

## Research Article

# Synthesis of Oxovanadium(IV) Complexes with Tetraaza Coordinating Ligands

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Oxovanadium(IV) complexes of the type  $[\text{VO}(\text{mac})]\text{SO}_4$  (where mac = tetraaza macrocyclic ligands derived by condensation of thenil with 1,4-diaminobenzene or 3,4-diaminopyridine and their reaction with  $\beta$ -diketones) have been prepared using vanadyl ion as kinetic template. The prepared macrocyclic complexes were characterized by elemental analyses, molar conductance, magnetic moments, and infrared, electronic, and electron spin resonance data. From the spectroscopic studies, five-coordinate square-pyramidal geometry for the  $\text{VO}^{2+}$  complexes have been proposed wherein derived ligands act as tetradentate chelating agents.

## 1. Introduction

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 [1–3]. The literature contains several reports about oxovanadium(IV) complexes which show modulating activities of various enzymes [4, 5]. Vanadium compounds with vanadyl ion having oxidation state +4 and +5 exist in the environment and in biological systems. These complexes also have biological activities such as antibacterial, antifungal, antiviral, and anticancer drugs [6–8]. Thenil is a versatile chelating agent having two reactive carbonyl groups capable of undergoing Schiff-base condensation with a variety of di- and polyamines. The use of metals as templates in such reaction has led to the synthesis of metal complexes of macrocyclic ligands [9]. Thus, thenil has played an important role in the development of macrocyclic complexes. Such complexes show unusual structure and stability and are known to have relevance to biological system. This provides an opportunity to design and study the model biological systems to understand the chemical changes taking place in

such cases [10]. However, in most cases, the template effect of metal ions of the first transition series has been studied and the chemistry of metal complexes with macrocyclic ligands of oxovanadium(IV) incorporating four nitrogen donor atoms has received less attention [11, 12].

With this aspect, some oxovanadium(IV) complexes with new denticity ligands derived from condensation of thenil with 1,4-diaminobenzene or 3,4-diaminopyridine, capable of undergoing cyclization with  $\beta$ -diketones via the metal template effect, have been prepared and characterized, and their tentative structures are ascertained in this communication.

## 2. Experimental

**2.1. Chemicals and Materials.** All the chemicals and the solvents used were of the reagent grade. Oxovanadium(IV) sulfate was procured from Aldrich Chemical Co. The  $\beta$ -diketones, namely, acetylacetone, benzoylacetone, thenoyl-trifluoroacetone and dibenzoylmethane, were SRL products and the diamines used were reagent-grade products. Thenil used was an Aldrich product.

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)	$\mu_{\text{eff}}$ BM (300°C)
[VO(L <sup>1</sup> )]SO <sub>4</sub>	C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> VS <sub>3</sub> O <sub>5</sub>	216	46.7 (46.6)	3.2 (3.2)	9.9 (9.8)	9.0 (9.0)	17.0 (16.9)	1.71
[VO(L <sup>2</sup> )]SO <sub>4</sub>	C <sub>20</sub> H <sub>16</sub> N <sub>6</sub> VS <sub>3</sub> O <sub>5</sub>	214	42.3 (42.1)	2.8 (2.7)	14.8 (14.7)	9.0 (9.0)	16.9 (16.8)	1.75
[VO(mac <sup>1</sup> )]SO <sub>4</sub>	C <sub>27</sub> H <sub>22</sub> N <sub>4</sub> VS <sub>3</sub> O <sub>5</sub>	218	51.5 (51.4)	3.5 (3.4)	8.9 (8.8)	8.1 (8.0)	15.3 (15.3)	1.72
[VO(mac <sup>2</sup> )]SO <sub>4</sub>	C <sub>32</sub> H <sub>24</sub> N <sub>4</sub> VS <sub>3</sub> O <sub>5</sub>	221	55.6 (55.6)	3.5 (3.4)	8.1 (8.1)	7.4 (7.3)	13.9 (13.8)	1.74
[VO(mac <sup>3</sup> )]SO <sub>4</sub>	C <sub>30</sub> H <sub>19</sub> N <sub>4</sub> VS <sub>4</sub> O <sub>5</sub> F <sub>3</sub>	220	47.9 (47.8)	2.5 (2.4)	7.5 (7.5)	6.8 (6.7)	17.0 (16.9)	1.76
[VO(mac <sup>4</sup> )]SO <sub>4</sub>	C <sub>37</sub> H <sub>26</sub> N <sub>4</sub> VS <sub>3</sub> O <sub>5</sub>	217	59.0 (58.9)	3.5 (3.4)	7.4 (7.3)	6.8 (6.8)	12.8 (12.7)	1.75
[VO(mac <sup>5</sup> )]SO <sub>4</sub>	C <sub>25</sub> H <sub>20</sub> N <sub>6</sub> VS <sub>3</sub> O <sub>5</sub>	215	47.5 (47.4)	3.2 (3.1)	13.3 (13.2)	8.1 (8.0)	15.2 (15.1)	1.73
[VO(mac <sup>6</sup> )]SO <sub>4</sub>	C <sub>30</sub> H <sub>22</sub> N <sub>6</sub> VS <sub>3</sub> O <sub>5</sub>	220	52.0 (51.9)	3.2 (3.1)	12.1 (12.1)	7.4 (7.3)	13.9 (13.8)	1.74
[VO(mac <sup>7</sup> )]SO <sub>4</sub>	C <sub>28</sub> H <sub>17</sub> N <sub>6</sub> VS <sub>4</sub> O <sub>5</sub> F <sub>3</sub>	216	44.6 (44.5)	2.3 (2.2)	11.2 (11.1)	6.8 (6.8)	17.0 (17.0)	1.75
[VO(mac <sup>8</sup> )]SO <sub>4</sub>	C <sub>35</sub> H <sub>24</sub> N <sub>6</sub> VS <sub>3</sub> O <sub>5</sub>	218	55.6 (55.4)	3.2 (3.2)	11.1 (11.2)	6.7 (6.6)	12.7 (12.6)	1.72

