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Oxidoalkoxidovanadium(V) complexes: Synthesis, characterization and comparison of X-ray crystal structures

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ABSTRACT

The reaction of $VO(acac)_2$ with the ONO-chelator obtained by the condensation of salicylaldehyde with 2-hydroxybenzoylhydrazine (H_2L) in a monohydric alcohol (ROH) medium produces [VO(OR)L]-type oxidoalkoxido complexes (**1**–**7**) where R = Me, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, ^{t}Bu and ^{n}Pen. All the complexes show the metal atom to have a five-coordinate square pyramidal environment, although in some complexes there is an additional weak V···O interaction in the sixth axial position. In acetonitrile medium and in the presence of a *cis*-diol (ethylene glycol), H_2L reacts with $VO(acac)_2$ to form a six-coordinate complex, $[VO(OCH_2CH_2OH)L]$ (**8**). When the reaction is carried out in acetonitrile medium in the presence of 2-amino ethanol, a completely different type of product containing the square pyramidal complex anion $[VO_2L]^-$ associated with the cation $[NH_3CH_2CH_2OH]^+$ is obtained. It was noted previously that on being reacted with monodentate nitrogen donor bases B (which are stronger than pyridine), the [VO(OR)L] complexes react to form the same complex anion $[VO_2L]^-$ associated with the corresponding cation $[BH]^+$. The coordination environment around the V(V) acceptor center of the water soluble $[BH]^+[VO_2L]^-$ satisfies one of the several requirements for an efficient antidiabetic vanadium species such as water solubility, nature of donor atoms of the ligand and their disposition around the VO^{2+} acceptor center.

1. Introduction

Sustained interest in the chemistry of vanadium stems mainly from the following: (i) recognition of its multifaceted biological activity observed in some low-order living systems like mushrooms [1–3], terrestrial fungi, algae [4–7] and sea squirts [8,9]; (ii) its active role in several enzymes such as vanadium-dependent nitrogenases, haloperoxidases [10–14] and its involvement in phosphate metabolizing enzymes [15] and phosphomutases [16]; (iii) its participation in a variety of non-enzymic industrially important reactions like α-olefin polymerization [17–21], oxidation of sulfides and thioethers [22–24] epoxidation of allylic alcohols [25,26], phenols [27], catechol [28–30] and α-hydroxy ethers [31–33], and hydroxylation of alkenes [34]; (iv) insulin mimesis exhibited by certain vanadium complexes of selected O,O and N,O donor [35–45] chelators; and last but not least, (v) the rather recent recognition that some oxidovanadium(IV) complexes exhibit important anticancer properties [46–48].

Strong preference of vanadium(V) for N–O donor ligands [49–53] in general, along with recent reports on the insulin mimetic activity of some vanadium(V) complexes of N–O chelating ligands attracted special attention of inorganic and bioinorganic chemists. Vanadium(V) complexes in an N–O donor environment are also considered to have the potential to act as models of vanadium dependent haloperoxidases [54–59]. It was noted that the alkoxido group has the tendency to stabilize the highest oxidation state (+5) of vanadium [60]. All of the above considerations, along with our own experience in vanadium(V) and (IV) complexes of multidentate ligands with N–O coordination sites [61–67], prompted us to undertake the present study. Herein we report the synthesis, structural characterization, spectroscopic, chemical and electrochemical studies of vanadium(V) monooxidoalkoxido complexes of the type [VO(OR)L] where H_2L is a tridentate ONO chelating donor ligand, salicylaldehyde-2-hydroxybenzoylhydrazone.

2. Experimental

2.1. Materials

$[VO(acac)_2]$ was prepared as described in the literature [68] and is used as the source of vanadium which is oxidized to vanadium(V) spontaneously under aerobic conditions [69]. Reagent grade solvents were dried and distilled prior to use. All other

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chemicals were reagent grade, obtained from commercial sources and used without further purification. Spectroscopic grade solvents were used for spectral measurements.

2.2. Preparations

2.2.1. Synthesis of the ligand H_2L

The tridentate ONO chelator salicylaldehyde-2-hydroxybenzoylhydrazone (H_2L) was prepared using a previously reported procedure [66].

Yield 70%; M.p. 170 °C. *Anal.* Calc. for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.94. Found: C, 65.58; H, 4.64; N, 10.92%. IR (KBr; cm^{-1}): 3195 ν(OH), 3075 ν(NH), 1660 ν(C=O), 1618 ν(C=N), 1H NMR (DMSO d_6, δ): 7.91–6.91 (m, 8H, C_6H_4), 8.68 (s, 1H, –CH=N), 11.18 (s, 1H, NH), 11.76 (s, 1H, OH), 12.02 (s, 1H, OH).

2.2.2. Synthesis of the mononuclear oxidovanadium(V) complexes

All of the mononuclear oxidovanadium(V) complexes of the type [VO(OR)L] (**1**–**7**) were synthesized by a simple general method reported earlier [66] using [VO(acac)$_2$] as the starting material.

0.26 g (1.0 mmol) of the ligand H_2L was dissolved in 30 ml of methanol for [VO(OMe)L] (**1**), propan-1-ol for [VO(O^n*Pr*)L] (**2**), propan-2-ol for [VO(O^i*Pr*)L] (**3**), 1-butanol for [VO(O^n*Bu*)L] (**4**), 2-methyl propan-2-ol for [VO(O^i*Bu*)L] (**5**), 2,2-dimethyl propan-1-ol [VO(O^t*Bu*)L] (**6**) and 1-pentanol for [VO(O^n*Pen*)L] (**7**), and then 0.27 g (1.0 mmol) of VO(acac)$_2$ was added to the corresponding ligand solution and refluxed for 4 h on steam bath in open air. The resultant solutions were filtered and the filtrates were kept in air over 3 days whereupon dark brown crystalline products were deposited, from which good single crystals could be collected.

