Research Article

New Insights into the Chemistry of Oxovanadium(IV) Complexes with N₄ Coordinating Ligands

Ashok Kumar Yadava,¹ Hardeo Singh Yadav,¹ Uma Shanker Yadav,² and Devendra Pratap Rao³

¹ Department of Chemistry, North Eastern Regional Institute of Science and Technology (NERIST), Arunachal Pradesh, Nirjuli 791109, India
² Department of Chemistry, J.P. University, Bihar, Chapra 841301, India
³ Department of Chemistry, D.A.-V. College, Uttar Pradesh, Kanpur 208001, India

Correspondence should be addressed to Devendra Pratap Rao; devendraprataprao@yahoo.com

Received 2 September 2012; Accepted 24 September 2012

Academic Editors: W. Ding and S. B. Etcheverry

Copyright © 2013 Ashok Kumar Yadava et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The syntheses of new oxovanadium(IV) complexes having general formula [VO(mac)]SO₄ have been carried out by using in situ method of preparation where vanadyl ion acts as kinetic template for the ligands derived by condensation of 2,2'-pyridil with 1,2-diaminopropane and 1,3-diaminopropane. The complexes were characterized by elemental analyses, molar conductance, magnetic moments, and spectral (infrared, electronic, and electron spin resonance) data. All the oxovanadium(IV) complexes are five coordinate wherein derived ligands act as tetradentate chelating agents.

1. Introduction

Vanadium is widely distributed in the biosphere and its essential role has been recognized in both plants and animals. The oxovanadium(IV) cation has been found to inhibit the plasma membrane ATPase of Neurospora crassa and Saccharomyces cerevisiae, the proton translocating ATPase of Mycobacterium phlei and Ca³⁺-ATPase of red cell membranes [1–3]. It has been observed that the free vanadyl ion is oxidized to vanadate within a few minutes in aqueous solution exposed to air at neutral pH [4–6]. However, the tetravalent state appears to be stable when complexed with intracellular proteins or smaller molecules. Thus the complex formation of the oxovanadium(IV) cation with tetraaza ligands appears to be interesting, particularly in order to explore the biochemical importance of the oxovanadium(IV) cation in vitro at neutral pH [7–9]. The coordination chemistry of vanadium has great interest 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 [10, 11]. 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 [12–14]. Many clinical trials of vanadium compounds have also been reported [15–17], in which vanadium salts such as VOSO₄ and NaVO₃ were administered to diabetic patients.

With this view, the oxovanadium(IV) complexes of ligands derived from condensation of 2,2'-pyridil with diamines, namely, 1,2-diaminopropane and 1,3-diaminopropane are synthesized. These complexes are characterized by elemental analyses, molar conductance, magnetic susceptibility, and spectral data. The tentative structures of these oxovanadium(IV) complexes are also ascertained on the basis of above characterization.
2. Experimental

2.1. Materials. Oxovanadium(IV) sulfate was procured from Aldrich. The diamines used were reagent grade products. 2,2'-pyridil used was Aldrich product.

2.2. Analytical Methods and Physical Measurements. Vanadium was estimated gravimetrically as its vanadate after decomposing the complex with concentrated nitric acid [18]. Sulfur was estimated as barium sulfate using standard procedure [19]. 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), Hg[Co(CNS)₄], (χₐ = 16.44 × 10⁻⁶ c.g.s. unit at 20°C), was used as a standard. The electronic spectra of the complexes were recorded on C 810 Russian spectrophotometer instrument in the ranges 700–400 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 were recorded in the range 4000–200 cm⁻¹, were recorded in KBr on Perkin-Elmer 621 spectrophotometers.

