



Chemistry of mixed-ligand methoxy bonded oxidovanadium(V) complexes with a family of hydrazone ligands containing VO³⁺ core and their substituent controlled methoxy-bridged dimeric forms

Bipul Mondal^a, Michael G.B. Drew^b, Rahul Banerjee^c, Tapas Ghosh^{a,*}

^a Department of Chemistry, Ramakrishna Mission Vivekananda Centenary College, Rahara, Kolkata 700 118, West Bengal, India

^b Department of Chemistry, The University of Reading, P.O. Box 224, Whiteknights, Reading RG6 6AD, UK

^c Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, United States

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ABSTRACT

[V^{IV}O(acac)₂] reacts with an equimolar amount of benzoyl hydrazones of 2-hydroxyacetophenone (H₂L¹), 2-hydroxy-5-methylacetophenone (H₂L²) and 5-chloro-2-hydroxyacetophenone (H₂L⁴) in methanol to afford the penta-coordinated mixed-ligand methoxy bonded oxidovanadium(V) complexes [V^{VO}(L¹)(OCH₃)] (**1**), [V^{VO}(L²)(OCH₃)] (**2**), and [V^{VO}(L⁴)(OCH₃)] (**4**), respectively, whereas, the similar reaction with the benzoyl hydrazone of 2-hydroxy-5-methoxyacetophenone (H₂L³) producing only the hexa-coordinated dimethoxy-bridged dimeric complex [V^{VO}(L³)(OCH₃)₂] (**3A**). Similar type of hexa-coordinated dimeric analogue of **1** i.e., [V^{VO}(L¹)(OCH₃)₂] (**1A**) was obtained from the reaction of [V^{IV}O(acac)₂] with the equimolar amount of H₂L¹ in presence of half equivalent 4,4'-bipyridine in methanol while the decomposition of [V^{VO}(L²)(bipy)] complex in methanol afforded the dimeric analogue of **2** i.e., [V^{VO}(L²)(OCH₃)₂] (**2A**). All these dimeric complexes **1A–3A** react with an excess amount of imidazole in methanol producing the respective monomeric complex. The X-ray structural analysis of **1–3** and their dimeric analogues **1A–3A** indicates that the geometry around the vanadium center in the monomeric form is distorted square-pyramidal while that of their respective dimeric forms is distorted octahedral, where the ligands are bonded to vanadium meridionally in their fully deprotonated enol forms. Due to the formation of bridge, the V–O(methoxy) bond in the dimeric complexes is lengthened to such an extent that it becomes equal in length with the V–O(phenolate) bond in **3A** and even longer in **1A** and **2A**, which is unprecedented. The ¹H NMR spectra of the complexes **1A–3A** in CDCl₃ solution, indicates that these dimeric complexes are converted appreciably into their respective monomeric form. Complexes are electro-active displaying one quasi-reversible reduction peak near +0.25 V versus SCE in CH₂Cl₂ solution. The E_{1/2} values of the complexes show linear relationship with the Hammett parameter (σ) of the substituents. All these VO³⁺-complexes are converted to the corresponding complexes with V₂O₃⁴⁺ motif simply on refluxing them in acetone and to the complexes with VO₂⁺ motif on reaction with KOH in methanol.

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1. Introduction

During the past twenty-five years or so, there is a dramatic development of the vanadium chemistry because of discoveries of many physiological [1,2] and catalytic [3–6] activities of its compounds. The rich chemistry of vanadium in its +V state is probably due to its ability to exist in three different forms: viz. mononuclear VO³⁺ and VO₂⁺ motifs and dinuclear V₂O₃⁴⁺ motif. In a mixed-ligand system, a tridentate and a monodentate ligands along with the oxido atom would provide the penta-coordinated environment to the vanadium center and being the coordinative unsaturated,

such type of complexes should have a tendency to attain the hexa-coordinated environment either through the coordination of a solvent molecule or by the formation of bridge through a suitable coordinated ligand atom of the neighbouring molecule resulting its dimerization provided, the bond (sixth) energy exceeds the steric repulsive force. We are interested with the chemistry and structure of new alkoxo-bonded mixed-ligand oxidovanadium(V) complexes with tridentate ONO donor hydrazone ligands. A literature search on the methoxy bonded mixed-ligand oxidovanadium(V) complexes with tridentate dibasic ONO donor hydrazone ligands indicates that the complexes with higher basic ligands have a tendency for the formation of dimethoxy-bridged dimeric complex [7–9] while the complexes with relatively lower basic ligands are monomeric in nature where the vanadium is either hexa-coor-

* Corresponding author. Tel.: +91 03 3256 85674.

E-mail address: ictg_64@yahoo.co.in (T. Ghosh).

minated by the incorporation of one methanol (solvent) molecule [7,10–12] in its coordination sphere or remains penta-coordinated [8,12] (where the coordination of the solvent molecule is inhibited probably due to steric repulsion between the methyl group attached to the carbonyl carbon instead of a hydrogen atom in the aryloxy ring of the hydrazone ligand and the OH group of the solvent alcohol).

