

# Synthesis and structural characterization of novel square pyramidal oxovanadium(IV) complexes with ligands having N and O donor atoms

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Oxovanadium(IV) complexes having the general formula [VO(L)] were designed and synthesized using vanadyl ion as kinetic template with ligands derived by condensation of  $\beta$ -diketones such as acetylacetone, benzoylacetone, thenoyltrifluoroacetone, and dibenzoylmethane with 2-amino-3-hydroxypyridine or 2-aminobenzoic acid or 2-aminonicotinic acid. Tentative structures of the complexes were proposed on the basis of elemental analysis, molar conductance, magnetic moments, and spectral (infrared, electronic and electron spin resonance) data. All the oxovanadium(IV) complexes are 5-coordinated wherein derived ligands act as tetradentate chelating agents.

**Key Words:** Oxovanadium(IV), tetradentate ligands,  $\beta$ -diketones, kinetic template

## Introduction

Interest in vanadium coordination chemistry over the past decade has been increasing because of its biological importance and its catalytic abilities.<sup>1</sup> Vanadium is found naturally in soil and water as a trace metal. Vanadium popular oxidation states are +4 and +5 existing in the environment and in biological systems. The literature contains several reports about oxovanadium(IV) complexes that influence modulating activities

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of various enzymes.<sup>2</sup> Polymer bound VO(acac)<sub>2</sub> has been used for the conversion of benzene to phenol and cyclohexane to cyclohexene oxide.<sup>3</sup> Vanadyl complexes having electron withdrawing substituents have been shown to catalyze olefin epoxidation with moderate selectivities.<sup>4</sup> Vanadium presence in biological systems particularly its accumulation in sea squirts and wild mushrooms like *Amanita muscaria* and others has been a curious area of study.<sup>5-7</sup> 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 the chemistry of vanadium complexes incorporating nitrogen and oxygen donor atoms has received less attention.<sup>8-10</sup> With this view, oxovanadium(IV) complexes were prepared using in-situ method of synthesis by condensation of  $\beta$ -diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone, and dibenzoylmethane with 2-amino-3-hydroxypyridine or 2-aminobenzoic acid or 2-aminonicotinic acid in molar ratio 1:2 in the presence of VO<sub>2</sub><sup>+</sup> cation as kinetic template.

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

## Experimental

### Materials and measurements

Oxovanadium(IV) sulfate was procured from Aldrich. The  $\beta$ -diketones, viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone, and dibenzoylmethane, were SRL products and the 2-amino-3-hydroxypyridine, 2-aminonicotinic acid, 2-aminobenzoic acid, and 2-aminonicotinic acid used were Aldrich products.

