Inorganica Chimica Acta 362 (2009) 3303–3308

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, structure and solution chemistry of quaternary oxovanadium(V) complexes incorporating hydrazone ligands

Bipul Mondal [a], Michael G.B. Drew [b], 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

ARTICLE INFO

Article history:
Received 25 December 2008
Received in revised form 20 February 2009
Accepted 28 February 2009
Available online 9 March 2009

Keywords:
Quaternary oxovanadium(V) complexes
Methoxy bonded oxovanadium(V) complexes
Hydrazone complexes
Pyridine complexes
Crystal structure
Cyclic voltammetry

ABSTRACT

$[V^{IV}O(acac)_2]$ reacts with an equimolar amount of benzoyl hydrazone of 2-hydroxyacetophenone (H_2L^1) or 5-chloro-2-hydroxyacetophenone (H_2L^2) in the presence of excess pyridine (py) in methanol to produce the quaternary $[V^VO(L^1)(OCH_3)(py)]$ (**1**) and $[V^VO(L^2)(OCH_3)(py)]$ (**2**) complexes, respectively, while under similar condition, the benzoyl hydrazones of 2-hydroxy-5-methylacetophenone (H_2L^3) and 2-hydroxy-5-methoxyacetophenone (H_2L^4) afforded only the methoxy bridged dimeric $[V^VO(L^3/L^4)(OCH_3)]_2$ complexes. The X-ray structural analysis of **1** and **2** indicates that the geometry around the metal is distorted octahedral where the three equatorial positions are occupied by the phenolate-O, enolate-O and the imine-N of the fully deprotonated hydrazone ligand in its enolic form and the fourth one by a methoxide-O atom. An oxo-O and a pyridine-N atom occupy two axial positions. Quaternary complexes exhibit one quasi-reversible one-electron reduction peak near 0.25 V versus SCE in CH_2Cl_2 and they decompose appreciably to the corresponding methoxy bridged dimeric complex in $CDCl_3$ solution as indicated by their ^1H NMR spectra. These quaternary VO^{3+} complexes are converted to the corresponding $V_2O_3^{4+}$-complexes simply on refluxing them in acetone and to the VO_2^+-complexes on reaction with KOH in methanol. An equimolar amount of 8-hydroxyquinoline (Hhq) converts these quaternary complexes to the ternary $[V^VO(L)(hq)]$ complexes in $CHCl_3$.

1. Introduction

The relative stability of two commonly occurring oxo motifs of vanadium viz. VO^{2+} and VO^{3+} in its two biologically important oxidation states (viz. +IV and +V) depends upon the basicity of the coordinated ligand. As a part of our programme on the synthesis and characterization of new oxovanadium(IV/V) complexes with a family of benzoyl hydrazones of 2-hydroxyacetophenone and its 5-substituted derivatives (H_2L^{1-4}; general abbreviation H_2L, Scheme 1), we have seen that this set of ligands (containing two intermediate basic phenolic and amide moieties and one neutral imine moiety) are very suitable in stabilizing the VO^{3+} motif in binary [1,2] as well as mixed-ligand [3–6] systems (in the presence of an auxiliary ligand containing at least one phenolic or alcoholic moiety). The presence of only a neutral bidentate *N,N* donor auxiliary ligand viz. 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen), stabilizes the VO^{2+} motif [7]. We have already reported that the reaction of $[V^{IV}O(acac)_2]$ with an equimolar amount of H_2L in methanol yielded either monomeric $[V^VO(L^1/L^2/L^3)(OCH_3)]$ or dimethoxy bridged dimeric $[V^VO(L^4)(OCH_3)]_2$ complexes depending upon the nature of substituent in the aryloxy ring [6]. The methyl group associated with the imine carbon in these ligands may be responsible in some way in discouraging the coordination of solvent methanol molecule at the axial position *trans* to vanadyl oxygen as such coordination is normally observed in the hydrazone complexes containing 2-hydroxybenzaldehyde instead of 2-hydroxyacetophenone, where the solvent alcohol molecule has been found to be coordinated with the vanadium [8–11]. We are interested in studying the above reaction in the presence of excess amount of pyridine (a weak basic ligand having $pK_a = 5.48$ [12]) and to see whether the $[V^{IV}O(L)(py)_2]$ or $[V^VO(L)(OCH_3)(py)]$ complexes are formed. In fact, it has been found that H_2L^1 and H_2L^2 ligands yielded the $[V^VO(L^1/L^2)(OCH_3)(py)]$ complexes while the other two ligands viz. H_2L^3 and H_2L^4 afforded only $[V^VO(L^3/L^4)(OCH_3)]_2$ complexes without the formation of any $[V^{IV}O(L)(py)_2]$ complex. The quaternary hydrazone complexes reported here represent the very rare example [13] in this area. The procedures for the transformation of these quaternary complexes to the ternary complexes with VO^{3+} and also to the corresponding binary complexes with $V_2O_3^{4+}$ and VO_2^+ motifs have also been described here which is important in connection with their catalytic activities. Such type of oxovanadium(V)-alkoxide complexes is important due to their biological relevance [14] and also for their catalytic activities [15,16].

