Polyhedron 27 (2008) 2233–2242

Contents lists available at ScienceDirect

Polyhedron

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

Novel supramolecular network in tri- and mono-nuclear oxovanadium(V)-salicyl-hydroximate: Synthesis, structure and catalytic oxidation of hydrocarbons using H_2O_2 as terminal oxidant

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ARTICLE INFO

Article history:
Received 20 January 2008
Accepted 31 March 2008
Available online 24 June 2008

Keywords:
Vanadium(V) complexes
Salicylhydroximates
Supramolecular structure
Hydrocarbon oxidation
Hydrogen peroxide

ABSTRACT

Two oxovanadium(V) salicylhydroximate complexes, $[VO(SHA)(H_2O)] \cdot 1.58H_2O$ (**1**) and $[V_3O_3(CSHA)_3(H_2O)_3] \cdot 3CH_3COCH_3$ (**2**) have been synthesized by reaction of VO_4^{3-} with *N*-salicyl hydroxamic acid ($SHAH_3$) and *N*-(5-chlorosalicyl) hydroxamic acid ($CSHAH_3$), respectively, in methanol medium. Compound **1** on reaction with pyridine 2,6-dicarboxylic acid ($PyDCH_2$) yields mononuclear complex $[VO(SHAH_2)(PyDC)]$ (**3**). Treatment of compound **3** with hydrogen peroxide at low pH (2-3) and low temperature (0–5 °C) yields a stable oxoperoxovanadium(V) complex $H[VO(O_2)(PyDC)(H_2O)] \cdot 2.5H_2O$ (**4**). All four complexes (**1**–**4**) have been characterized by spectroscopic (IR, UV–Vis, ^{51}V NMR) and single crystal X-ray analyses. Intermolecular hydrogen bonds link complex **1** into hexanuclear clusters consisting of six $\{VNO_5\}$ octahedra surrounded by twelve $\{VNO_5\}$ octahedra to form an annular ring. While the molecular packing in **2** generates a two-dimensional framework hydrogen bonds involving the solvent acetone molecules, the mononuclear complexes **3** and **4** exhibit three-dimensional supramolecular architecture. The compounds **1** and **2** behave as good catalysts for oxygenation of benzylic, aromatic, carbocyclic and aliphatic hydrocarbons to their corresponding hydroxylated and oxygenated products using H_2O_2 as terminal oxidant; the process affords very good yield and turnover number. The catalysis work shows that cyclohexane is a very easily oxidizable substrate giving the highest turnover number (TON) while *n*-hexane and *n*-heptane show limited yield, longer time involvement and lesser TON than other hydrocarbons.

1. Introduction

Activation of C–H bond is one of the challenging problems in homogeneous catalysis research since it involves conversion of crude oil and natural gas constituents into oxygenated derivatives such as alcohols or carbonyl compounds. In this respect dioxygen and hydrogen peroxide are two most useful oxidants from economic and environmental standpoints [1–3]. Interest in oxovanadium(V) chemistry has recently been accelerated due to high potentiality of dioxygen activation along with the ability of oxo-peroxo vanadium(V) species to function as important intermediates in the in vivo enzymatic processes [4–7]. Also synthetic oxoperxovanadium(V) complexes are known to exhibit stoichiometric and in some cases catalytic oxidation of various organic substrates to their oxidized products [8–10]. Mimoun et al. [11] reported oxovanadium(V) peroxo complexes of the types $[VO(O_2)(O–N)(L)]$ and $[VO(O_2)(O–N)_2]^-$, where L = solvent molecule; O–NH = pyridine 2-carboxylic acid and pyrazine 2-carboxylic acid and the complexes were shown to be good oxidizing agents for the stoichiometric hydroxylation of aromatic hydrocarbons. The first catalytic hydrocarbon oxidation using oxovanadium(V) compounds was furnished by Shul'pin et al. [12] using the Mimoun type compounds [11]. Using those catalysts Shul'pin et al. [13] also succeeded in the oxidation of methane to methanol, formaldehyde or formic acid with tertiary butyl hydroperoxides (TBHP) as oxidant [14]. Remias et al. [8] reported oxidation of benzene and cyclohexane using $[V(acac)_3]$, $[VO(acac)_2]$ and $[VO(O_2)(2\text{-picolinate})(H_2O)_2]$ as catalysts and H_2O_2 as oxidant. We described [15] the synthesis and crystal structure of a hydroxamato[1] complex, namely $[VO(BPHA)_2(Cl)]$; (BPHAH = *N*-benzoyl *N*-phenyl hydroxamic acid [16]) which was shown to act as catalyst for the oxidation of wide variety of hydrocarbons. Besides, being good analytical reagents [17,18] and having siderophoric role, the hydroxamic acids are also important for numerous biological functions [19]. In this paper, we report the

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[1] Fisher et al. (D.C. Fisher, S.J. Barclay-Peet, C.A. Balfe, K.N. Raymond, Inorg. Chem. 28 (1989) 4399, isolated and structurally characterized a couple of hydroximato (derived from primary hydroxamic acid where one of the hydroxylamine protons is substituted) complexes but erratically described as hydroxamato complexes.

