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## Synthesis, structure and characterization of oxovanadium(IV) Schiff base complexes with tetradentate macrocyclic ligands

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### ABSTRACT

Two types of new oxovanadium(IV) complexes having general formula [VO(mac)]SO<sub>4</sub> were designed and synthesized using vanadyl ion as template with ligands derived from condensation of 2,2'-pyridil or 1,1'-oxalyldiimidazole with 2,3-diamino-5-bromopyridine and their reactions with  $\beta$ -diketones such as acetylacetone, bezoylacetone, thenoyltrifluoroacetone and dibenzoylmethane are carried out to get macrocyclic complexes. Tentative structures of the complexes have been proposed on the basis of elemental analyses, molar conductance, magnetic moments and spectral (infrared, electronic and electron spin resonance) data. All the oxovanadium(IV) complexes are five coordinate wherein the ligands act as tetradentate chelating agents.

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**Keywords:** Vanadyl ion,  $\beta$ -Diketones, Condensation, template.

### 1. INTRODUCTION

The coordination chemistry of vanadium has been interesting since the discovery of vanadium in organisms such as certain ascidians and Amanita mushrooms and as a constituent of the cofactors in vanadate-dependent haloperoxidases and vanadium nitrogenases [1-4]. The literature contains several reports about oxovanadium(IV) complexes which show modulating activities on various enzymes [5]. Vanadium is found naturally in soil and water as a trace metal. Vanadium compounds in oxidation state IV and V exist in the environment and in biological systems. The biochemical aspects of oxovanadium(IV) complexes have further promoted the coordination chemistry of vanadium [6]. Vanadium is not only an important trace element for organisms but also the necessary element for human body [7]. Heyliger et al. first reported the insulin mimetic activity of oral vanadate in vivo in 1985 [8]. Since then, extensive studies have been carried out to explore vanadium chemistry, including the synthesis of novel complexes and their anti-diabetic activities both in vitro and in vivo [9–11]. Many clinical trials of vanadium compounds have also been reported [12–14] in which vanadium salts such as VOSO<sub>4</sub> and NaVO<sub>3</sub> were administered to diabetic patients. 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 have been studied but chemistry of vanadium complexes with macrocyclic ligands incorporating four nitrogen donor atoms

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resulting controlled geometry has received less attention [15-16]. Giving considerations to these facts, a new series of oxovanadium(IV) complexes have been prepared by condensation of 2,2'-pyridil or 1,1'-oxalyldiimidazole with 2,3-diamino-5-bromopyridine in 1:2 molar ratio in the presence of  $\text{VO}^{2+}$  cation as template. The reactions of these oxovanadium(IV) complexes with  $\beta$ -diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane have been carried out which lead to the formation of 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

