadium(IV) complexes with tetradentate Schiff base ligands derived by reaction of dibenzoylmethane with amino acids such as glycine, alanine, serine, cysteine and valine were synthesised where VO⁺² cation appears to act as kinetic template.

2. EXPERIMENTAL

2.1. Materials

The materials and reagents used in the synthesis were analytical grade reagent and were used without further purification. The used chemicals like dibenzoylmethane, amino acids such as glycine, alanine, serine, cysteine and valine were obtained from Sisco Research Laboratory Pvt. Ltd. The vanadyl sulphate was Aldrich product.

2.2. Measurements

The C, H, N elemental analysis of oxovanadium(IV) complexes was done at Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Bombay, India by using CHN analyser (Model : FLASH EA 1112 series). Sulphur was estimated as Barium Sulphate gravimetrically by standard method(Vogel,

1972). Vanadium was estimated in digested sample of vanadium(IV) complex using volumetric analysis based on redox reaction involving iodometry (Jeffery et al., 1989). Infrared spectra of the vanadyl complexes were recorded using KBr pellet in the range $4000 - 667 \text{ cm}^{-1}$ on a Perkin-Elmer Paragon 1000 Fourier-transform spectrometer. ESR spectra were recorded at liquid nitrogen temperature at SAIF, Indian Institute of Technology, Bombay by using Electron Spin Resonance Spectrometer (Make: VARIAN, USA, Model : E-112 ESR Spectrometer, Specification : X- band microwave frequency 9.5 GHz) and at room temperature at Central Instrument Facility, Indian Institute of Technology, Guwahati, India.

2.3. In- situ synthesis of Schiff base oxovanadium(IV) complexes

In the ethanolic solution (15 mL) of dibenzoylmethane (2 mmol) and glycine (4 mmol), vanadium(IV) sulphate (2 mmol) solution in ethanol was added. The mixture was refluxed for 6 hours, when the colour of the solution turned green and precipitated compound was filtered, washed several times with ethanol and dried over anhydrous CaCl_2 . Same procedure was adopted to obtain oxovanadium (IV) complexes with ligands derived by condensation of dibenzoylmethane with alanine, serine, cysteine and valine.

3. RESULTS AND DISCUSSION

The tetradentate Schiff base oxovanadium(IV) complexes were formed using the *in-situ* method involving reflux of a reaction mixture having molar ratio of dibenzoylmethane, amino acids and vanadyl sulphate as 1 : 2 : 1 in aqueous ethanol medium. The reaction appears to proceed according to the Reaction Scheme shown in the figure 1. The elemental analysis of the vanadyl complexes as in Table 1 show 1:1 metal to ligand stoichiometry.

Fig 1: In-situ synthesis of oxovanadium(IV) complexes with Schiff base derived by condensation of dibenzoylmethane with amino acids

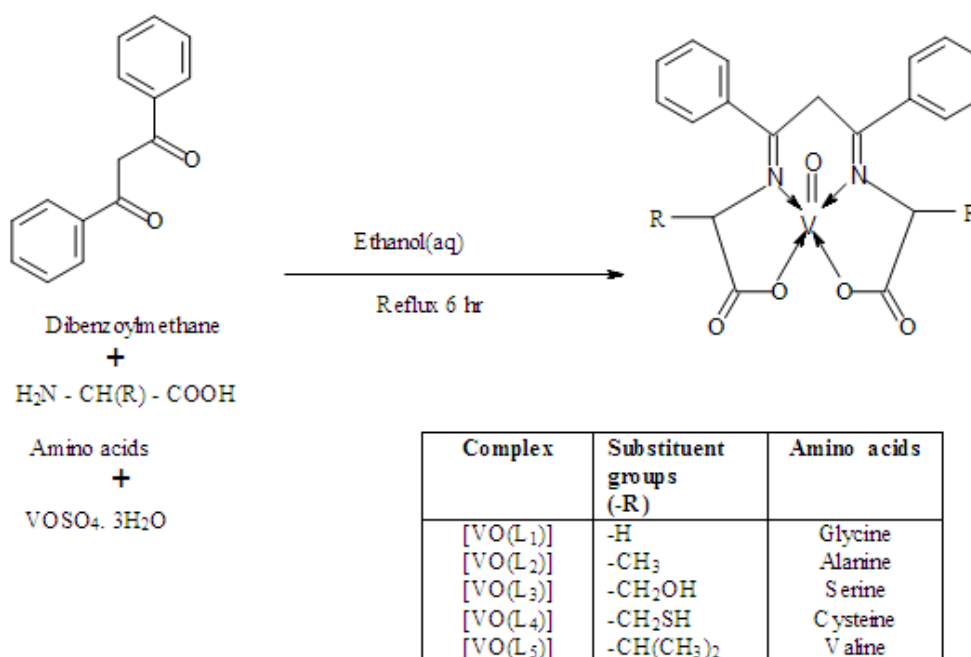


Table 1 : Elemental analysis and melting point of Schiff base vanadyl complexes

Complex	Empirical formula	m.p (°C)	Calc.(found)				
			C %	H %	N %	S %	V %
[VO(L ₁)]	VC ₁₉ H ₁₆ O ₅ N ₂	279	56.58	3.97	6.94	-	12.64
			56.60	4.00	6.91	-	12.66
[VO(L ₂)]	VC ₂₁ H ₂₀ N ₂ O ₅	288	58.48	4.64	6.50	-	11.82
			58.50	4.66	6.49	-	11.79
[VO(L ₃)]	VC ₂₁ H ₂₀ N ₂ O ₇	276	54.43	4.32	6.05	-	11.00
			54.45	4.30	6.00	-	10.98
[VO(L ₄)]	VC ₂₁ H ₂₀ N ₂ O ₅ S ₂	281	50.91	4.04	5.65	12.93	10.29
			50.93	4.07	5.67	12.96	10.30
[VO(L ₅)]	VC ₂₅ H ₂₈ N ₂ O ₅	269	61.61	5.75	5.75	-	10.46
			61.59	5.78	5.70	-	10.48