### Analytical methods and physical measurements

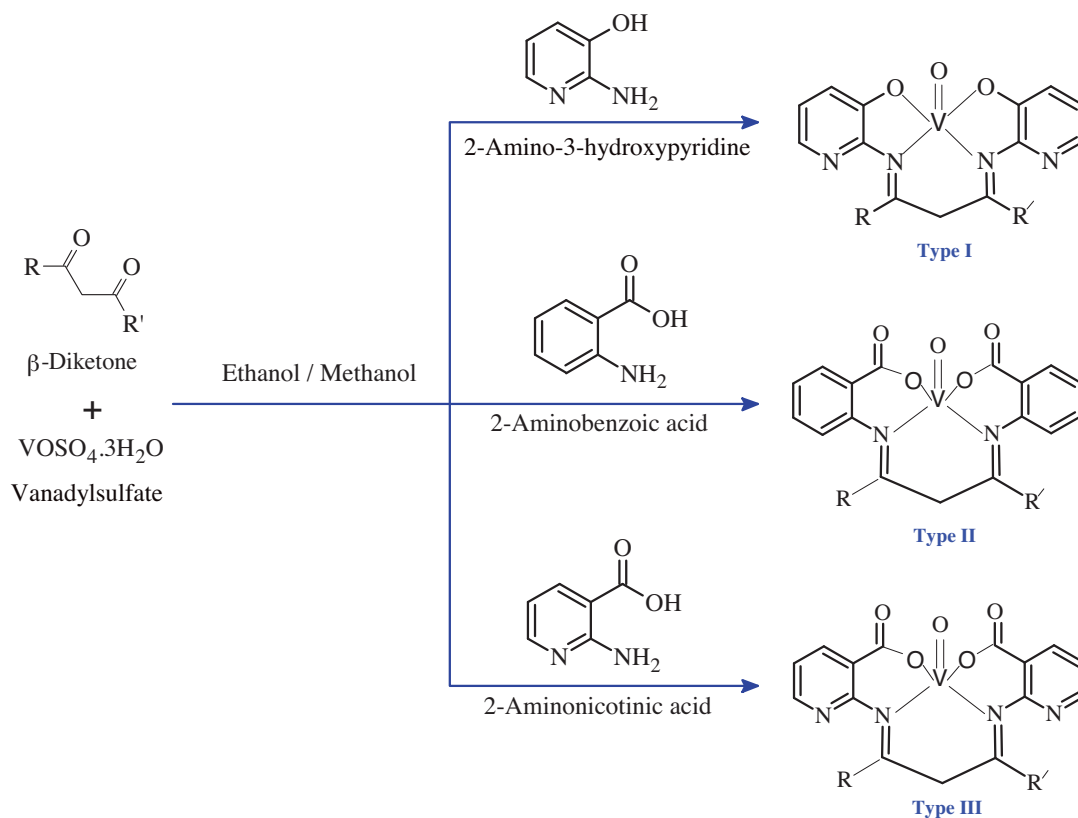
Vanadium was estimated gravimetrically as its vanadate, after decomposing the complex with concentrated nitric acid.<sup>11</sup> Sulfur was estimated as barium sulfate in the laboratory.<sup>12</sup> The standard technique of melting point (uncorrected) determination using a sulfuric acid bath was employed. A Toshniwal conductivity bridge, model no. CLO102A, was used for conductance measurements at room temperature. The magnetic susceptibility of the complexes in powder form was measured at room temperature using a 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 a Beckmann DU-2 spectrophotometer and a  $\Phi$ 10 Russian spectrophotometer instrument in the ranges 2000-185 nm and 700-400 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 recorded in KBr on Perkin-Elmer 621 and Beckmann Acculab-9 spectrophotometers.

### In-situ preparation of oxovanadium(IV) complexes with ligands derived by condensation of $\beta$ -diketones with 2-amino-3-hydroxypyridine or 2-aminobenzoic acid or 2-aminonicotinic acid

Vanadyl sulfate (0.02 mol) dissolved in methanol (25 mL) was added to a refluxing solution of acetylacetone (0.02 mol) and 2-aminonicotinic acid (0.04 mol) respectively in ethanol (25 mL). The mixture was refluxed for 5 h, when the color of the solution turned green. The solvent was removed under vacuo at room temperature

and a dark green product was isolated. The complex was thoroughly washed with methanol/ethanol mixture (1:1). The yield was 68%.

A similar procedure was adopted to prepare oxovanadium(IV) complexes using benzoylacetone, thenoyl-trifluoroacetone and dibenzoylmethane with the precursor molecules such as 2-amino-3-hydroxypyridine or 2-aminobenzoic acid or 2-aminonicotinic acid.



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

## Results and discussion

The oxovanadium(IV) complexes were synthesized using an in-situ method by refluxing the reaction mixture of the  $\beta$ -diketones and 2-amino-3-hydroxypyridine or 2-aminobenzoic acid or 2-aminonicotinic acid and vanadyl sulfate in 1:2:1 molar ratio in aqueous ethanol. The reaction appears to proceed according to the given Scheme.

The elemental analyses of complexes show 1:1 metal to ligand stoichiometry (Table 1).

### Infrared spectra

The important bands of the infrared spectra for the complexes are listed in Table 2. The complexes of oxovanadium(IV) exhibit  $>\text{C}=\text{N}$  absorption around  $1625\text{--}1610\text{ cm}^{-1}$ , which normally appears at  $1660\text{ cm}^{-1}$  in free ligands.<sup>13–15</sup> The lowering of this band in the complexes indicates the coordination of nitrogen atoms