2.3. In Situ Preparation of Oxovanadium(IV) Complexes with Ligands Derived by Condensation of 2,2'-Pyridil with 1,2-Diaminopropane or 1,3-Diaminopropane and Their Reactions with β-Diketones. Vanadyl sulfate (0.002 mmol) dissolved in methanol (25 mL) was added to a refluxing solution mixture of 2,2'-pyridil (0.002 mmol) with 1,2-diaminopropane (0.004 mmol) in ethanol (25 mL) and the reaction was allowed for 5 hours. Then the solvent was removed under vacuum at room temperature and the dark green color product was isolated. The complex was thoroughly washed with methanol/ethanol mixture. The yield was 64%. (Type I). The reaction mixture of I suspended in methanol/ethanol mixture was further reacted for 5 h with β-diketones such as acetylaceton or benzoylaceton or thienyltrifluoroacetone or dibenzoylmethane (1:1) to get macrocyclic products (Type II), which were isolated under vacuum and their purity was checked by TLC. The yield was found to be 60%. The similar procedure was adopted to prepare the oxovanadium(IV) complexes using 1,3-diaminopropane and solid products were isolated. The pH value of a stock solution of [VO(mac)]SO₄ was 10.2. 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 2,2'-pyridil with diamines and vanadyl sulfate in 1:2:1 molar ratio in aqueous ethanol. The reactions appear to proceeds according to Scheme 1.

3.1. Infrared Spectra. The important bands of the infrared spectra for the complexes are listed in Table 2. The complexes of oxovanadium(IV) exhibit >C=N absorption around 1618–1608 cm⁻¹, which normally appears at 1650 cm⁻¹ in free ligands [20–23]. The lowering of this band in the complexes (Type-I and II) indicates the coordination of nitrogen atoms of the azomethine groups to the VO³⁺ [23–25]. The presence of a band at around 300 cm⁻¹ may be assigned to υ(V=N) vibration [26]. The appearance of >C=N band and the absence of the >C=O band around 1710 cm⁻¹ is a conclusive evidence for condensation of the diamines with the two keto group of 2,2'-pyridil [25]. The bands appearing at 3350 and 3180 cm⁻¹ may be assigned to asymmetrical and symmetrical N-H stretching modes of the coordinated terminal amino group [27]. The oxovanadium(IV) complexes show a band at around 978–984 cm⁻¹, which is assigned to υ(V=O) vibration [28–30]. The presence of an ionic sulfate group in the complexes is confirmed by the appearance of three bands at ca. 1130–1135 cm⁻¹ (υ₁), 955–960 cm⁻¹ (υ₂), and 602–608 cm⁻¹ (υ₃). The absence of a υ₂ band and nonsplitting band of υ₃ band confirms that tetrahedral symmetry is retained [31].

3.2. Electronic Spectra. The electronic spectra show bands in the regions 11,040–11,980 cm⁻¹, 15,035–15,910 cm⁻¹, and 21,080–22,380 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. for distorted five coordinate square pyramidal oxovanadium(IV) complexes [32]. Accordingly, the observed bands can be assigned to 2B₂ → ⁴E, 2B₂ → ⁴B₁, and 2B₂ → ⁴A₂ transitions, respectively. One more band is observed in the region 35,260–35,760 cm⁻¹, which may be due to transition of the azomethine linkages [33].

3.3. Molar Conductance Measurements. The molar conductivity (Λₘ) values of all the oxovanadium(IV) complexes were measured in dimethylformamide and the obtained values lie between 95–105 ohm⁻¹ cm² mol⁻¹ indicating their 1:1 electrolytic nature.

3.4. Magnetic Moment Measurements. Magnetic moments of oxovanadium(IV) complexes were measured at room temperature and effective magnetic moment (μₑffective) 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 3d⁵ system of square-pyramidal oxovanadium(IV) [32].