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* Corresponding author. Tel.: +91 03325685674.
E-mail address: ictg_64@yahoo.co.in (T. Ghosh).

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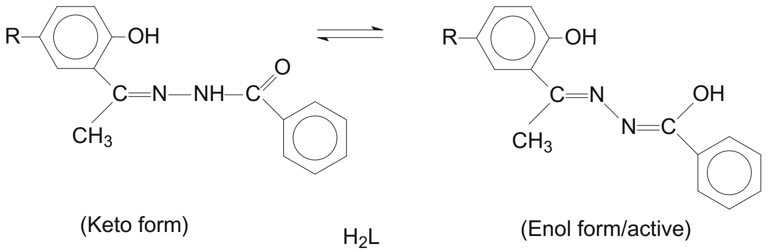
doi:10.1016/j.ica.2009.02.043



H_2L	R
H_2L^1	H
H_2L^2	Cl
H_2L^3	CH_3
H_2L^4	OCH_3

Scheme 1.

2. Experimental

2.1. Materials

$[V^{IV}O(acac)_2]$ [17] and the hydrazone ligands (H_2L^{1-4}) [3] (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 $[V^VO(L)(OCH_3)(py)]$ (**1**) and (**2**)

These two complexes were synthesized by a simple general method using $[V^{IV}O(acac)_2]$ as the starting material.

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

To a methanolic solution (20 cm^3) of $[V^{IV}O(acac)_2]$ (0.265 g, 1 mmol) was added a methanolic solution (20 cm^3) of H_2L^1 (0.254 g, 1 mmol) with stirring. To this solution ~1 cm^3 pyridine was added and the mixture was heated under reflux for 1 h and the resulting solution was kept for slow evaporation at room temperature. Brown crystals of **1**, suitable for X-ray diffraction analysis were obtained which were collected by filtration after washing with methanol and dried over silica gel. Yield: 0.36 g (84%). *Anal.* Calc. for $C_{21}H_{20}N_3O_4V$ (429.34): C, 58.69; H, 4.66; N, 9.78. Found: C, 58.63; H, 4.64; N, 9.77%. Selected IR data (cm^{-1}): $\nu = 1588$ (s, $C{=}N_{azomethine}$); 1249 (s, $C–O_{enolate}$); 1060 (m, N–N); 962 (s, V=O). ^1H NMR (300 MHz; $CDCl_3$): $\delta = 7.03–7.18$ (m, 3H, H-3, H-5, H-13); 7.49–7.52 (m, 1H, H-4); 7.84–7.88 (m, 1H, H-6); 2.96 (s, 3H, 3 × H-8); 7.53–7.56 (m, 2H, H-11, H-15); 7.23–7.25 (m, 2H, H-12, H-14); [3.46 (s, H-16) + 5.28 (s, H-16(bridged)), total 3H, 4:7]; 8.58 (d, 2H, H-17, H-21, $J = 4.1$ Hz); 7.44–7.47 (m, 2H, H-18, H-20); 8.17 (d, 1H, H-19, $J = 6.7$ Hz) ppm. UV–Vis (CH_2Cl_2): λ_{max} (ε, $dm^3\ mol^{-1}\ cm^{-1}$) = 373^{sh} nm (11366), 325 nm (17940).

