



# SYNTHESES AND SPECTRAL CHARACTERIZATION OF SOME NOVEL MACROCYCLIC COMPLEXES OF OXOVANADIUM(IV) WITH 1,1'-OXALYLDIIMIDAZOLE

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A new series of five complexes of oxovanadium(IV) with the general formula [VO(mac)]SO<sub>4</sub> (where mac = tetraazamacrocyclic ligands derived by condensation of 1,1'-oxalyldiimidazole with 1,2-diaminopropane and their reactions with β-diketones) have been prepared using oxometal ion as kinetic template. The prepared complexes have been characterized on the basis of electrical conductance, molecular weight, magnetic moment, elemental analyses, infrared, e.s.r. and electronic spectral data. The probable coordination number of central metal is five (distorted square-pyramid).

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## Introduction

Schiff bases play an important role in chemistry as they easily form stable complexes with most of transition metal ions. Schiff base complexes may serve as models for biologically important species. Vanadium is an essential element for biological systems. Vanadium is reported to participate in some enzymatic reactions such as nitrogen fixation.<sup>1,2</sup> Vanadium is found naturally in soil and water as trace metal. "Accumulated" vanadium in the form ores such as vanadinite or patronite is rare. Vanadium is actually the second most abundant transition metal in sea water, only surpassed by molybdenum as molybdate. Vanadium compounds with oxidation state IV and V exist in the biological systems. The oral administration of vanadate is reported to reduce hyperglycemia in diabetic rats. The chemistry of oxovanadium complexes has attracted due to their insulinomimetic properties in the therapeutics of diabetes.<sup>3-5</sup> 1,1'-oxalyldiimidazole is a versatile chelating agent having two reactive carbonyl groups capable of undergoing Schiff-base condensation with a variety of amines. Studies on the macrocyclic ligands of oxovanadium(IV) incorporating four nitrogen donor atoms have received less attention.<sup>5-7</sup> Oxovanadium(IV) complexes have been commonly utilized as precatalysts for olefin epoxidation and sulfide oxidation when combined with peroxide co-oxidants.<sup>8-10</sup> The 1,2-diaminopropane can form chelate ring using in-situ method of synthesis in presence of metal cation due to kinetic template effect.<sup>11-13</sup>

Considering these facts a new series of oxovanadium(IV) complexes were synthesized using in-situ method of synthesis by condensation of β-diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and

dibenzoylmethane with 1,2-diaminopropane in molar ratio 1:2 in the presence of VO<sup>2+</sup> cation as kinetic template using 1,1'-oxalyldiimidazole. These complexes were isolated in solid state. We report here the synthesis of these complexes and their tentative structures on the basis of elemental analyses, molar conductance, magnetic susceptibility measurements and spectral (ir, esr and electronic) data.

## Experimental

### Materials

Oxovanadium(IV) sulfate was purchased from Aldrich. The β-diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane were obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. 1,1'-oxalyldiimidazole and 1,2-diaminopropane used were Aldrich products. The solvents were purified before use by standard techniques.

### Analytical and Physical Measurements

Estimation of vanadium was done by gravimetrically as its vanadate, after decomposing the complex with concentrated nitric acid.<sup>14</sup> Sulfur was estimated as BaSO<sub>4</sub> in the laboratory.<sup>15</sup> Melting point (uncorrected) determination of the complexes were done by the standard technique using sulfuric acid bath. Molar conductance were measured using Toshniwal conductivity bridge (Model CL-01-02A, cell constant 0.5 cm<sup>-1</sup>) using 1x10<sup>-3</sup> M solution of the complexes in DMF at room temperature. Carbon, hydrogen and nitrogen microanalyses of the complexes were estimated at CRF, NERIST, Nirjuli-791109, Itanagar, Arunachal Pradesh, India.