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doi:10.1016/j.poly.2008.03.031

synthesis, spectroscopic and structural characterization of salicylhydroximato-oxovanadium(V) complexes, $[VO(SHA)(H_2O)] \cdot 1.58H_2O$ (**1**) and $[V_3O_3(CSHA)_3(H_2O)_3] \cdot 3CH_3COCH_3$ (**2**) ($SHAH_3$ = *N*-salicyl hydroxamic acid and $CSHAH_3$ = *N*-(5-chlorosalicyl) hydroxamic acid along with their catalytic properties in functionalization of hydrocarbons. This work also reports the synthesis and structural characterization of two mononuclear oxovanadium(V) complexes, $[VO(SHAH_2)(PyDC)]$ (**3**) and the other is a peroxovanadium(V) complex $H[VO(O_2)(PyDC)(H_2O)] \cdot 2.5H_2O$ (**4**), [20]. Complex **3** is obtained by reaction of complex **1** with $PyDCH_2$ and is the second example of an oxovanadium(V) complex containing uninegetive bidentate (O,O donor) salicylhydroximate ligands [21,22] whereas complex **4** is obtained by the reaction of **3** with hydrogen peroxide. Notably, oxoperoxovanadium(V) complexes with $PyDC^{2-}$ ligand [23] exhibits poor catalytic properties in the oxidation of hydrocarbons due to their unusual stability.

2. Experimental

2.1. Physical measurements

The IR spectra were recorded as KBr pallets on a Nicolet 520 FTIR spectrometer and Electronic spectra on a Hitachi U-3410 UV–Vis–NIR spectrophotometer. ^1H NMR spectra was measured in $CDCl_3$ on a Bruker AM 360 (300 MHz) FT NMR spectrometer using TMS as an internal standard. The 51 V NMR was recorded in CD_3CN on a GEOL 400 MHz NMR spectrometer and a systronics (India) model 335 digital conductivity bridges where a bottle type cell was used to determine the molar conductance values of the isolated complexes at 25 °C using a thermostatic arrangement. The magnetic susceptibilities at 298 K were obtained by the Gouy method using $Hg[Co(NCS)_4]$ as a standard. Elemental analyses were performed with the help of a Perkin–Elmer 240C elemental analyzer. GLC measurements were done in an Agilent model 6890N gas chromatograph using HP-1 and INNOWAX capillary column in FID mode with dinitrogen as carrier gas.

2.2. Materials

Ammonium metavanadate and hydroxylamine hydrochloride were of extrapure variety and obtained from Sisco Research Laboratory (India). Methyl Salicylate was obtained from S.D. Fine-Chem. Ltd (India). 5-Chloro salicylic acid and 2,6-pyridine dicarboxylic acid ($PyDCH_2$) were obtained from Aldrich Chemicals. Potassium hydroxide pellets and methanol (G.R.) were the products of E. Merck (India) and were directly used. Ethanol (95%) was obtained from Bengal Chemical and Pharmaceutical Works (Calcutta), and was lime distilled before use. All other chemicals needed were obtained from E. Merck (India). *N*-Salicyl hydroxamic acid ($SHAH_3$) and *N*-(5-chloro salicyl) hydroxamic acid ($CSHAH_3$) were synthesized following the literature method [16]. Acetonitrile, dichloromethane and acetone were further purified by the literature method [24] for physico-chemical studies. Iolar II grade dioxygen, dihydrogen, zero air, and dinitrogen gas used for chromatographic analysis were obtained from Indian Refrigeration Stores, Calcutta. Cyclohexane and ethylbenzene were obtained from S.D. Fine-Chem. Ltd (India) while cyclohexanol, cyclohexanone, tetralin and tetralone were obtained from Sisco Research Laboratory, India (extrapure AR grade). Toluene, benzene, *n*-hexane, *n*-heptane and *n*-pentane, diphenylmethane, *n*-heptanol, *n*-hexanol, *n*-pentanol, benzaldehyde and phenol were obtained from E. Merck (India) (G.R grade). Triply distilled (all glass) water was used whenever necessary. All the solvents used for chromatographic analysis were either of HPLC, spectroscopic, or GR grade and in all cases their purity was confirmed by GC analysis before use.