L<sup>1</sup>: ligand derived by condensation of thenil with 1,4-diaminobenzene (1 : 2); L<sup>2</sup>: ligand derived by condensation of thenil with 3,4-diaminopyridine (1 : 2); Mac<sup>1</sup>: macrocyclic ligand derived by condensation of L<sup>1</sup> with acetylacetone; Mac<sup>2</sup>: macrocyclic ligand derived by condensation of L<sup>1</sup> with benzoylacetone; Mac<sup>3</sup>: macrocyclic ligand derived by condensation of L<sup>1</sup> with thenoyltrifluoroacetone; Mac<sup>4</sup>: macrocyclic ligand derived by condensation of L<sup>1</sup> with dibenzoylmethane; Mac<sup>5</sup>: macrocyclic ligand derived by condensation of L<sup>2</sup> with acetylacetone; Mac<sup>6</sup>: macrocyclic ligand derived by condensation of L<sup>2</sup> with benzoylacetone; Mac<sup>7</sup>: macrocyclic ligand derived by condensation of L<sup>2</sup> with thenoyltrifluoroacetone; Mac<sup>8</sup>: macrocyclic ligand derived by condensation of L<sup>2</sup> with dibenzoylmethane. The elemental analyses (Table 1) of complexes show 1 : 1 metal to ligand stoichiometry.

**2.2. Analytical Methods and Physical Measurements.** Vanadium was estimated gravimetrically as its vanadate after decomposing the complex with concentrated nitric acid [13]. Sulfur was estimated as barium sulfate in the laboratory [14]. The standard technique of melting point (uncorrected) determination using sulfuric acid bath was employed. Toshniwal conductivity bridge, model number 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), Hg[Co(CNS)<sub>4</sub>] ( $\chi_g = 16.44 \times 10^{-6}$  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. The room temperature and liquid nitrogen temperature ESR spectra were recorded at RSIC, IIT, Chennai, India. The infrared spectra of the complexes in the range 4000–200 cm<sup>-1</sup> were measured on Perkin-Elmer 621 using KBr medium.

**2.3. In-Situ Preparation of Oxovanadium(IV) Complexes with Ligands Derived by Condensation of Thenil with 1,4-Diaminobenzene or 3,4-Diaminopyridine.** Vanadyl sulfate (2 mmol) dissolved in methanol (25 mL) was added to a refluxing solution of thenil (2 mmol) and 1,4-diaminobenzene (4 mmol) or 3,4-diaminopyridine (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 vacuo at room temperature and the dark green color product was isolated. The complex was 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 thenil (2 mmol) and 1,4-diaminobenzene or 3,4-diaminopyridine (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 (2 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 60%. The same procedure was adopted for the synthesis of other oxovanadium(IV) macrocyclic complexes using benzoylacetone, thenoyltrifluoroacetone, and dibenzoylmethane. The physical and analytical data of the complexes are presented in Table 1.

