Int. J. Chem. Sci.: 10(4), 2012, 1969-1976
ISSN 0972-768X
www.sadgurupublications.com

SYNTHESIS, CHARACTERIZATION AND ANTIFUNGAL STUDIES OF OXOVANADIUM (IV) COMPLEXES WITH TETRADENTATE SCHIFF BASE LIGANDS

PROBIN BORA* and HARDEO S. YADAV

Department of Chemistry, North Eastern Regional Institute of Science & Technology,
NIRJULI – 791109 (Ar.P.) INDIA

ABSTRACT

A series of oxovanadium (IV) complexes were synthesised with tetradentate ligands derived by condensation of thenoyltrifluoroacetone with amino acids such as glycine, alanine, serine, cysteine and valine. Antifungal studies of the complexes were carried out against the fungi *Aspergillus flavus* and *Candida glaberata* and it was found that all the compounds are moderate antifungal agent. All the complexes were characterized by elemental analysis, magnetic moment measurements, infer-red, UV and esr spectral data.

Key words: Thenoyltrifluoroacetone, Amino acids, Antifungal, ESR spectroscopy.

INTRODUCTION

In recent years, vanadium chemistry has attracted attention due to its interesting structural features and biological relevance[1-4]. It is found in both anionic and cationic forms having oxidation states from -1 to +5 in its compounds[5]. Vanadium compounds have been found to bring normal level of high blood glucose in both type-1 and type-2 diabetic animals[6-7]. The role of vanadium as a biometal is well established and encompasses stimulating and regulating as well as inhibitory function[8]. The VO^{+2} ions are reported to be adsorbed by plant roots (Allium Sativum L.) and accumulated as soluble low molecular weight complex of o-diphenolic compounds[9]. Oxovanadium (IV) Schiff base complexes derived from C-substituted diamines and pyridexal-5-phosphate act as antitumor agents[10]. Vanadium compounds were used as catalysts in the various organic synthesis and an ecofriendly solid catalyst has been synthesised by anchoring vanadium (IV) into organically MCM-41[11,12]. It was established by the different research groups that Schiff base oxovanadium (IV) complexes have potential antibacterial and antifungal activity[13-16]. In view of the importance of vanadium

*Author for correspondence; E-mail: boraprobin@yahoo.in, Ph.: + 919856382821

compounds, a series of oxovanadium (IV) complexes with ligands derived by reaction of thenoyltrifluoroacetone 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

The oxovanadium (IV) complexes were synthesised by standard method using hydrated salt of vanadyl sulphate. All the chemicals and solvents used were analytical grade reagents and thenoyltrifluoroacetone was Aldrich product. ESR spectra were recorded at room temperature and at liquid nitrogen temperature by ESR Spectrometer (X-band microwave frequency 9.5 GHz) at IIT Bombay. The micro analysis of carbon, hydrogen and nitrogen were carried out at SAIF, Indian Institute of Technology, Bombay. 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. Sulphur was estimated as barium sulphate gravimetrically by standard method. Vanadium was estimated in digested sample of vanadium (IV) complex using volumetric analysis based on redox reaction involving iodometry.

Preparation of the oxovanadium (IV) complexes

Vanadium sulphate (2 mmol) dissolved in ethanol (20 mL) was added into refluxing solution mixture of thenoyltrifluoroacetone (2 mmol) and glycine (4 mmol) in ethanol (20 mL). The mixture was refluxed for about 5 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. Other oxovanadium (IV) complexes with ligand derived by condensation of thenoyltrifluoroacetone with alanine, serine, cysteine and valine were prepared by the same method. The physical and analytical data of the complexes are reported in Table 1.