Room temperature magnetic susceptibilities of the complexes in powder form were measured by Gouy's balance using mercury tetrathiocyanatocobaltate(II), Hg[Co(NCS)<sub>4</sub>], ( $\chi_g = 16.44 \times 10^{-6}$  c.g.s. unit at 20 °C), as calibrant. The UV-Vis electronic spectra of the complexes were obtained by using Beckmann DU-2 spectrophotometer in the range 2000-185 nm.

**Table 1.** Physical and analytical data of the complexes

Complex	Empirical Formula	T <sub>dec</sub> , °C	Elem. Anal., Calcd./ (Found)				μ <sub>eff.</sub> BM, 300 °K	
			C %	H %	N %	V %		S %
[VO(L)]SO <sub>4</sub>	C <sub>14</sub> H <sub>22</sub> N <sub>8</sub> VSO <sub>5</sub>	221	36.1 (35.8)	4.7 (4.5)	24.0 (23.8)	11.0 (10.9)	6.9 (6.6)	1.75
[VO(mac <sup>1</sup> )]SO <sub>4</sub>	C <sub>19</sub> H <sub>26</sub> N <sub>8</sub> VSO <sub>5</sub>	220	43.1 (42.9)	5.0 (4.9)	21.2 (21.0)	9.6 (9.4)	6.1 (5.9)	1.72
[VO(mac <sup>2</sup> )]SO <sub>4</sub>	C <sub>24</sub> H <sub>28</sub> N <sub>8</sub> VSO <sub>5</sub>	216	48.7 (48.3)	4.8 (4.7)	18.9 (18.7)	8.6 (8.5)	5.4 (5.2)	1.72
[VO(mac <sup>3</sup> )]SO <sub>4</sub>	C <sub>22</sub> H <sub>23</sub> N <sub>8</sub> VSO <sub>5</sub> F <sub>3</sub>	215	40.6 (40.2)	3.6 (3.3)	17.2 (16.9)	7.8 (7.6)	9.8 (9.7)	1.71
[VO(mac <sup>4</sup> )]SO <sub>4</sub>	C <sub>29</sub> H <sub>30</sub> N <sub>8</sub> VSO <sub>5</sub>	220	53.3 (53.0)	4.6 (4.3)	17.1 (16.8)	7.8 (7.6)	4.9 (4.7)	1.74

The room temperature and liquid nitrogen temperature ESR spectra were recorded at RSIC, IIT, Chennai, India. The FTIR spectra of the complexes in the range 4000-200 cm<sup>-1</sup> were measured in KBr pellets on Perkin-Elmer 621. Purity of the complexes was tested by TLC on silica.

### Synthesis of oxovanadium(IV) complexes

The Schiff base ligand (L) was prepared by mixing ethanolic solutions of 1,1'-oxalyldiimidazole (4 mmol, 25 mL) with 1,2-diaminopropane (8 mmol, 50 mL) and refluxing the mixture for about 3 h. After completion of the reaction, green solid product was filtered and washed with ethanol. The purity of compound was checked by TLC. Yield: 60 %, m.p. 255 °C; UV-Vis (CH<sub>3</sub>OH) λ<sub>max</sub> /nm: 242, 265. Vanadyl sulfate (4 mmol) dissolved in ethanol (25 mL) was added to the refluxing solution of ligand and again this mixture was refluxed for 3 h, when the color of the solution is intensified and turned to green. The solid which separated at room temperature was washed with ethanol and dried over P<sub>4</sub>O<sub>10</sub> in vacuo. The purity of complex was checked by TLC. The yield was 65 % (Type I).

The reaction mixture of I suspended in ethanol was further reacted with β-diketones such as acetylacetone or benzoylacetone or thenoyltrifluoroacetone or dibenzoylmethane (1:1) to get macrocyclic complexes (Type II). These macrocyclic complexes were isolated under vacuo.