Where

L₁ = Ligand obtained by the condensation of Dibenzoylmethane and Glycine (molar ratio 1:2)

L₂ = Ligand obtained by the condensation of Dibenzoylmethane and Alanine (molar ratio 1:2)

L₃ = Ligand obtained by the condensation of Dibenzoylmethane and Serine (molar ratio 1:2)

L₄ = Ligand obtained by the condensation of Dibenzoylmethane and Cystine (molar ratio 1:2)

L₅ = Ligand obtained by the condensation of Dibenzoylmethane and Valine (molar ratio 1:2)

3.1. Infrared spectra of the complexes

The infra-red spectral bands of the complexes at about 1595 – 1622 cm⁻¹, which are shifted towards lower value indicate that ν(C=N) group has coordinated to vanadium centre which is normally found at 1660 cm⁻¹ to 1670 cm⁻¹ in free ligands (Rana et al.,1982, Chandra and Sharma,1983, Malik et al. 1983). The bands in the range 680 – 690 cm⁻¹ is assigned to ν(V – O) stretching vibration, indicating the coordination of β- diketone ligand to oxovanadium(IV) ion . The IR band found at about 306 to 310 cm⁻¹ is assigned to ν(V-N) stretching(Ferraro, 1971). An intense bands in the oxovanadium(IV) complexes in the region 975 - 985 cm⁻¹ are assigned to the ν (V=O) vibration(Sakata et al.,1989).

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 115 cm⁻¹. The respective ν_{asym} (COO⁻) and ν_{sym}(COO⁻) in case of oxovanadium(IV) complexes occurs at ca. 1555cm⁻¹ and 1420cm⁻¹, giving Δ(COO⁻) value at 135 cm⁻¹, which is higher than the free amino acids. Such an enhancement in the Δ(COO⁻) values support the monodentate coordination(Chow and Mc Auliffa, 1975) of the amino acids via carboxyl groups to the vanadium centre.

3.2. Electronic spectra and magnetic moments of the complexes

The magnetic moment values, μ_{eff} at room temperature for Schiff base oxovanadium(IV) complexes are found in the range 1.65 – 1.74 B.M. These values

are in agreement with the reported values of oxovanadium(IV) complexes with one unpaired electron (Michael et al., 1984). The electronic spectra of vanadyl complexes in the region 11425 – 11780, 15112 – 15856 and 21230 – 22500 cm^{-1} comparable to other five coordinated Schiff base oxovanadium(IV) complexes with tetradentate ligands. These bands are due to ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions (Maurya et al., 2006). The band observed in the region 35190 – 35680 cm^{-1} is assigned to electronic transition of azomethine linkage (Mishra and Panday, 2005). These transitions as well as the measured values of magnetic moments suggest square pyramidal geometry of the complexes.

3.3. EPR spectra

ESR spectra of the Schiff base oxovanadium(IV) complexes recorded in DMSO show eight lines at room temperature and at liquid nitrogen temperature which are due to hyperfine splitting arising from the interaction of the unpaired electron with a ${}^{51}\text{V}$ nucleus having the nuclear spin number $I = 7/2$ (Nejati and Rezvani, 2003). Room temperature esr spectra result g- average values but lower temperature esr pattern show eight bands due to g_{\parallel} and g_{\perp} and anisotropy is clearly visible at liquid nitrogen temperature in frozen solution. The measured value of g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp} are in good agreement for a square pyramidal structure (Sasmal et al., 2010) and are reported in Table 2.

Table 2 : g average value at room temperature and g and A values at frozen temperature of the oxovanadium(IV) complexes

Complex	Room temp.	Liquid nitrogen temperature					
	g	g_{\parallel}	g_{\perp}	g	A_{\parallel}	A_{\perp}	A
[VO(L ¹)]	1.975	1.933	1.972	1.959	189.73	66.40	107.51
[VO(L ²)]	1.972	1.935	1.973	1.960	190.75	66.40	107.85
[VO(L ³)]	1.973	1.931	1.975	1.960	189.72	66.43	107.51
[VO(L ⁴)]	1.974	1.932	1.970	1.961	190.70	66.00	107.57
[VO(L ⁵)]	1.976	1.934	1.975	1.961	189.76	65.97	107.23

3.4. Biological Study

The prepared Schiff base oxovanadium(IV) complexes were screened against the *Aspergillus flavus* and *Candida glabrata* by the well diffusion method (Muhammad et al., 2008) in which the *Amphotericin B* and *Miconazole* were used as standard drugs and results are reported in Table 3.

Table 3 : Antifungal Activity of oxovanadium(IV) complexes

Compound	Zone of inhibition in %		Conc. ($\mu\text{g/ml}$)
	<i>Aspergillus flavus</i>	<i>Candida glabrata</i>	
[VO(L ¹)]	50	60	100
[VO(L ²)]	59	62	100
[VO(L ³)]	51	47	100
[VO(L ⁴)]	72	70	100
[VO(L ⁵)]	49	56	100
Standard ^a	100	-	100
Standard ^b	-	100	100

Amphotericin B^a, Miconazole^b

CONCLUSIONS

The spectral data show that tetradentate Schiff bases are bonded with vanadyl ion in complexes through the azomethine nitrogen atoms and o-donor atoms of carboxylate group of the amino acids. The analytical data suggest the mononuclear structure of the complexes having square pyramidal geometry and one metal ion per ligand molecule. All the oxovanadium (IV) complexes show significant antifungal activity.

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