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New insights into the chemistry of oxovanadium (IV) complexes with tetradentate macrocyclic ligands

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ABSTRACT

Macrocyclic ligands derived from condensation of 1,2-diaminopropane or 1,4-diaminobutane with furil and their reaction with β -diketones (viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane) in the presence of vanadyl ion is reported. The oxovanadium(IV) complexes having general formula $[\text{VO}(\text{mac})]\text{SO}_4$ have been designed and synthesized using vanadyl ion as template without which these complexes might not be formed. The prepared macrocyclic complexes were characterized by elemental analyses, molar conductance, magnetic moments, infrared, electronic and electron spin resonance data. From the spectroscopic studies, five coordinated with square-pyramidal geometry for the VO(IV) complexes have been proposed wherein derived ligands act as tetradentate chelating agents.

Keywords: *oxovanadium (IV), furil, Schiff-base, macrocyclic complexes.*

1. INTRODUCTION

The coordination chemistry of vanadium with Schiff base ligands has attracted continuous attention for the chemists due to their ease of synthesis, stability under a variety of oxidative and reductive conditions and wide biological relevance of the metal. The chemistry of vanadium has generated great interest since the discovery of vanadium in organisms such as certain ascidians and Amanita mushrooms and being a constituent of the cofactors in vanadate-dependent haloperoxidases and vanadium nitrogenase [1-4]. Synthesis of homo- and heterometallic complexes having Schiff base ligands which can accommodate different metal centers involving various coordination modes with variety of stereochemistry are studied [5]. This feature is applied for modeling active sites in biological systems [6]. The literature contains several reports about oxovanadium(IV) complexes which show modulating activities of various enzymes [7]. Vanadium is found naturally in soil and water as a trace metal. Vanadium compounds with oxidation state IV and V exist in the environment and in biological systems. These complexes also have biological activities such as antibacterial, antifungal, antiviral and anticancer [8-10]. The biochemical aspects of vanadium complexes have further promoted the coordination chemistry of vanadium [11]. Vanadium is not only an important trace element for organisms, but also the necessary element for human body [12]. Heyliger et al. first reported the insulin mimetic activity of oral vanadate *in vivo* in 1985 [13]. Since then, extensive studies have been carried out to explore vanadium chemistry, including the synthesis of novel complexes and their antidiabetic activities both *in vitro* and *in vivo* [14-16]. Many clinical trials of vanadium compounds have also been reported [17-19], in which vanadium salts such as VOSO_4 and

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NaVO_3 were administered to diabetic rats. The oral administration of vanadate has been proved to reduce hyperglycemia in diabetic rats. However, in most cases, the template effect of metal ions of the first transition series has been studied, but chemistry of vanadium complexes with macrocyclic ligands incorporating four nitrogen donor atoms has received less attention [20,21]. Considering these facts, a new series of oxovanadium(IV) complexes have been prepared by condensation of furil with 1,2-diaminopropane or 1,4-diaminobutane in the presence of VO^{2+} cation in 1:2:1 molar ratio where in oxovanadium(IV) act as template. The reactions of oxovanadium(IV) complexes with β -diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane have been carried out which result macrocyclic complexes.

The complexes have been isolated in solid state and their tentative structures have been assigned on the basis of their elemental analyses, molar conductance, magnetic susceptibility measurements and spectral data.

2. EXPERIMENTAL SECTION

2.1 Materials and Methods: All the chemicals and the solvents used were of the reagent grade. Furil and oxovanadium(IV) sulfate were Aldrich products. The β -diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane were Sisco Research Laboratory products and 1,2-diaminopropane, 1,4-diaminobutane used were Aldrich product.