2.2.2. $[V^VO(L^2)(OCH_3)(py)]$ (**2**)

Complex **2** was also prepared similarly to **1**, replacing H_2L^1 by H_2L^2. Yield: 0.38 g (82%). *Anal.* Calc. for $C_{21}H_{19}ClN_3O_4V$ (463.78): C, 54.34; H, 4.10; N, 9.06. Found: C, 54.32; H, 4.07; N, 9.04%. Selected IR data (cm^{-1}): $\nu = 1586$ (s, $C{=}N_{azomethine}$); 1240 (s, $C–O_{enolate}$); 1060 (m, N–N); 962 (s, V=O). ^1H NMR (300 MHz; $CDCl_3$): $\delta = 7.07–7.10$ (m, 1H, H-3); 7.55–7.72 (m, 3H, H-4, H-11, H-15); 7.77 (d, 1H, H-6, $J = 0.8$ Hz); 2.91 (s, 3H, 3 × H-8); 7.36–7.46 (m, 4H, H-12, H-14, H-18, H-20); 7.22–7.24 (m, 1H, H-13); [3.45 (s, H-16) + 5.34 (s, H-16 (bridged)), total 3H, 6:13]; 8.57 (d, 2H, H-17, H-21, $J = 3.80$ Hz); 8.15 (d, 1H, H-19, $J = 6.8$ Hz) ppm. UV–Vis (CH_2Cl_2): λ_{max} (ε, $dm^3\ mol^{-1}\ cm^{-1}$) = 382^{sh} nm (9143), 321 nm (16360).

Under similar reaction condition, the H_2L^3 and H_2L^4 ligands yielded only $[V^VO(L^3/L^4)(OCH_3)]_2$ complexes (confirmed from their IR and NMR spectra) which were synthesized by using different method and reported very recently [6].

2.3. Conversion of these quaternary VO^{3+} complexes to the ternary VO^{3+} complexes

The conversions of these quaternary VO^{3+} complexes to the corresponding ternary complexes were done by using a simple general method and for this reason only one representative method is described here.

2.3.1. Conversion to $[V^VO(L^1)(hq)]$ complex

To the chloroform solution (30 cm^3) of $[VO(L^1)(OCH_3)(py)]$ (**1**) (0.100 g, 0.23 mmol) was added chloroform solution (5 cm^3) of 8-hydroxyquinoline (0.035 g, 0.23 mmol) at room temperature. It was then stirred for 1 h. A deep violet solution was obtained which was kept for slow evaporation at room temperature. A shiny black microcrystalline solid was obtained. Yield: 88%. This compound was found to be identical in all respects (confirmed from its IR, NMR and UV–Vis spectra) with the recently reported $[V^VO(L^1)(hq)]$ complex [3] (synthesized by using different method).

2.4. Conversion of these quaternary VO^{3+} complexes to the complexes with $V_2O_3^{4+}$ motif

These quaternary VO^{3+} complexes smoothly transformed to the complexes with $V_2O_3^{4+}$ motif on refluxing them in acetone and a representative method is described below.

2.4.1. Conversion to $[V_2O_3(L^1)_2]$

0.100 g (0.23 mmol) of $[VO(L^1)(OCH_3)(py)]$ (**1**) was dissolved in 40 ml acetone on warming. The solution was then heated under reflux for 2 h and the resulting red-brown solution was kept for slow evaporation at room temperature. A deep brown microcrystalline compound was obtained. Yield: 85%. This compound was found to be identical in all respects (confirmed from its IR and NMR spectra) with the $[V_2O_3(L^1)_2]$ complex which was synthesized by using different method [1].