Table 1: Physical and analytical data of the prepared complexes

Empirical formula	M.P. (^{0}C)	Calc. (found)%					Yield (%)
		C	H	N	V	S	
I : $C_{12}H_9N_2O_5F_3SV$	280	35.91 35.82	2.24 2.27	6.98 7.00	12.71 12.50	7.98 8.00	64
II : $C_{14}H_{13}N_2O_5F_3SV$	286	39.17 39.21	3.03 3.00	6.53 6.50	11.87 11.94	7.46 7.40	70

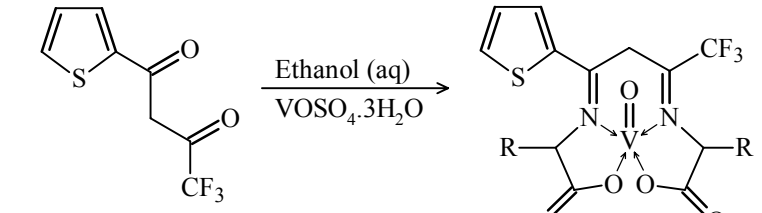
Cont…

Empirical formula	M.P. (^{0}C)	Calc. (found)%					Yield (%)
		C	H	N	V	S	
III: $C_{14}H_{13}N_2O_7F_3SV$	278	36.44 36.38	2.82 2.80	6.07 6.02	11.05 11.00	6.94 6.97	65
IV: $C_{14}H_{13}N_2O_5F_3S_3V$	267	34.11 34.15	2.64 2.56	5.68 5.70	10.33 10.30	19.47 19.50	63
V : $C_{18}H_{21}N_2O_5F_3SV$	270	44.54 44.60	4.33 4.21	5.77 5.87	10.50 10.54	6.60 6.56	56

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

RESULTS AND DISCUSSION

The oxovanadium (IV) complexes were synthesized using in-situ method by refluxing the reaction mixture of oxovanadium (IV) sulphate, thenoyltrifluoroacetone (2 mmol) and glycine or alanine or serine or cysteine or valine (4 mmol) in the molar ratio of 1 : 1 : 2 in aqueous ethanol medium and the reaction proceeds as Scheme 1 shown as below.



Scheme 1: Preparation of the oxovanadium (IV) complex, I, II, III, IV and V

Complex	Substituent group	Amino acids
I	-H	Glycine
II	-CH_3	Alanine
III	-CH_2OH	Serine
IV	-CH_2SH	Cysteine
V	-CH $(CH_3)_3$	Valine

Biological study

All the complexes were screened against the fungi *Aspergillus flavus* and *Candida glaberata* by using standard method. It was observed that complexes have significant antifungal activity and results are recorded in Table 2. It is also observed that the complex, **IV** has more antifungal activity than other complexes **I**, **II**, **III** and **V** which may be due to the sulphur atom of cysteine.

Table 2: Antifungal results of the complexes

Complex	Percentage inhibition		Conc. (μgmL^{-1})
	Aspergillus flavus	*Candida glaberata*	
I	54	50	100
II	65	65	100
III	62	59	100
IV	72	76	100
V	63	65	100
Standard[a]	100	-	100
Standard[b]	-	100	100

Amphotericin [a] , Miconazole [b]

Infrared spectra of the complexes

Infrared spectra of the oxovanadium (IV) complexes were recorded in KBr and observed characteristics IR spectral bands are reported.

Table 3: IR spectral bands and magnetic moment of oxovanadium (IV) complexes

Complex	IR spectral bands (KBr, cm^{-1})				Magnetic moment (B.M.)
	>C=N	V-N	V-O	V=O	
I	1620	305	418	980	1.72
II	1618	304	420	983	1.71
III	1616	305	420	981	1.70
IV	1623	306	421	981	1.72
V	1625	306	419	989	1.70