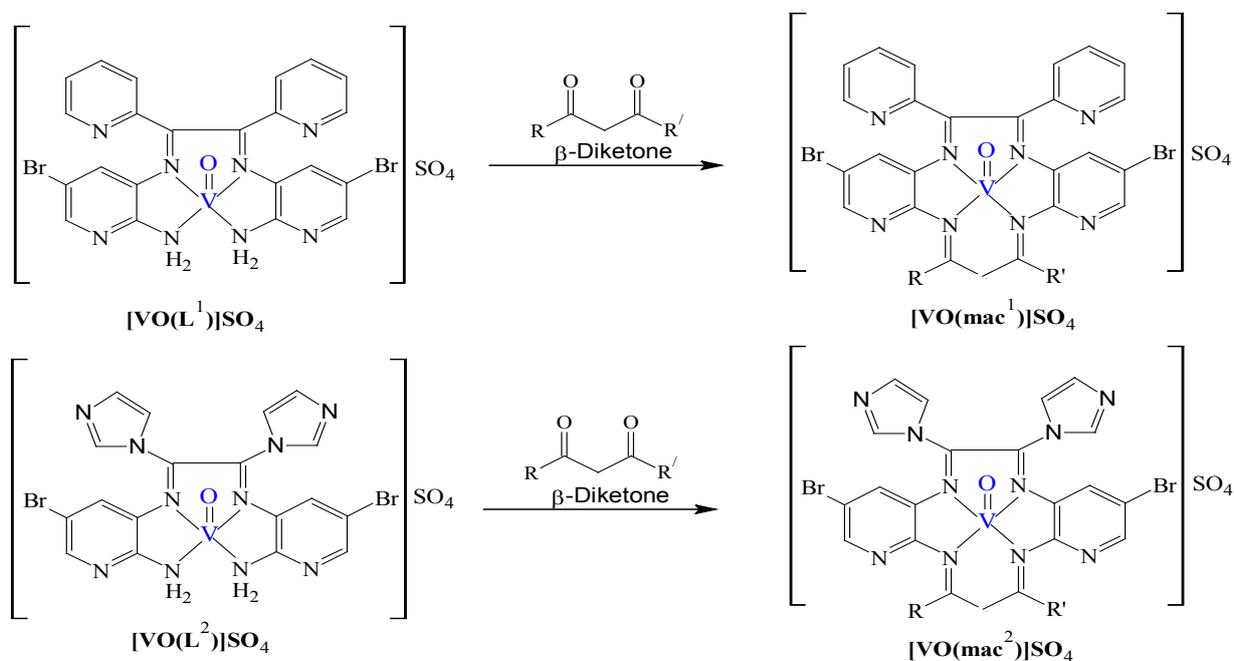
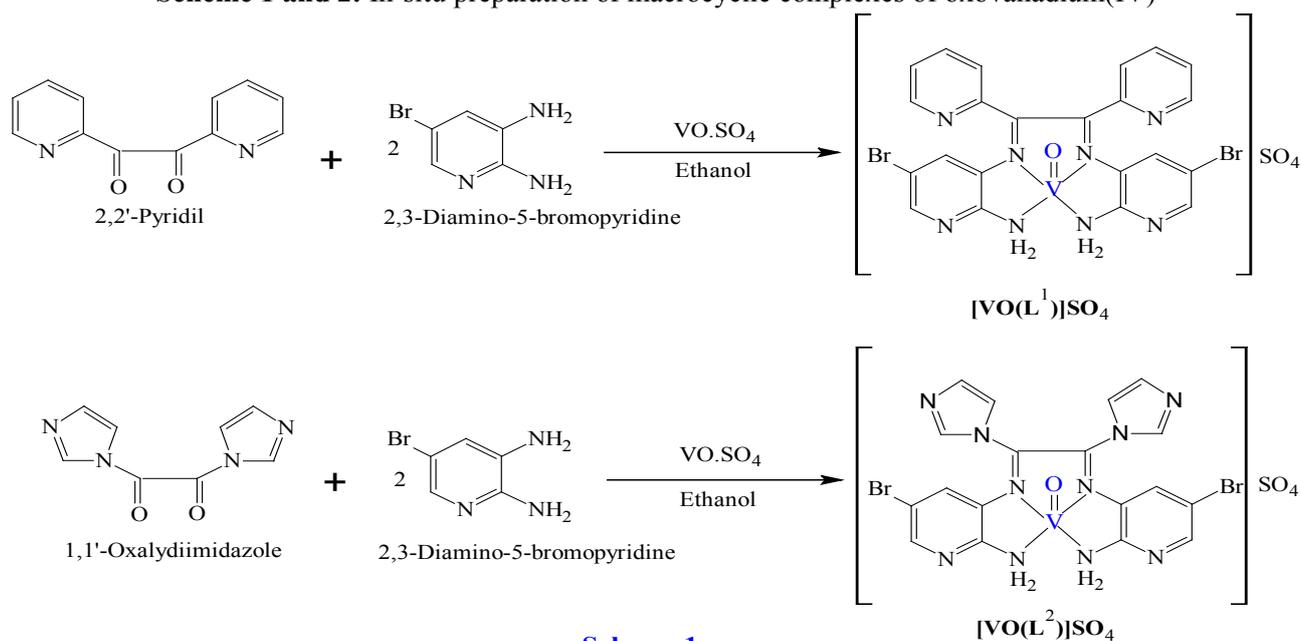
**2.1 Materials and Methods:** Oxovanadium(IV) sulfate was procured from Aldrich. The  $\beta$ -diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane were obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India and 2,2'-pyridil, 1,1'-oxalyldiimidazole and 2,3-diamino-5-bromopyridine used were Aldrich products.

**2.2 Analytical and Physical Measurements:** Vanadium was estimated gravimetrically as its vanadate, after decomposing the complex with concentrated nitric acid [17]. Sulfur was estimated as barium sulfate in the laboratory [18]. 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  $20^\circ\text{C}$ ), was used as calibrant. The electronic spectra of the complexes were recorded on Beckmann DU-2 spectrophotometer in the range 2000-185 nm. 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 recorded in KBr on Perkin-Elmer 621.