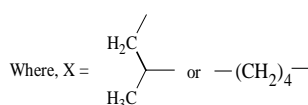
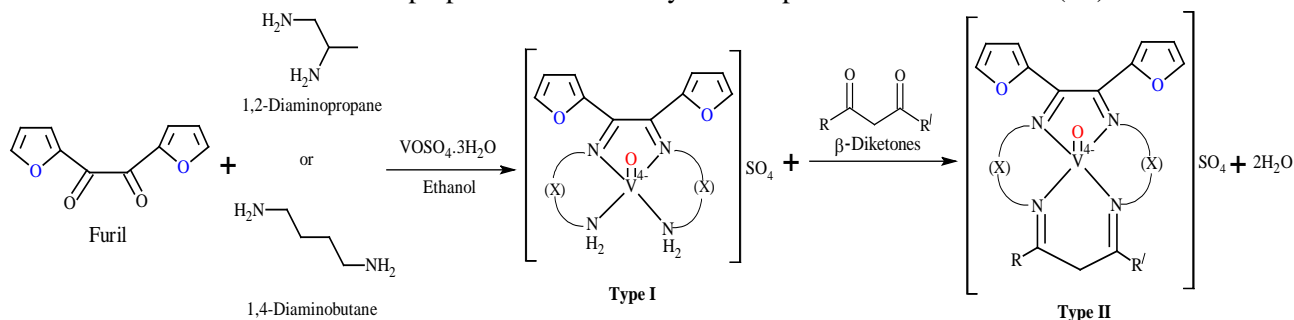
2.2 Analytical and Physical Measurements: Vanadium was estimated gravimetrically as its vanadate after decomposing the complex with concentrated nitric acid [22]. Sulfur was estimated as barium sulfate in the laboratory [23]. The standard technique of melting point (uncorrected) determination using sulfuric acid bath was employed. Toshniwal conductivity bridge, model no. CLO102A was used for conductance measurements at room temperature. The magnetic susceptibility of the complexes in powder form was carried out at room temperature using Gouy's balance. Mercury tetrathiocyanatocobaltate(II), $\text{Hg}[\text{Co}(\text{CNS})_4]$, ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. unit at 20°C) was used as calibrant. The electronic spectra of the complexes were recorded on Beckmann DU-2 spectrophotometer in the ranges 2000-185 nm using methanol as solvent. The room temperature and liquid nitrogen temperature e.s.r. spectra were recorded at RSIC, IIT, Chennai, India. The infrared spectra of the complexes in the range $4000\text{-}200\text{ cm}^{-1}$ were measured on Perkin-Elmer 621 using CsI pellets.

2.3 In-situ preparation of oxovanadium(IV) complexes with ligands derived by condensation of 1,2-diaminopropane or 1,4-diaminobutane with furil: Vanadyl sulfate (2 mmol) dissolved in methanol (25 mL) was added to a refluxing solution of furil (2 mmol) and 1,2-diaminopropane or 1,4-diaminobutane (4 mmol) in ethanol (25 mL). The mixture was refluxed for 6 h, when the color of the solution turned green. The solvent was removed under vacuum at room temperature and the dark green color product was isolated. The complexes were thoroughly washed with methanol/ethanol mixture. The yield was 70%.

2.4 In-situ preparation of macrocyclic complexes of oxovanadium(IV): Vanadyl sulfate (2 mmol) dissolved in methanol (25 mL) was added to a refluxing solution of furil (2 mmol) and 1,2-diaminopropane or 1,4-diaminobutane (4 mmol) in ethanol (25 mL). The mixture was refluxed for 5 h, when the color of the solution intensified and turned green. To this reaction mixture, an ethanolic solution (10 mL) of acetylacetone (2 mmol) and glacial acetic acid (1 mL) were added. The reaction mixture was refluxed for about 5 h then green precipitate was obtained. The complex was purified by washing with the mixture (10 mL) of methanol/ethanol (1:1). The yield was 55%. The same procedure was adopted for the synthesis of other oxovanadium(IV) macrocyclic complexes using

benzoylacetone, thenoyltrifluoroacetone and dibenzolylmethane. The physical and analytical data of the complexes are presented in Table 1.

Scheme 1: *In-situ* preparation of macrocyclic complexes of oxovanadium(IV)



R	R'	β -Diketone
CH ₃	CH ₃	Acetylacetone
C ₆ H ₅	CH ₃	Benzoylacetone
C ₄ H ₃ S	CF ₃	Thenoyltrifluoroacetone
C ₆ H ₅	C ₆ H ₅	Dibenzolylmethane

Scheme: *In-situ* preparation of macrocyclic complexes of oxovanadium(IV)

3. RESULTS SECTION

The oxovanadium(IV) complexes were synthesized using in-situ method by refluxing the reaction mixture of furil, 1,2-diaminopropane or 1,4-diaminobutane and vanadyl sulfate in 1:2:1 molar ratio in aqueous methanol/ethanol medium. The reactions appear to proceed according to the given scheme.