The ligand L is derived by condensation of 1,1'-oxalyldiimidazole with 1,2-diaminopropane (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> =

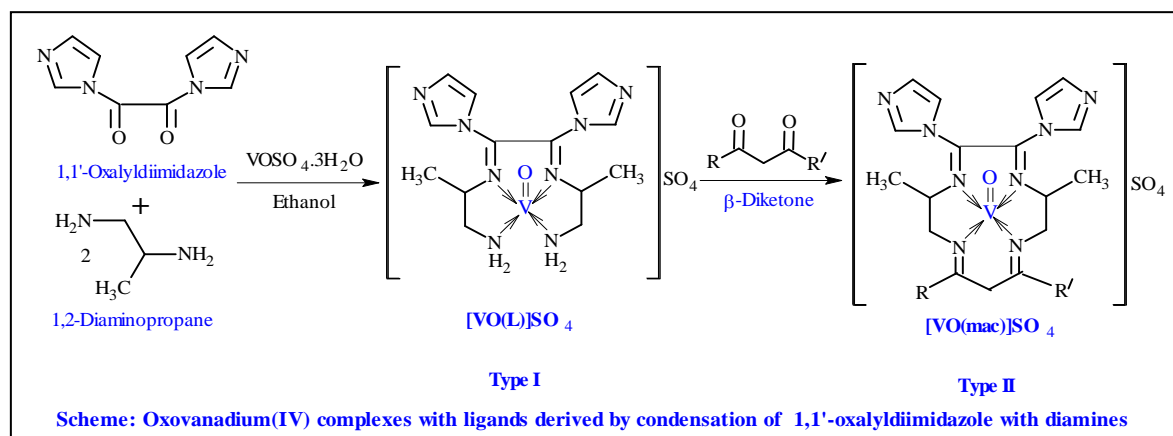
macrocyclic ligand derived by condensation of L<sup>1</sup> with thenoyltrifluoroacetone; Mac<sup>4</sup> = macrocyclic ligand derived by condensation of L<sup>1</sup> with dibenzoylmethane.

### Results and Discussion

The oxovanadium(IV) complexes were synthesized using in-situ method by refluxing the reaction mixture of 1,1'-oxalyldiimidazole with diamines and vanadylsulfate in 1:2:1 molar ratio in aqueous ethanol. The reactions appear to proceed according to the given scheme.

#### Infrared spectra

Important infrared spectral bands of the complexes and their tentative assignments are given in Table 2. In all complexes of oxovanadium(IV), the coordination of nitrogen atoms of azomethine groups to the VO<sup>2+</sup> is evidenced by the shift of ν<sub>C=N</sub> to lower frequencies.<sup>16-21</sup> Here >C=N absorption is observed around 1620 - 1615 cm<sup>-1</sup>, which normally appears at 1650 cm<sup>-1</sup> in free ligands. The presence of a band at around 300 cm<sup>-1</sup> may be assigned to ν<sub>V-N</sub> vibration.<sup>22</sup> The appearance of >C=N band and the absence of the >C=O band around 1710 cm<sup>-1</sup> is a conclusive evidence for condensation of the diamines with the two keto group of 1,1'-oxalyldiimidazole.<sup>21</sup> The bands appearing at 3345 and 3175 cm<sup>-1</sup> may be assigned to asymmetrical and symmetrical N-H stretching modes of the coordinated terminal amino group.<sup>23</sup> The oxovanadium(IV) complexes show a band at around 975 - 980 cm<sup>-1</sup>, which is assigned to ν<sub>V=O</sub> vibration.<sup>24-26</sup> The presence of an ionic sulfate group in the complexes is confirmed by the appearance of three bands at ca. 1130-1135 cm<sup>-1</sup> (ν<sub>3</sub>), 945-952 cm<sup>-1</sup> (ν<sub>1</sub>) and 600-604 cm<sup>-1</sup> (ν<sub>4</sub>). The absence of a ν<sub>2</sub> band and non-splitting of ν<sub>3</sub> band confirms that tetrahedral symmetry is retained.<sup>27</sup>