**2.3 In-situ preparation of oxovanadium(IV) complexes with ligands derived by condensation of 2,2'-pyridil or 1,1'-oxalyldiimidazole with 2,3-diamino-5-bromopyridine:** Vanadyl sulfate (0.002 mmol) dissolved in methanol (20 mL) was added to a refluxing solution mixture of 2,2'-pyridil or 1,1'-oxalyldiimidazole (0.002 mmol) with 2,3-diamino-5-bromopyridine (0.004 mmol) in ethanol (20 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 products were isolated. The complexes were thoroughly washed with methanol/ethanol mixture (1:1). The yield was 70 % (Scheme 1).

**2.3 In-situ preparation of macrocyclic complexes of oxovanadium(IV):** Vanadyl sulfate (0.002 mmol) dissolved in methanol (20 mL) was added to a refluxing solution mixture of 2,2'-pyridil or 1,1'-oxalyldiimidazole (0.002 mmol) with 2,3-diamino-5-bromopyridine (0.004 mmol) in ethanol (20 mL). The mixture was refluxed for 5 h to get the parent complex and to this reaction mixture, an ethanolic solution (10 mL) of acetylacetone (0.002 mmol) and glacial acetic acid (5 mL) were added. The reaction mixture was further allowed to react under mild reflux for about 4 h giving green precipitate. The complex was purified by the mixture (10 mL) of methanol/ethanol (1:1). The yield was found to be 60 % (Scheme 2).

## Scheme 1 and 2: In-situ preparation of macrocyclic complexes of oxovanadium(IV)



The above procedure was adopted for the synthesis of other oxovanadium(IV) macrocyclic complexes using benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane.

### 3. RESULTS SECTION

The oxovanadium(IV) complexes were synthesized using in-situ method by refluxing the reaction mixture of 2,2'-pyridil or 1,1'-oxalyldiimidazole with 2,3-diamino-5-bromopyridine and vanadyl sulfate in 1:2:1 molar ratio in aqueous ethanol.

#### 3.1 Physical and Analytical data of the vanadium complexes

$[VO(L^1)]SO_4$ : Yield: 62 %; decomp. temp. 212 °C; Anal. Calcd. for  $C_{22}H_{16}N_8VSO_5Br_2$ (%): C, 36.9; H, 2.3; N, 15.7; V, 7.1; S, 4.5. Found: C, 36.8; H, 2.2; N, 15.7; V, 7.1; S, 4.4. (FW 715.26).

$[VO(L^2)]SO_4$ : Yield: 64 %; decomp. temp. 211 °C; Anal. Calcd. for  $C_{18}H_{14}N_{10}VSO_5Br_2$ (%): C, 31.2; H, 2.0; N, 20.2; V, 7.4; S, 4.6. Found: C, 31.1; H, 1.9; N, 20.1; V, 7.3; S, 4.5. (FW 693.19).

$[VO(\text{mac}^{1A})]SO_4$ : Yield 65 %; decomp. temp. 218 °C; Anal. Calcd. for  $C_{27}H_{20}N_8VSO_5Br_2$ (%): C, 41.6; H, 2.6; N, 14.4; V, 6.5; S, 4.1. Found: C, 41.6; H, 2.5; N, 14.4; V, 6.5; S, 4.0. (FW 779.32).

$[VO(\text{mac}^{1B})]SO_4$ : Yield 62 decomp. temp. 217 °C; Anal. Calcd. for  $C_{32}H_{22}N_8VSO_5Br_2$ (%): C, 45.7; H, 2.6; N, 13.3; V, 6.1; S, 3.8. Found: C, 45.6; H, 2.5; N, 13.2; V, 6.0; S, 3.7. (FW 841.39).

$[VO(\text{mac}^{1C})]SO_4$ : Yield: 65 %; decomp. temp. 215 °C; Anal. Calcd. for  $C_{30}H_{17}N_8VS_2O_5Br_2F_3$ (%): C, 40.0; H, 1.9; N, 12.4; V, 5.7; S, 7.1. Found: C, 39.9; H, 1.8; N, 12.4; V, 5.6; S, 7.0. (FW 901.39).

$[VO(\text{mac}^{1D})]SO_4$ : Yield 67 %; decomp. temp. 220 °C; Anal. Calcd. for  $C_{37}H_{24}N_8VSO_5Br_2$ (%): C, 49.2; H, 2.7; N, 12.4; V, 5.6; S, 3.6. Found: C, 49.2; H, 2.6; N, 12.4; V, 5.6; S, 3.5. (FW 903.46).