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

Complex	Empirical formula	Decomp. temp. (°C)	C% Found (Calcd)	H% Found (Calcd)	N% Found (Calcd)	V% Found (Calcd)	S% Found (Calcd)	$\mu_{\text{eff}}$ . BM (300 °C)
[VO(L <sup>1</sup> )]	C <sub>17</sub> H <sub>14</sub> N <sub>4</sub> VO <sub>5</sub>	217	50.3 (50.4)	3.4 (3.5)	13.8 (13.8)	12.5 (12.6)		1.76
[VO(L <sup>2</sup> )]	C <sub>22</sub> H <sub>16</sub> N <sub>4</sub> VO <sub>3</sub>	214	60.6 (60.7)	3.6 (3.7)	12.8 (12.9)	11.6 (11.7)		1.72
[VO(L <sup>3</sup> )]	C <sub>24</sub> H <sub>18</sub> N <sub>2</sub> VO <sub>5</sub>	216	61.8 (61.9)	3.8 (3.9)	5.9 (6.0)	10. (11.0)		1.74
[VO(L <sup>4</sup> )]	C <sub>22</sub> H <sub>16</sub> N <sub>4</sub> VO <sub>5</sub>	216	56.5 (56.5)	3.4 (3.5)	11.9 (12.0)	10.8 (10.9)		1.74
[VO(L <sup>5</sup> )]	C <sub>18</sub> H <sub>11</sub> N <sub>4</sub> VO <sub>3</sub> SF <sub>3</sub>	213	45.9 (45.9)	2.3 (2.4)	11.8 (11.9)	10.8 (10.8)	6.8 (6.7)	1.74
[VO(L <sup>6</sup> )]	C <sub>22</sub> H <sub>13</sub> N <sub>2</sub> VO <sub>5</sub> SF <sub>3</sub>	219	50.2 (50.3)	2.4 (2.5)	5.3 (5.3)	9.6 (9.7)	6.8 (6.7)	1.71
[VO(L <sup>7</sup> )]	C <sub>20</sub> H <sub>11</sub> N <sub>4</sub> VO <sub>5</sub> SF <sub>3</sub>	218	45.5 (45.6)	2.0 (2.1)	10.5 (10.6)	9.7 (9.7)	6.8 (6.7)	1.76
[VO(L <sup>8</sup> )]	C <sub>25</sub> H <sub>18</sub> N <sub>4</sub> VO <sub>3</sub>	215	63.3 (63.4)	3.8 (3.8)	11.7 (11.8)	10.8 (10.8)		1.73
[VO(L <sup>9</sup> )]	C <sub>29</sub> H <sub>20</sub> N <sub>2</sub> VO <sub>5</sub>	220	66.0 (65.9)	3.8 (3.7)	5.2 (5.3)	9.6 (9.7)		1.73
[VO(L <sup>10</sup> )]	C <sub>27</sub> H <sub>18</sub> N <sub>4</sub> VO <sub>5</sub>	220	61.2 (61.3)	3.3 (3.4)	10.5 (10.6)	9.5 (9.6)		1.74

where

L<sup>1</sup> = ligand derived by condensation of acetylacetone with 2-aminonicotinic acid (1:2)

L<sup>2</sup> = ligand derived by condensation of benzoylacetone with 2-amino-3-hydroxypyridine (1:2)

L<sup>3</sup> = ligand derived by condensation of benzoylacetone with 2-aminobenzoic acid (1:2)

L<sup>4</sup> = ligand derived by condensation of benzoylacetone with 2-aminonicotinic acid (1:2)

L<sup>5</sup> = ligand derived by condensation of thenoyltrifluoroacetone with 2-amino-3-hydroxypyridine (1:2)

L<sup>6</sup> = ligand derived by condensation of thenoyltrifluoroacetone with 2-aminobenzoic acid (1:2)

L<sup>7</sup> = ligand derived by condensation of thenoyltrifluoroacetone with 2-aminonicotinic acid (1:2)

L<sup>8</sup> = ligand derived by condensation of dibenzoylmethane with 2-amino-3-hydroxypyridine (1:2)

L<sup>9</sup> = ligand derived by condensation of dibenzoylmethane with 2-aminobenzoic acid (1:2)

L<sup>10</sup> = ligand derived by condensation of dibenzoylmethane with 2-aminonicotinic acid (1:2)

of the azomethine groups to the vanadium.<sup>15-17</sup> The band at around 300 cm<sup>-1</sup> may be assigned to  $\nu(\text{V-N})$  vibration.<sup>17</sup> The  $\nu_{\text{asym}}(\text{OCO})$  and  $\nu_{\text{sym}}(\text{OCO})$  stretching vibrations of free carboxyl groups are normally observed at ca. 1530 cm<sup>-1</sup> and 1415 cm<sup>-1</sup>, respectively, giving a  $\Delta(\text{OCO})$  value of 115 cm<sup>-1</sup>, which is lower than that of the oxovanadium(IV) complexes occurring at ca. 1560 cm<sup>-1</sup> and 1425 cm<sup>-1</sup> giving a  $\Delta(\text{OCO})$