Such an observation indicates that there should be ligands of intermediate basicity, which would be able to form both the penta-coordinated monomeric and the hexa-coordinated methoxy-bridged dimeric complexes. For this purpose, a family of tridentate ligands with varying basicity will be ideal and on this ground, the hydrazone ligands derived from the condensation of aliphatic/aromatic acid hydrazide with aromatic 2-hydroxycarbonyl compound containing a substitution in the aromatic ring may be suitable, where, the basic property of the ligands can be finely tuned through the incorporation of suitable substituent. With a view to searching for suitable ligand(s) of borderline basicity, we have chosen the benzoyl hydrazones of 2-hydroxyacetophenone and its 5-substituted derivatives (H_2L^{1-4} , general abbreviation H_2L , Scheme 1) for this study. There are two reasons behind the selection of this family of ligands: (i) these hydrazone ligands contain two interme-

mediate basic phenolic and amide (which binds through their enol forms) groups, which are very suitable for the stabilization of +V state of vanadium [13–15] and (ii) due to presence of one methyl group with the carbonyl carbon (in stead of hydrogen in 2-hydroxybenzaldehyde), the coordination of solvent molecule is inhibited for steric reason. Utilizing this family of ligands we have been able to identify three suitable hydrazone ligands which are able to form both the methoxy bonded monomeric complexes and their dimethoxy-bridged dimeric analogues, which, to the best of our knowledge, represent the first report in this area. We also report the procedure for the transformation of these complexes to the corresponding complexes with $V_2O_3^{4+}$ and VO_2^+ motifs, which is important in connection with their catalytic activities. Such type of oxidovanadium(V)-alkoxide complexes are important due to their biological relevance [16] and also for their catalytic activities [17,18].

2. Experimental

2.1. Materials

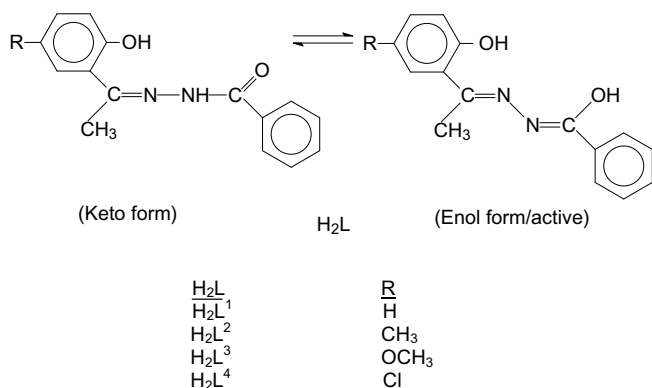
$[V^{IV}O(acac)_2]$ [19] and the hydrazone ligands (H_2L^{1-4}) [20] (Scheme 1) were prepared by the reported methods. Reagent grade solvents were dried and distilled prior to use. All other chemicals were reagent grade, obtained from commercial sources and used without further purification. Spectroscopic grade solvents were used for spectral measurements.

2.2. Synthesis of the complexes $[VO(L)(OCH_3)]$, (1)–(4)

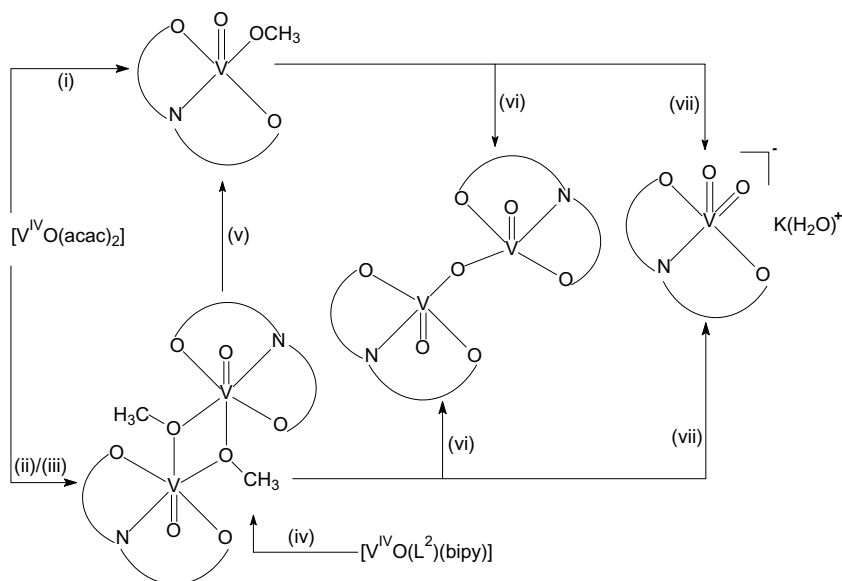
All these complexes except **3** were synthesized by a simple general method using $[V^{IV}O(acac)_2]$ (where $acac^-$ represents the acetyl acetonate ion) as the starting material (Scheme 2).

2.2.1. $[VO(L^1)(OCH_3)]$ (**1**)

A total of 0.254 g (1.0 mmol) of H_2L^1 was dissolved in 30 ml of methanol and 0.265 g (1.0 mmol) of $[V^{IV}O(acac)_2]$ was added to the ligand solution. The mixture was then heated under reflux for 2 h. A reddish brown solution was obtained which was kept



Scheme 1.



Scheme 2. (i) Heated under reflux in methanol with one equivalent H_2L^1 or H_2L^2 or H_2L^4 ; (ii) on heating under reflux in methanol with one equivalent H_2L^3 ; (iii) on heating under reflux in methanol with one equivalent H_2L^1 in presence of half-equivalent 4,4'-bipyridine; (iv) on keeping its methanol solution for ~7 days; (v) heated under reflux with the excess amount of imidazole in methanol; (vi) on heating under reflux in acetone; (vii) on reaction with the methanolic solution of KOH at slightly warm condition.

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