**Table 2.** Infrared spectral bands of complexes

Complex	Bands (cm <sup>-1</sup> )							
	$\nu_{C=N}$	$\nu_{V-N}$	$\nu_{V=O}$	$\nu_3(SO_4^{2-})$	$\nu_1(SO_4^{2-})$	$\nu_4(SO_4^{2-})$	$\nu_{as}(NH)$	$\nu_s(NH)$
[VO(L)]SO <sub>4</sub>	1620	300	975	1130	950	602	3345	3172
[VO(mac <sup>1</sup> )]SO <sub>4</sub>	1615	303	975	1132	952	602	3345	3175
[VO(mac <sup>2</sup> )]SO <sub>4</sub>	1620	300	975	1130	950	604	3348	3180
[VO(mac <sup>3</sup> )]SO <sub>4</sub>	1618	301	980	1135	950	600	3345	3180
[VO(mac <sup>4s</sup> )]SO <sub>4</sub>	1616	302	978	1135	952	602	3345	3178

### Electronic Spectra

The electronic spectra of oxovanadium(IV) complexes were recorded in 10<sup>-3</sup> mol L<sup>-1</sup> DMF solution. The electronic spectra show bands in the regions 11,030 – 11,960 cm<sup>-1</sup>, 15,020 – 15,850 cm<sup>-1</sup> and 21,030 – 22,340 cm<sup>-1</sup>. 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. for distorted five coordinate square pyramidal oxovanadium(IV) complexes.<sup>28</sup> Accordingly, the observed bands can be assigned to <sup>2</sup>B<sub>2</sub> → <sup>2</sup>E, <sup>2</sup>B<sub>2</sub> → <sup>2</sup>B<sub>1</sub> and <sup>2</sup>B<sub>2</sub> → <sup>2</sup>A<sub>2</sub> transitions, respectively. One more band is observed in the region 35,150 – 35,680 cm<sup>-1</sup>, which may be due to transition of the azomethine linkages<sup>29,30</sup>.

### Molar conductance measurements

The molar conductivity ( $\Lambda_M$ ) values of all the oxovanadium(IV) complexes were measured in dimethylformamide and the obtained values lie between 90 – 102 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating their 1:1 electrolytic nature.

### Magnetic moment measurements

Magnetic moments of oxovanadium(IV) complexes were measured at room temperature and effective magnetic moment ( $\mu_{eff}$ ) values are given in Table 1. The magnetic moment values of the vanadyl complexes ranges from 1.71–1.76 B.M which correspond to a single electron of the 3d<sup>1</sup> system of square-pyramidal oxovanadium(IV) complexes.<sup>28</sup>

### ESR spectra

The X-band ESR spectra of an oxovanadium(IV) complex was recorded in DMSO at room temperature and at liquid nitrogen temperature (177 K). ESR spectra of the complexes were analyzed by the method of Mishra, Yadava Sand and Ando et al.<sup>29–32</sup> ESR spectra at room temperature show eight lines, which are due to hyperfine splitting arising from the interaction of the unpaired electron with a <sup>51</sup>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<sub>||</sub> and g<sub>⊥</sub> are observed separately which are in good agreement for a square pyramidal vanadyl complexes.<sup>33–35</sup>

The g<sub>||</sub>, g<sub>⊥</sub>, A<sub>||</sub> and A<sub>⊥</sub> values are measured from the spectra, which are in good agreement for a square-pyramidal structure. The g<sub>iso</sub> value from mobile solution at room temperature and g<sub>av</sub> 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 these studies, the tentative structures are proposed for these oxovanadium(IV) complexes of the type (I) and (II).

### Conclusions

The present study demonstrates simple synthetic routes to 5 new oxovanadium(IV) complexes with tetraaza macrocyclic ligands. The obtained spectral data suggest that the 1,1'-oxalyldiimidazole is good chelating agents having two reactive carbonyl groups capable of undergoing Schiff base condensation with a variety of diamine. Schiff bases behave as tetradentate ligands by bonding to the metal ion through the azomethine nitrogen and amino group. The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for the VO<sup>2+</sup> complexes. The electrical conductance, magnetic moment values, infrared, e.s.r. and electronic data are in the favour of square pyramidal structure for VO(IV) complexes.

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