Table 1: Physical and analytical data of the complexes

Complex	Empirical Formula	Decomp. Temp. (°C)	C% Calcd. (found)	H% Calcd. (found)	N% Calcd. (found)	V% Calcd. (found)	S% Calcd. (found)	μ_{eff} . B.M. (300 K)
[VO(L ¹)] SO ₄	C ₁₆ H ₃₂ N ₄ VSO ₇	210	41.3 (41.2)	4.7 (4.6)	12.1 (12.0)	11.0 (11.0)	6.9 (6.8)	1.72
[VO(L ²)] SO ₄	C ₁₈ H ₂₆ N ₄ VSO ₇	216	43.8 (43.7)	5.3 (5.2)	11.4 (11.3)	10.3 (10.2)	6.5 (6.4)	1.75
[VO(mac ¹)] SO ₄	C ₂₁ H ₂₆ N ₄ VSO ₇	215	47.6 (47.5)	4.9 (4.8)	10.6 (10.5)	9.6 (9.5)	6.0 (5.9)	1.74
[VO(mac ²)] SO ₄	C ₂₆ H ₂₈ N ₄ VSO ₇	218	52.8 (52.7)	4.7 (4.6)	9.5 (9.5)	8.6 (8.5)	5.4 (5.3)	1.75
[VO(mac ³)] SO ₄	C ₂₄ H ₂₃ N ₄ VS ₂ O ₇ F ₃	217	44.2 (44.1)	3.5 (3.4)	8.6 (8.5)	7.8 (7.7)	9.8 (9.7)	1.76
[VO(mac ⁴)] SO ₄	C ₃₁ H ₃₀ N ₄ VSO ₇	212	57.0 (56.9)	4.6 (4.5)	8.6 (8.5)	7.8 (7.7)	4.9 (4.9)	1.73
[VO(mac ⁵)] SO ₄	C ₂₃ H ₃₀ N ₄ VSO ₇	220	49.6 (49.5)	5.4 (5.3)	10.1 (10.0)	9.1 (9.0)	5.7 (5.6)	1.74
[VO(mac ⁶)] SO ₄	C ₂₈ H ₃₂ N ₄ VSO ₇	221	54.3 (54.2)	5.2 (5.1)	9.0 (9.0)	8.2 (8.2)	5.2 (5.1)	1.73
[VO(mac ⁷)] SO ₄	C ₂₆ H ₂₇ N ₄ VS ₂ O ₇ F ₃	217	46.0 (45.9)	4.0 (3.9)	8.2 (8.2)	7.5 (7.4)	9.4 (9.3)	1.75
[VO(mac ⁸)] SO ₄	C ₃₃ H ₃₄ N ₄ VSO ₇	215	58.2 (58.1)	5.0 (4.9)	8.2 (8.1)	7.5 (7.4)	4.7 (4.6)	1.74

L^1 = Ligand derived by condensation of furil with 1,2-diaminopropane (1:2); L^2 = Ligand derived by condensation of furil with 1,4-diaminobutane (1:2); mac^1 = macrocyclic ligand derived by condensation of L^1 with acetylacetone; mac^2 = macrocyclic ligand derived by condensation of L^1 with benzoylacetone; mac^3 = macrocyclic ligand derived by condensation of L^1 with thenoyltrifluoroacetone; mac^4 = macrocyclic ligand derived by condensation of L^1 with dibenzoylmethane; mac^5 = macrocyclic ligand derived by condensation of L^2 with acetylacetone; mac^6 = macrocyclic ligand derived by condensation of L^2 with benzoylacetone; mac^7 = macrocyclic ligand derived by condensation of L^2 with thenoyltrifluoroacetone; mac^8 = macrocyclic ligand derived by condensation of L^2 with dibenzoylmethane. The elemental analyses (Table 1) of complexes show 1:1 metal to ligand stoichiometry.

3.1 Infrared spectra: The important bands of the infrared spectra for the complexes are listed in table 2. The macrocyclic complexes of oxovanadium(IV) exhibit $>C=N$ absorption around 1625-1616 cm^{-1} , which normally appears at 1660 cm^{-1} in free ligands [24-26]. The lowering of this band in the complexes (type-I) indicate the coordination of nitrogen atoms of the azomethine groups to the vanadium [26-28]. The presence of a band around 302 cm^{-1} may be assigned to ν (V-N) vibration [29]. The presence of $>C=N$ band and the absence of the $>C=O$ band at around 1700 cm^{-1} is a conclusive evidence for condensation of the diamines with the keto group of furil [28]. The band appearing at 3350 and 3180 cm^{-1} may be assigned to asymmetrical and symmetrical N-H stretching modes of the coordinated terminal amino group [30]. The oxovanadium(IV) complexes show a band at around 980 cm^{-1} , which is assigned to ν (V=O) vibration [31]. The presence of an ionic sulfate group in the appearance of three bands at ca. 1132-1135 cm^{-1} (ν_3), 955-960 cm^{-1} (ν_1) and 600-608 cm^{-1} (ν_4). The absence of a ν_2 band and non-splitting of ν_3 band indicate that T_d symmetry is retained [32]. The infrared spectra of macrocyclic complexes of type-II show the same pattern of bands but the asymmetrical and symmetrical N-H stretching modes of terminal amino groups disappear due to condensation of these amino groups with carbonyl group β -diketones in cyclization reactions.