2.3. Preparation of the complexes

2.3.1. $[VO(H_2O)(SHA)] \cdot 1.58H_2O$ (**1**) and $[V_3O_3(H_2O)_3(CSHA)_3] \cdot 3CH_3COCH_3$ (**2**)

NH_4VO_3 (0.586 g, 5 mmol) was dissolved in 15 mL of distilled water by stirring at 40–55 °C. The pH of the solution was adjusted at 3–4 by adding 4(M) HCl. $SHAH_3$ (0.76 g, 5 mM; 0.94 g $CSHAH_3$ for compound **2**) was dissolved in minimum volume of methanol (ca.15 mL) and the resulting solution was added to vanadate solution, with stirring (15 min) when the solution becomes deep blue which was kept at room temperature. After 2–3 days, deep blue cubes separated. The crystals were collected (for **1**), washed off with distilled water and dried in vacuo. Yield: 1.05 g (77.5%). *Anal.* Calc. for $C_7H_6NO_{6.58}V$: C, 32.25; H, 2.32; N, 5.41; V, 19.60. Found: C, 32.03; H, 2.43; N, 5.10; V, 19.15%. IR (KBr disc, cm^{-1}): 3441(broad), 1626(w), 1598(s): ν(C=O), 1566(w), 1468(s), 1365(s), 1240(m), 1157(w), 1108(w), 1044(w), 971(s): ν(V=O), 757(m), 678(m), 644(m), 582(w), 508(w), 451(w). ^{51}V NMR (105.03 MHz, CD_3CN, 296 K): δ ppm, −236.58. UV–Vis, λ_{max} nm (ε $M^{-1}cm^{-1}$): 625(18 380), 493(sh), 294(34 690), 247(sh). The crude compound (**2**) was recrystallized by slow diffusion of acetone solution of the compound in light petroleum (40–60 °C). Yield: 1.2 g (73%). *Anal.* Calc. for $C_{30}H_{33}Cl_3N_3O_{18}V_3$: C, 36.6; H, 3.38; N, 4.27; Cl, 10.83; V, 15.56. Found: C, 36.47; H, 3.40; N, 4.16; Cl, 11.42; V, 15.13%. IR (KBr disc, cm^{-1}): 3367(broad), 1627(w), 1596(s): ν(C=O), 1556(w), 1500(s), 1458(s), 1429(m), 1334(s), 1294(m), 1230(m), 1161(w), 1122(w), 1051(w), 977(s) and 962(s): ν(V=O), 894(w), 862(w), 825(m), 763(w), 739(s), 669(w), 626(m), 601(w), 541(w), 499(w), 455(w), 375(w). UV–Vis λ_{max} nm (ε M^{-1} cm^{-1}): 629(14 360), 488(sh), 292(27 300), 239(35 700).

2.3.2. $[VO(SHAH_2)(PyDC)]$ (**3**)

Complex **1**, 0.403 g (0.5 mmol) was dissolved in methanol (25 mL) and 10 mL aqueous solution of $PyDCH_2$ (0.250 g, 1.5 mmol) was mixed with stirring. After 30 min a deep purple solid was separated. The crude solid was filtered off, washed with water and dried in vacuo. Yield: 0.362 g (62%). Good crystals were obtained by slow diffusion of acetone solution of the complex in light petroleum (40–60 °C). *Anal.* Calc. for $C_{14}H_9N_2O_8V$: C, 43.75; H, 2.34; N, 7.29; V, 13.28. Found: C, 43.15; H, 2.35; N, 6.99; V, 12.92%. IR (KBr disc, cm^{-1}) 3103(m), 2879(w), 1684(s): ν(C=O), 1606(m), 1527(m), 1469(w), 1425(w), 1332(s), 1290(w), 1240(m), 1176(w), 1147(w), 1140(w), 1085(w), 979(s): ν(V=O), 919(m), 842(w), 755(m), 682(w), 669(w), 605(w), 449(w), 387(w). ^{51}V NMR (105.03 MHz, CD_3CN, 296 K): δ ppm, −423.80. UV–Vis λ_{max} nm (ε M^{-1} cm^{-1}): 478(8000); 289(6100); 243(18 000).

2.3.3. $H[VO(O_2)(PyDC)(H_2O)] \cdot 2.5H_2O$ (**4**)

Compound **3** (0.401 g, 1.05 mmol) was treated with 30% aqueous H_2O_2 (1 ml, 12.5 mmol) by maintaining the pH of the solution at 2–3 with 4(M) HCl at 0–5 °C. The solution became orange red and was allowed stand in the deep freeze. After 15 days, orange red crystals separated. *Anal.* Calc. for $C_7H_{11}NO_{10.5}V$: C, 25.60; H, 3.34; N, 4.26; V, 15.54. Found: C, 25.27; H, 3.27; N, 4.13; V, 14.98 IR (KBr disc, cm^{-1}): 3209(broad), 3089(w), 2846(w), 1645(s): ν(C=O), 1437(m), 1380(s), 1273(w), 1188(m), 1151(w), 1081(m), 1037(w), 974(s): ν(V=O), 925(s): ν[O–O], 858(w), 837(w), 777(m), 750(m), 682(m), 605(w), 569(m), 451(w). UV–Vis λ_{max} nm (ε M^{-1} cm^{-1}): 427(2700), 270(26 500).

2.4. X-ray structure analyses for complexes **1**, **2**, **3** and **4**

Intensity data of complexes were recorded on a Bruker SMART CCD area detector (for **1** and **3**) and an Oxford diffraction X-Calibur CCD system (for **2** and **4**) using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data analyses were carried out with the