$[VO(\text{mac}^{2A})]SO_4$ : Yield: 65 %; decomp. temp. 221 °C; Anal. Calcd. for  $C_{23}H_{18}N_{10}VSO_5Br_2$ (%): C, 36.5; H, 2.4; N, 18.5; V, 6.7; S, 4.3. Found: C, 36.4; H, 2.3; N, 18.4; V, 6.6; S, 4.2. (FW 757.28).

$[VO(\text{mac}^{2B})]SO_4$ : Yield: 67 %; decomp. temp. 217 °C; Anal. Calcd. for  $C_{28}H_{20}N_{10}VSO_5Br_2$ (%): C, 41.1; H, 2.5; N, 17.1; V, 6.2; S, 3.9. Found: C, 41.0; H, 2.4; N, 17.0; V, 6.2; S, 3.8. (FW 819.35).

$[VO(\text{mac}^{2C})]SO_4$ : Yield: 62 %; decomp. temp. 218 °C; Anal. Calcd. for  $C_{26}H_{15}N_{10}VS_2O_5Br_2F_3$ (%): C, 35.5; H, 1.7; N, 15.9; V, 5.8; S, 7.3. Found: C, 35.5; H, 1.6; N, 15.9; V, 5.8; S, 3.6. (FW 879.35).

$[VO(\text{mac}^{2D})]SO_4$ : Yield: 65 %; decomp. temp. 216 °C; Anal. Calcd. for  $C_{33}H_{22}N_{10}VSO_5Br_2$ (%): C, 45.0; H, 2.5; N, 15.9; V, 5.8; S, 4.2. Found: C, 44.9; H, 2.4; N, 15.9; V, 5.8; S, 3.5. (FW 881.42).

Where,  $L^1$  = Ligand derived by condensation of 2,2'-pyridil and 2,3-diamino-5-bromopyridine(1:2);  $L^2$  = Ligand derived by condensation of 1,1'-oxalydiimidazole and 2,3-diamino-5-bromopyridine (1:2);  $\text{Mac}^{1A}$  = macrocyclic ligand derived by condensation of  $L^1$  with acetylacetone;  $\text{Mac}^{1B}$  = macrocyclic ligand derived by condensation of  $L^1$  with benzoylacetone;  $\text{Mac}^{1C}$  = macrocyclic ligand derived by condensation of  $L^1$  with thenoyltrifluoroacetone;  $\text{Mac}^{1D}$  = macrocyclic ligand derived by condensation of  $L^1$  with dibenzoylmethane;  $\text{Mac}^{2A}$  = macrocyclic ligand derived by condensation of  $L^2$  with acetylacetone;  $\text{Mac}^{2B}$  = macrocyclic ligand derived by condensation of  $L^2$  with benzoylacetone;  $\text{Mac}^{2C}$  = macrocyclic ligand derived by condensation of  $L^2$  with thenoyltrifluoroacetone;  $\text{Mac}^{2D}$  = macrocyclic ligand derived by condensation of  $L^2$  with dibenzoylmethane. The elemental analyses of complexes show 1:1 metal to ligand stoichiometry.

**3.2 Infrared spectra.** The important bands of the infrared spectra for the complexes are listed in table. The macrocyclic complexes of oxovanadium(IV) exhibit  $>C=N$  absorption around 1620-1610  $\text{cm}^{-1}$ , which normally appears at 1660  $\text{cm}^{-1}$  in free ligands [19-21]. The lowering of this band in the complexes  $[VO(L^1)]SO_4$  and  $[VO(L^2)]SO_4$  indicate the coordination of nitrogen atoms of the azomethine groups to the vanadium[21-23]. The presence of a band around 302  $\text{cm}^{-1}$  may be assigned to  $\nu$  (V-N) vibration [24]. The presence of  $>C=N$  band and the absence of the  $>C=O$  band at around 1700  $\text{cm}^{-1}$  indicates the condensation of the diamines with the keto group of 2,2'-pyridil or 1,1'-oxalyliimidazoles[23]. The band appearing at 3345 and 3175  $\text{cm}^{-1}$  may be assigned to asymmetrical and symmetrical N-H stretching modes of the coordinated terminal amino group (Nonoyama et al) [25]. The oxovanadium(IV) complexes show a band at around 982  $\text{cm}^{-1}$ , which is assigned to  $\nu$  (V=O) vibration[26]. The presence of an ionic sulfate group in the complexes is indicated by the appearance of three bands at ca. 1130-1135  $\text{cm}^{-1}$  ( $\nu_3$ ), 955-960  $\text{cm}^{-1}$  ( $\nu_1$ ) and 600-610  $\text{cm}^{-1}$  ( $\nu_4$ ). The absence of a  $\nu_2$  band and non-splitting band of  $\nu_3$  band indicate the retention of tetrahedral symmetry [27]. The infrared spectra of macrocyclic complexes of the type  $[VO(\text{mac}^1)]SO_4$  and  $[VO(\text{mac}^2)]SO_4$  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 groups of  $\beta$ -diketones in cyclization reactions.