The complexes show ν (>C = N) absorption at about 1625-1616 cm^{-1}, which is normally observed at 1660 cm^{-1} in free ligands[17,18]. The lowering of this band in the oxovanadium (IV) complexes support coordination N-atoms of azomethine groups to the vanadyl ion[19,20]. The IR absorption bands at about 304-307 cm^{-1} and 418-420 cm^{-1} are assigned to ν (V-N) and ν (V-O) vibrations, respectively[21]. The presence of ν (>C=N) band and the absence of ν (>C=O) band at about 1700 cm^{-1} support the coordination of – NH_2 group of amino acids with the keto group of theonyltrifluoroacetone. Oxovanadium (IV) complexes show an intense band at around 980-989 cm^{-1}, which are assigned to the ν (V= O) vibration[22]. The respective streching vibrations ν_{asym} (COO^-) and ν_{sym} (COO^-) in case of oxovanadium (IV) complexes occurs at ca. 1556 cm^{-1} and 1410 cm^{-1}, giving Δ (COO^-) value at 136 cm^{-1}, which is higher than the free amino acids. Such increase in the Δ (COO^-) values support the monodentate coordination of the amino acids through carboxyl group. Thus, these observations indicate that the monovalent anionic carboxylate ion of the amino acids are coordinated to the vanadium centre.

EPSR spectra

ESR spectra of all the oxovanadium (IV) complexes were recorded in dimethylsulphoxide at room temperature and at liquid nitrogen temperature. The complexes show eight ESR lines which are due to the hyperfine splitting arising from the interaction of the d^1 electron with a ^{51}V nucleus (nuclear spin, I = 7/2). It confirms that complexes are mononuclear. At liquid nitrogen temperature, anisotropy is clearly visible in the spectra and eight bands each due to $g_{\|}$ and $g_{\perp}$ are observed separately, which are in good agreement for a square pyramidal structure. The $g_{\|}$, $g_{\perp}$, $A_{\|}$, and $A_{\perp}$ values are measured from the spectra, which are in good agreement for a square pyramidal structure[23,24]. The ESR parameters were calculated using the 298 K and 77 K spectra, which are shown in Table 4.

Table 4: At room temperature g-values and at liquid nitrogen temperature g and A values of the oxovanadium (IV) complexes

Complex	Room temp.	Liquid nitrogen temperature					
	$\|g\|$	$g_{\|}$	$g_{\perp}$	$\|g\|$	$A_{\|}$	$A_{\perp}$	$\|A\|$
I	1.969	1.920	1.979	1.959	190.90	66.98	108.28
II	1.972	1.921	1.980	1.960	190.78	65.80	107.46
III	1.987	1.922	1.978	1.959	190.97	65.79	107.52
IV	1.978	1.920	1.972	1.954	190.62	65.79	107.40
V	1.977	1.921	1.979	1.959	190.92	65.86	107.55

On the basis of the above studies, tentative structures are proposed for these oxovanadium (IV) complexes in the reaction Scheme 1.

Electronic spectra and magnetic moments of the complexes

The observed values of magnetic moment, μ_{eff} at room temperature (298 K) for Schiff base oxovanadium (IV) complexes were found in the range 1.70-1.72 B. M. and are reported in Table 3. These values are in agreement with the reported values of oxovanadium (IV) complexes with one unpaired electron[25,26].

The electronic spectra of vanadyl complexes in the region 11430-11790 cm^{-1} for $^2B_2 \rightarrow {}^2E$ transition, 15123-15873 cm^{-1} for $^2B_2 \rightarrow {}^2B_1$ transition and 21239-22508 cm^{-1} for $^2B_2 \rightarrow {}^2A_1$ transition are comparable to the other five coordinated Schiff base oxovanadium (IV) complexes with tetradentate ligands. The band observed in the region 35200-35700 cm^{-1} is assigned to electronic transition of azomethine linkage[27-29]. These transitions as well as the measured values of magnetic moments suggest square pyramidal geometry of the complexes.

CONCLUSION

The spectral data show that the tetradentate ligands derived by condensation of thenoyltrifluoroacetone with amino acids 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.

ACKNOWLEDGEMENT

The authors are thankful to the Head, SAIF, IIT Bombay, India for providing ESR facilities to record spectra and microanalysis of carbon, hydrogen and nitrogen. The fungal species provided by research group of Dr. R. S. S. Yadav, Department of Chemistry, DDU Gorakhpur University is highly acknowledged.

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Revised : 16.08.2012 *Accepted : 19.08.2012*