3.2 Electronic spectra: The electronic spectra show bands in the regions 11,030 – 11,970 cm^{-1} , 15,038 - 15,916 cm^{-1} and 21,085 – 22,388 cm^{-1} . These spectra are similar to other five coordinate oxovanadium(IV) complexes involving nitrogen donor atoms. These spectral bands are interpreted according to an energy level scheme [32,33] for distorted, five coordinate square pyramidal oxovanadium(IV) complexes [34]. Accordingly, the observed bands can be assigned to ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions, respectively. One more band is observed in the region 35,268 – 35,766 cm^{-1} , which may be due to transition of the azomethine linkages [35].

3.3 Molar conductance measurements: The molar conductivity (Λ_M) values of all the oxovanadium(IV) complexes were measured in dimethylformamide and the obtained values between 100-106 $ohm^{-1} cm^2 mol^{-1}$ indicate their 1:1 electrolytic nature.

3.4 Magnetic moment measurements: Effective magnetic moments (μ_{eff}) of oxovanadium(IV) complexes were measured at room temperature. The effective magnetic moment of complexes were found in the range 1.71-1.73 B.M which correspond to a single electron of the d^1 -system of square-pyramidal oxovanadium(IV) [34].

3.5 ESR spectra: The X-band ESR spectra of an oxovanadium(IV) complexes were recorded in DMSO at room temperature and at liquid nitrogen temperature(177K). ESR spectra of the complexes were analyzed by the method of Mishra, Sand and Ando et al [36-38] The room temperature ESR spectra show eight lines, which are due to hyperfine splitting arising from the interaction of the unpaired electron with a ${}^{51}V$ nucleus having the nuclear spin $I = 7/2$. This confirms the presence of a single electron in 3d-orbital of oxovanadium(IV) cation as the metallic centre in the complex. The anisotropy is not observed due to rapid tumbling of molecules in solution at room temperature and

only g-average values are obtained. The anisotropy is clearly visible in the spectra at liquid nitrogen temperature and eight bands each due to g_{\parallel} and g_{\perp} are observed separately which are in good agreement for a square pyramidal structure [39-41]. The g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} values are measured from the spectra, which are in good agreement for a square-pyramidal structure. The g_{iso} value from mobile solution at room temperature and g_{av} from frozen solution at liquid nitrogen temperature do not agree very closely since the g and A tensors are corrected for second-order. Further, g values are all very close to the spin-only value (free electron value) of 2.0023, suggesting little spin-orbit coupling. On the basis of the above studies, the following tentative structures may be proposed for these oxovanadium(IV) complexes of the type-I and type-II.

Table 2: Infrared spectral bands (ν / cm^{-1}) of vanadium complexes. All spectra were recorded using KBr in the range 4000-200 cm^{-1} .

Complex	$\nu(\Delta\text{C}=\text{N})$	$\nu(\text{V}-\text{N})$	$\nu(\text{V}=\text{O})$	ν_3 of SO_4^{2-}	ν_1 of SO_4^{2-}	ν_4 of SO_4^{2-}	$\nu_{\text{asym}}(\text{N}-\text{H})$	$\nu_{\text{sym}}(\text{N}-\text{H})$
[VO(L ¹)]SO ₄	1625	301	982	1135	958	600	3350	3178
[VO(L ²)]SO ₄	1624	304	981	1132	958	602	3348	3180
[VO(mac ¹)]SO ₄	1622	302	980	1135	956	604		
[VO(mac ²)]SO ₄	1620	304	980	1135	955	606		
[VO(mac ³)]SO ₄	1622	302	982	1133	958	608		
[VO(mac ⁴)]SO ₄	1618	302	982	1134	958	604		
[VO(mac ⁵)]SO ₄	1622	301	980	1134	960	606		
[VO(mac ⁶)]SO ₄	1616	302	981	1135	958	604		
[VO(mac ⁷)]SO ₄	1622	304	982	1134	960	606		
[VO(mac ⁸)]SO ₄	1624	302	981	1132	956	606		

4. CONCLUSIONS

The spectral data show that the Schiff base condensation of furil is a versatile chelating agent having two reactive carbonyl groups with of 1,2-diaminopropane or 1,4-diaminobutane and their cyclisation reaction with β -diketones are achieved by virtue of template effect of oxovanadium(IV) cation in aqueous ethanol medium. Schiff bases behave as tetradentate ligands by bonding to the metal ion through the azomethine nitrogen atoms. The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for complexes. The molar conductance, magnetic moment values, infrared, e.s.r. and electronic data are in the favour of distorted square-pyramidal structure for VO(IV) complexes.

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