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

Complex	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{V}-\text{N})$	$\nu(\text{V}=\text{O})$	$\nu_3$ of $\text{SO}_4^-$	$\nu_1$ of $\text{SO}_4^-$	$\nu_4$ of $\text{SO}_4^-$	$\nu_{\text{asym}}(\text{N}-\text{H})$	$\nu_{\text{sym}}(\text{N}-\text{H})$
$[\text{VO}(\text{L}^1)]\text{SO}_4$	1620	300	980	1134	955	602	3352	3182
$[\text{VO}(\text{L}^2)]\text{SO}_4$	1624	302	982	1132	956	604	3350	3180
$[\text{VO}(\text{mac}^{1\text{A}})]\text{SO}_4$	1622	303	981	1135	958	606		
$[\text{VO}(\text{mac}^{1\text{B}})]\text{SO}_4$	1618	302	982	1134	956	604		
$[\text{VO}(\text{mac}^{1\text{C}})]\text{SO}_4$	1624	300	981	1135	960	606		
$[\text{VO}(\text{mac}^{1\text{D}})]\text{SO}_4$	1616	302	982	1135	958	602		
$[\text{VO}(\text{mac}^{2\text{A}})]\text{SO}_4$	1624	304	980	1134	956	606		
$[\text{VO}(\text{mac}^{2\text{B}})]\text{SO}_4$	1620	303	982	1132	958	602		
$[\text{VO}(\text{mac}^{2\text{C}})]\text{SO}_4$	1616	302	980	1135	960	606		
$[\text{VO}(\text{mac}^{2\text{D}})]\text{SO}_4$	1622	304	981	1134	955	608		

**3.3 Electronic spectra:** The electronic spectra show bands in the regions 11,040 – 11,980  $\text{cm}^{-1}$ , 15,035 - 15,910  $\text{cm}^{-1}$  and 21,080 – 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 [27] for distorted, five coordinate square pyramidal oxovanadium(IV) complexes [28]. 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  ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$  transitions, respectively. One more band is observed in the region 35,260 – 35,760  $\text{cm}^{-1}$ , which may be due to transition of the azomethine linkages [29].

**3.4 Molar conductance measurements:** The oxovanadium(IV) complexes are soluble in dimethylformamide and their molar conductivity ( $\Lambda_{\text{M}}$ ) values were measured in DMF and the obtained values are between 85-95  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  indicating their 1:1 electrolytic nature.

**3.4 Magnetic moment measurements:** Effective magnetic moments ( $\mu_{\text{eff}}$ ) values of oxovanadium(IV) complexes were measured at room temperature and the observed values were found in the range 1.71-1.75 B.M. which are in agreement to a  $3d^1$ -system of square-pyramidal oxovanadium(IV) centre [28].

**3.5 ESR spectra:** The X-band ESR spectra of 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, Tan and Ando et al [30-32]. 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 complexes. The anisotropy is not observed due to rapid tumbling of molecules in solution at room temperature and only g-average values at about 1.937 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 at about 1.931 and 1.971 separately which are in good agreement for a square pyramidal structure [33-35]. 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.

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 are proposed for these oxovanadium(IV) complexes of the type  $[\text{VO}(\text{L}^1)]\text{SO}_4$ ;  $[\text{VO}(\text{L}^2)]\text{SO}_4$ ;  $[\text{VO}(\text{mac}^1)]\text{SO}_4$  and  $[\text{VO}(\text{mac}^2)]\text{SO}_4$  respectively.

#### **4. CONCLUSIONS**

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The infra red spectral data show that the Schiff base condensation of keto group of 2,2'-pyridil or 1,1'-oxalyldiimidazole with amino group of 2,3-diamino-5-bromopyridine in the presence of oxovanadium(IV) takes place and the cyclisation reaction of these parent complexes with  $\beta$ -diketones such as acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane are achieved by virtue of template effect of oxovanadium(IV) cation in aqueous ethanol medium. Schiff bases behave as tetradentate ligands by coordinating to vanadyl 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 these complexes. The magnetic moment values, infrared, e.s.r. and electronic data are in agreement to the distorted square pyramidal structure for VO(IV) complexes.

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