value of  $135\text{ cm}^{-1}$ . Such an increase in the  $\Delta(\text{OCO})$  value in vanadyl complexes supports the monodentate coordination of the carboxyl group.<sup>18</sup> The oxovanadium(IV) complexes show a band at around  $980\text{ cm}^{-1}$ , which is assigned to  $\nu(\text{V}=\text{O})$  vibration. The absence of an ionic sulfate group in the complexes is confirmed by the disappearance of 3 bands at ca.  $1130\text{-}1135\text{ cm}^{-1}$  ( $\nu_3$ )  $955\text{-}960\text{ cm}^{-1}$  ( $\nu_1$ ), and  $600\text{-}610\text{ cm}^{-1}$  ( $\nu_4$ ).

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

Complex	Bands ( $\text{cm}^{-1}$ )				
	$\nu(>\text{C}=\text{N})$	$\nu(\text{V}-\text{N})$	$\nu(>\text{V}=\text{O})$	$\nu_{asym}(\text{O}-\text{C}-\text{O})$	$\nu_{sym}(\text{O}-\text{C}-\text{O})$
[VO(L <sup>1</sup> )]	1625	302	978	1530	1415
[VO(L <sup>2</sup> )]	1622	302	981	1528	1414
[VO(L <sup>3</sup> )]	1620	301	981	1532	1416
[VO(L <sup>4</sup> )]	1618	300	979	1528	1413
[VO(L <sup>5</sup> )]	1620	301	981	1532	1416
[VO(L <sup>6</sup> )]	1618	300	982	1529	1414
[VO(L <sup>7</sup> )]	1616	301	980	1526	1412
[VO(L <sup>8</sup> )]	1618	300	979	1528	1413
[VO(L <sup>9</sup> )]	1622	302	980	1530	1415
[VO(L <sup>10</sup> )]	1618	300	979	1528	1413

## Electronic spectra

The electronic spectra show bands in the regions  $11,040\text{-}11,980\text{ cm}^{-1}$ ,  $15,035\text{-}15,910\text{ cm}^{-1}$ , and  $21,080\text{-}22,380\text{ cm}^{-1}$ . These spectra are similar to those of other 5-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, 5-coordinate square pyramidal oxovanadium(IV) complexes.<sup>19,20</sup> Accordingly, the observed bands can be assigned to  ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ ,  ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ , and  ${}^2\text{B}_2 \rightarrow {}^2\text{A}_2$  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.<sup>21</sup>

## Molar conductance measurements

The molar conductivity ( $\Lambda_M$ ) values of all the oxovanadium(IV) complexes were measured in dimethylformamide and the obtained values are between  $120\text{-}138\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$  indicating their 1:1 electrolytic nature.

## Magnetic moment measurements

Magnetic moments of oxovanadium(IV) complexes were measured at room temperature and the values are given in Table 1. The magnetic moments of complexes were in the range  $1.71\text{-}1.76\text{ B.M.}$ , which correspond to a single electron of the  $d^1$ -system of square-pyramidal oxovanadium(IV) center.<sup>20</sup>

## ESR spectra

The X-band ESR spectra of an oxovanadium(IV) complexes were 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, Sand, and Ando *et al.*<sup>22-24</sup> The room temperature ESR spectra show 8 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 center in the complex. Isotropy is observed due to rapid tumbling of molecules in solution at room temperature and only g-average values are obtained. Anisotropy is clearly visible in the spectra at liquid nitrogen temperature and 8 bands each due to  $g_{||}$  and  $g_{\perp}$  are observed separately, which are in good agreement for a square pyramidal structure<sup>25-27</sup>. The  $g_{||}$ ,  $g_{\perp}$ ,  $A_{||}$ , and  $A_{\perp}$  values are measured from the spectra, which are in good agreement for a square-pyramidal structure. The giso 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, tentative structures are proposed for these oxovanadium(IV) complexes as Type I, II, and III in the reaction scheme.

## Conclusions

The spectral data show that tetradentate ligands derived by condensation of  $\beta$ -diketones with 2-amino-3-hydroxypyridine or 2-aminobenzoic acid or 2-aminonicotinic acid are versatile chelating agents. 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, ESR, and electronic data support a square pyramidal structure for all oxovanadium(IV) complexes.

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