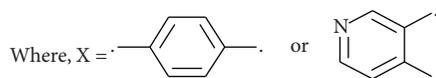
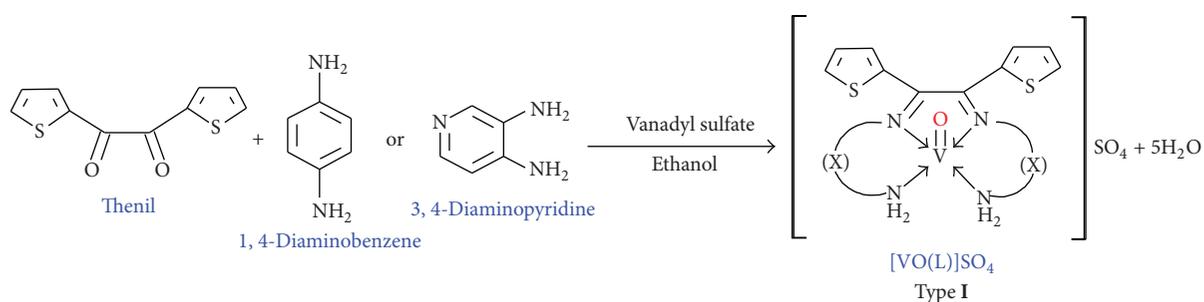
### 3. Results and Discussion

The oxovanadium(IV) complexes were synthesized using *in situ* method by refluxing the reaction mixture of thenil, diamines, and vanadylsulfate in 1 : 2 : 1 molar ratio in aqueous ethanol. The reaction appears to proceed according to Schemes I and II given in Figure 1.

**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 1625–1618 cm<sup>-1</sup>, which normally appears at 1660 cm<sup>-1</sup> in free ligands [15–18]. The lowering of this band in the complexes (type I) indicates the coordination of nitrogen atoms of the azomethine groups to the vanadium [19, 20]. The presence of a band at around 302 cm<sup>-1</sup> may be assigned to  $\nu$  (V–N) vibration [21]. The appearance of >C=N band and the absence of the >C=O band around 1700 cm<sup>-1</sup> are a conclusive evidence for condensation of the diamines with the two keto group of thenil [18]. The bands appearing at 3350 and 3180 cm<sup>-1</sup> may be assigned to asymmetrical

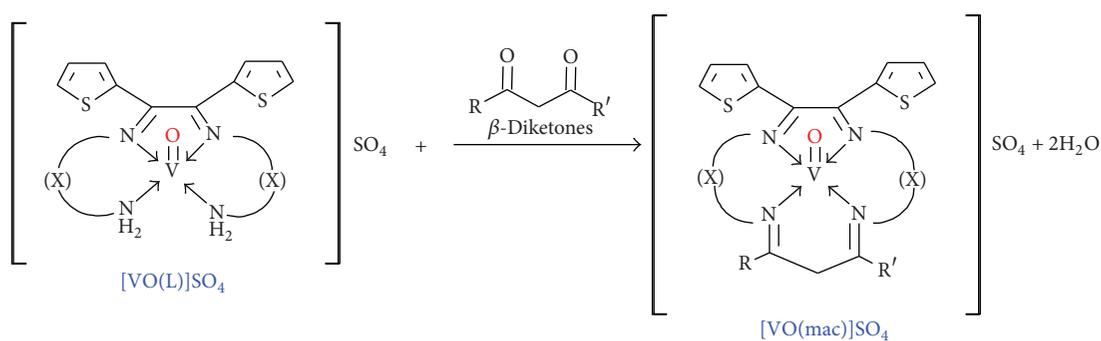
TABLE 2: Infrared spectral bands of complexes.

Complex	Bands (cm <sup>-1</sup> )							
	$\nu$ (C=N)	$\nu$ (V-N)	$\nu$ (V=O)	$\nu_3$ SO <sub>4</sub> <sup>-2</sup>	$\nu_1$ SO <sub>4</sub> <sup>-2</sup>	$\nu_4$ SO <sub>4</sub> <sup>-2</sup>	$\nu_{as}$ (N-H)	$\nu_s$ (N-H)
[VO(L <sup>1</sup> )]SO <sub>4</sub>	1618	301	981	1132	956	603	3350	3180
[VO(L <sup>2</sup> )]SO <sub>4</sub>	1624	302	982	1134	960	605	3348	3182
[VO(mac <sup>1</sup> )]SO <sub>4</sub>	1618	302	982	1133	958	604		
[VO(mac <sup>2</sup> )]SO <sub>4</sub>	1622	304	981	1134	956	606		
[VO(mac <sup>3</sup> )]SO <sub>4</sub>	1624	304	980	1131	955	605		
[VO(mac <sup>4</sup> )]SO <sub>4</sub>	1622	302	981	1134	960	604		
[VO(mac <sup>5</sup> )]SO <sub>4</sub>	1625	304	980	1134	958	606		
[VO(mac <sup>6</sup> )]SO <sub>4</sub>	1620	302	982	1133	960	602		
[VO(mac <sup>7</sup> )]SO <sub>4</sub>	1624	303	981	1132	958	606		
[VO(mac <sup>8</sup> )]SO <sub>4</sub>	1618	302	982	1135	960	604		



L<sup>1</sup> = thenil + 1, 4-diaminobenzene; L<sup>2</sup> = thenil + 3, 4-diaminopyridine

The parent complexes [VO(L)]SO<sub>4</sub> react with  $\beta$ -diketones to yield [VO(mac)]SO<sub>4</sub> as given below



where, mac = tetraaza macrocyclic ligands derived by condensation of L<sup>1</sup> or L<sup>2</sup> with  $\beta$ -diketones in presence of oxovanadium (IV) cation.