3.5. ESR Spectra. The X-band ESR spectra of an oxovanadium(IV) complex was recorded in DMSO at room temperature and at nitrogen temperature (177 K). ESR spectra of the complexes were analyzed by the method of Mishra, Sand, and Ando et al. [34, 35]. The room temperature ESR
Table 1: Physical and analytical data of the complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Empirical formula</th>
<th>Decomp. temp. (°C)</th>
<th>% C Calcd. (found)</th>
<th>% H% Calcd. (found)</th>
<th>% N% Calcd. (found)</th>
<th>% V% Calcd. (found)</th>
<th>% S% Calcd. (found)</th>
<th>$\mu_{\text{eff}}$ BM (300°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[VO(L^1)]SO_4</td>
<td>C_{28}H_{24}N_6VSO_5</td>
<td>210</td>
<td>44.6 (44.3)</td>
<td>5.0 (4.9)</td>
<td>17.2 (17.2)</td>
<td>10.5 (10.5)</td>
<td>6.5 (6.4)</td>
<td>1.71</td>
</tr>
<tr>
<td>[VO(L^2)]SO_4</td>
<td>C_{18}H_{24}N_6VSO_5</td>
<td>212</td>
<td>44.6 (44.3)</td>
<td>5.0 (4.9)</td>
<td>17.2 (17.2)</td>
<td>10.5 (10.5)</td>
<td>6.5 (6.4)</td>
<td>1.72</td>
</tr>
<tr>
<td>[VO(mac^{a*})]SO_4</td>
<td>C_{23}H_{28}N_6VSO_5</td>
<td>216</td>
<td>50.1 (50.0)</td>
<td>5.1 (5.0)</td>
<td>15.2 (15.1)</td>
<td>9.2 (9.1)</td>
<td>5.8 (5.7)</td>
<td>1.72</td>
</tr>
<tr>
<td>[VO(mac^{b*})]SO_4</td>
<td>C_{28}H_{30}N_6VSO_5</td>
<td>212</td>
<td>54.8 (54.7)</td>
<td>4.9 (4.7)</td>
<td>13.7 (13.6)</td>
<td>8.3 (8.2)</td>
<td>5.2 (5.2)</td>
<td>1.72</td>
</tr>
<tr>
<td>[VO(mac^{c*})]SO_4</td>
<td>C_{26}H_{25}N_6VS_2O_5F_3</td>
<td>214</td>
<td>58.7 (58.6)</td>
<td>4.8 (4.8)</td>
<td>12.4 (12.3)</td>
<td>7.5 (7.4)</td>
<td>4.7 (4.6)</td>
<td>1.73</td>
</tr>
<tr>
<td>[VO(mac^{d*})]SO_4</td>
<td>C_{23}H_{28}N_6VSO_5</td>
<td>214</td>
<td>58.7 (58.6)</td>
<td>4.8 (4.8)</td>
<td>12.4 (12.3)</td>
<td>7.5 (7.4)</td>
<td>4.7 (4.6)</td>
<td>1.73</td>
</tr>
<tr>
<td>[VO(mac^{e*})]SO_4</td>
<td>C_{28}H_{30}N_6VSO_5</td>
<td>212</td>
<td>50.1 (50.0)</td>
<td>5.1 (5.0)</td>
<td>15.2 (15.2)</td>
<td>9.2 (9.1)</td>
<td>5.8 (5.7)</td>
<td>1.72</td>
</tr>
<tr>
<td>[VO(mac^{f*})]SO_4</td>
<td>C_{26}H_{25}N_6VS_2O_5F_3</td>
<td>214</td>
<td>58.7 (58.6)</td>
<td>4.8 (4.8)</td>
<td>12.4 (12.3)</td>
<td>7.5 (7.4)</td>
<td>4.7 (4.6)</td>
<td>1.73</td>
</tr>
<tr>
<td>[VO(mac^{g*})]SO_4</td>
<td>C_{33}H_{32}N_6VSO_5</td>
<td>218</td>
<td>58.7 (58.6)</td>
<td>4.8 (4.8)</td>
<td>12.4 (12.3)</td>
<td>7.5 (7.4)</td>
<td>4.8 (4.7)</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Where, L^1: ligand derived by condensation of 2,2'-pyridil with 1,2-diaminopropane (1:2); L^2: ligand derived by condensation of 2,2'-pyridil with 1,3-diaminopropane (1:2); Mac^{a*}: macrocyclic ligand derived by condensation of L^1 with acetylacetone; Mac^{b*}: macrocyclic ligand derived by condensation of L^1 with benzoylacetone; Mac^{c*}: macrocyclic ligand derived by condensation of L^1 with thenoyltriﬂuoroacetone; Mac^{d*}: macrocyclic ligand derived by condensation of L^1 with dibenzoylmethane; Mac^{e*}: macrocyclic ligand derived by condensation of L^2 with acetylacetone; Mac^{f*}: macrocyclic ligand derived by condensation of L^2 with benzoylacetone; Mac^{g*}: macrocyclic ligand derived by condensation of L^2 with thenoyltriﬂuoroacetone; Mac^{h*}: macrocyclic ligand derived by condensation of L^2 with dibenzoylmethane.