R	R'	$\beta$ -Diketones
CH <sub>3</sub>	CH <sub>3</sub>	Acetylacetone
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	Benzoylacetone
C <sub>4</sub> H <sub>3</sub> S	CF <sub>3</sub>	Thenoyltrifluoroacetone
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Dibenzoylmethane

FIGURE 1: *In situ* preparation of macrocyclic complexes of oxovanadium(IV).

and symmetrical N–H stretching modes of the coordinated terminal amino group [21]. The oxovanadium(IV) complexes show a band at around  $981\text{ cm}^{-1}$ , which is assigned to  $\nu$  (V=O) vibration [22]. The presence of an ionic sulfate group in the complexes is confirmed by the appearance of three bands at ca.  $1131\text{--}1135\text{ cm}^{-1}$  ( $\nu_3$ ),  $955\text{--}960\text{ cm}^{-1}$  ( $\nu_1$ ) and  $602\text{--}606\text{ cm}^{-1}$  ( $\nu_4$ ). The absence of a  $\nu_2$  band and nonsplitting of  $\nu_3$  band indicate that Td symmetry is retained [23, 24]. 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 of  $\beta$ -diketones in cyclization reactions.

**3.2. Electronic Spectra.** The electronic spectra show bands in the regions  $11,040\text{--}11,980\text{ cm}^{-1}$ ,  $15,038\text{--}15,916\text{ cm}^{-1}$ , and  $21,080\text{--}22,380\text{ cm}^{-1}$ . 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 reported by Tsuchimoto et al. [25] for distorted, five-coordinate square pyramidal oxovanadium(IV) complexes [26, 27]. 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  $35,260\text{--}35,760\text{ cm}^{-1}$ , which may be due to transition of the azomethine linkages [28, 29].

**3.3. Molar Conductance Measurements.** The molar conductivity ( $\Lambda_M$ ) values of all the oxovanadium(IV) complexes were measured in dimethylformamide and the obtained values were between  $100$  to  $106\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$  indicating their 1 : 1 electrolytic nature.

**3.4. Magnetic Moment Measurements.** Effective magnetic moments ( $\mu_{\text{eff}}$ ) of oxovanadium(IV) complexes were measured at room temperature and the values are given in Table 1. The effective magnetic moments of complexes were found in the range  $1.71\text{--}1.76\text{ BM}$  which correspond to a single electron of the  $d^1$  system of square-pyramidal oxovanadium(IV) [26].

**3.5. ESR Spectra.** The X-band ESR spectra of an oxovanadium(IV) complex were recorded in DMSO at room temperature and at liquid nitrogen temperature ( $177\text{ K}$ ). ESR spectra of the complexes were analyzed by the method of Mishra and Pandey [30], Sands [31], and Ando et al. [32]. The room temperature ESR spectra show eight lines, which are due to hyperfine splitting arising from the interaction of the unpaired electron with a  ${}^{51}\text{V}$  nucleus having the nuclear spin  $I = 7/2$ . This confirms the presence of a single 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. The  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$ , and  $A_{\perp}$  values (RT/LNT) are measured from the spectra, which are in good agreement for a square-pyramidal

structure [33–35]. The  $g_{\text{iso}}$  value from mobile solution at room temperature and  $g_{\text{av}}$  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 tentative structures may be proposed for these oxovanadium(IV) complexes of the type (I) and macrocyclic complexes of the type (II) are shown in Figure 1.

## 4. Conclusions

The spectral data show that the Schiff base condensation has been possible due to thenil being a versatile chelating agent having two reactive carbonyl groups with 1,4-diaminobenzene or 3,4-diaminopyridine and their cyclization reaction with  $\beta$ -diketones is achieved by virtue of kinetic 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 and amine nitrogen providing controlled geometry. The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for complexes. The magnetic moment values and electronic data are in the favour of square pyramidal structure for oxovanadium(IV) complexes. The purpose of synthesizing oxovanadium(IV) complexes is to provide new vanadyl centres in controlled geometry to explore biological importance as few vanadyl complexes are reported showing DNA cleavage activity in near-IR light.

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