Table 2: Infrared spectral bands of complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$v (&gt;C=N)$ cm$^{-1}$</th>
<th>$v (V-N)$ cm$^{-1}$</th>
<th>$v (V=O)$ cm$^{-1}$</th>
<th>$v_1$ of SO$_4^{2-}$ cm$^{-1}$</th>
<th>$v_2$ of SO$_4^{2-}$ cm$^{-1}$</th>
<th>$v_3$ of SO$_4^{2-}$ cm$^{-1}$</th>
<th>$v_4$ of SO$_4^{2-}$ cm$^{-1}$</th>
<th>$v_{\text{asym}}$ (N–H) cm$^{-1}$</th>
<th>$v_{\text{sym}}$ (N–H) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[VO(L^1)]SO_4</td>
<td>1614</td>
<td>300</td>
<td>980</td>
<td>1133</td>
<td>956</td>
<td>602</td>
<td>3349</td>
<td>3178</td>
<td></td>
</tr>
<tr>
<td>[VO(L^2)]SO_4</td>
<td>1612</td>
<td>302</td>
<td>978</td>
<td>1134</td>
<td>955</td>
<td>604</td>
<td>3350</td>
<td>3179</td>
<td></td>
</tr>
<tr>
<td>[VO(mac^{a*})]SO_4</td>
<td>1610</td>
<td>302</td>
<td>982</td>
<td>1133</td>
<td>955</td>
<td>602</td>
<td>3350</td>
<td>3179</td>
<td></td>
</tr>
<tr>
<td>[VO(mac^{b*})]SO_4</td>
<td>1618</td>
<td>300</td>
<td>982</td>
<td>1135</td>
<td>956</td>
<td>608</td>
<td>3350</td>
<td>3180</td>
<td></td>
</tr>
<tr>
<td>[VO(mac^{c*})]SO_4</td>
<td>1610</td>
<td>303</td>
<td>981</td>
<td>1134</td>
<td>956</td>
<td>604</td>
<td>3349</td>
<td>3178</td>
<td></td>
</tr>
<tr>
<td>[VO(mac^{d*})]SO_4</td>
<td>1608</td>
<td>303</td>
<td>982</td>
<td>1134</td>
<td>955</td>
<td>606</td>
<td>3348</td>
<td>3179</td>
<td></td>
</tr>
<tr>
<td>[VO(mac^{e*})]SO_4</td>
<td>1610</td>
<td>302</td>
<td>984</td>
<td>1133</td>
<td>956</td>
<td>602</td>
<td>3348</td>
<td>3179</td>
<td></td>
</tr>
<tr>
<td>[VO(mac^{f*})]SO_4</td>
<td>1612</td>
<td>303</td>
<td>981</td>
<td>1133</td>
<td>955</td>
<td>604</td>
<td>3350</td>
<td>3180</td>
<td></td>
</tr>
<tr>
<td>[VO(mac^{g*})]SO_4</td>
<td>1618</td>
<td>302</td>
<td>984</td>
<td>1135</td>
<td>956</td>
<td>604</td>
<td>3349</td>
<td>3178</td>
<td></td>
</tr>
</tbody>
</table>

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 oxovanadium(IV) cation as the metallic center 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 $g_{||}$ and $g_\perp$ are observed separately which are in good agreement for a square pyramidal vanadyl complexes [36–38]. 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 $g_{\text{iso}}$ 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 following tentative structures may be proposed for these oxovanadium(IV) complexes of the type (I) and (II).

4. Conclusions

The spectral data show that the 2,2′-pyridil is a good chelating agents having two reactive carbonyl groups capable of undergoing Schiff base condensation with a variety of diamines. Schiff bases behave as tetradebate 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$^{2+}$ 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.

Acknowledgments

The authors are very much obliged to the Director, NERIST, Nirjuli, Itanagar, Arunachal Pradesh, India for providing laboratory facilities and to the Department of Chemistry for microanalysis of carbon, hydrogen, and nitrogen.

References