Complexes **8** and **9** were prepared by slight modification of the above method as mentioned below.

0.26 g (1.0 mmol) of the ligand H_2L was dissolved in 30 ml of acetonitrile and 5 ml ethylene glycol mixture for [VO(OCH$_2$CH$_2$OH)L] **8**, 30 ml of acetonitrile and 5 ml 2-amino ethanol mixture for $[NH_3CH_2CH_2OH]^+[VO_2L]^-$ **9**, and 0.27 g (1.0 mmol) of VO(acac)$_2$ was added to the corresponding ligand solution. After refluxing 4 h on a steam bath in open air, the solution was filtered and the filtrate kept in air for 3 days whereupon dark brown and yellow brown crystalline products, respectively for complexes **8** and **9**, containing good single crystals, were obtained.

*2.2.2.1. [VO(OMe)L] (**1**).* Yield 79%. *Anal.* Calc. for $C_{15}H_{13}N_2O_5V$: C, 51.14; H, 3.69; N, 7.95; V, 14.49. Found: C, 51.10; H, 3.72; N, 7.92; V, 14.46%. ^{1}H NMR ($CDCl_3$, δ): 10.17 (s, 1H, OH), 8.59 (s, 1H, –CH=N), 7.99–6.80 (m, 8H, C_6H_4), 5.34 (s, 3H, CH_3, O*Me*). IR (KBr; cm^{-1}): 3180 ν(OH), 1604 ν(C=N), 1238 ν(C–O)$_{enolic}$, 1034 ν(N–N), 988 ν(V=O).

*2.2.2.2. [VO(O^{n}Pr)L] (**2**).* Yield 79%. *Anal.* Calc. for $C_{17}H_{15}N_2O_5V$: C, 53.68; H, 4.47; N, 7.36; V, 13.42. Found: C, 53.62; H, 4.43; N, 7.37; V, 13.38%. ^{1}H NMR ($CDCl_3$, δ): 10.17 (s, 1H, OH), 8.54 (s, 1H, –CH=N), 7.97–6.84 (m, 8H, C_6H_4), 5.12 (t, 2H, CH_2, O^n*Pr*), 2.42–2.54 (m, 2H, CH_2, O^n*Pr*), 1.27 (m, 3H, CH_3, O^n*Pr*). IR (KBr; cm^{-1}): 3070 ν(OH), 1606 ν(C=N), 1238 ν(C–O)$_{enolic}$, 1032 ν(N–N), 988 ν(V=O).

*2.2.2.3. [VO(O^{i}Pr)L] (**3**).* Yield 79%. *Anal.* Calc. for $C_{17}H_{15}N_2O_5V$: C, 53.68; H, 4.47; N, 7.36; V, 13.42. Found: C, 53.64; H, 4.44; N, 7.34; V, 13.40%. ^{1}H NMR ($CDCl_3$, δ): 10.16 (s, 1H, OH), 8.57 (s, 1H, –CH=N), 7.93–6.88 (m, 8H, C_6H_4), 4.01 (m, H, CH, O^i*Pr*), 1.24 (d, 6H, CH_3, O^i*Pr*). IR (KBr; cm^{-1}): 2973 ν(OH), 1609 ν(C=N), 1252 ν(C–O)$_{enolic}$, 1038 ν(N–N), 990 ν(V=O).

*2.2.2.4. [VO(O^{n}Bu)L] (**4**).* Yield 65%. *Anal.* Calc. for $C_{18}H_{19}N_2O_5V$: C, 54.82; H, 4.82; N, 7.11; V, 12.94. Found: C, 54.80; H, 4.78; N, 7.13; V, 12.91%. ^{1}H NMR ($CDCl_3$, δ): 10.18 (s, 1H, OH), 8.58 (s, 1H, –CH=N), 7.96–6.93 (m, 8H, C_6H_4), 5.59 (t, 2H, CH_2, O^n*Bu*), 2.05 (m, 2H, O^n*Bu*), 1.5 (m, 2H, CH_2, O^n*Bu*), 1.06 (t, 3H, CH_3, O^n*Bu*). IR (KBr; cm^{-1}): 3187 ν(OH), 1605 ν(C=N), 1251 ν(C–O)$_{enolic}$, 1048 ν(N–N), 995 ν(V=O).

*2.2.2.5. [VO(O^{i}Bu)L] (**5**).* Yield 68%. *Anal.* Calc. for $C_{18}H_{19}N_2O_5V$: C, 54.82; H, 4.82; N, 7.11; V, 12.94. Found: C, 54.80; H, 4.84; N, 7.11; V, 12.92%. ^{1}H NMR ($CDCl_3$, δ): 10.16 (s, 1H, OH), 8.54 (s, 1H, –CH=N), 7.92–6.87 (m, 8H, C_6H_4), 5.27 (m, 1H, CH, O^i*Bu*), 2.71 (d, 3H, O^i*Bu*), 1.68 (m, 2H, CH_2, O^i*Bu*), 1.12 (t, 3H, CH_3, O^i*Bu*). IR (KBr; cm^{-1}): 3433 ν(OH), 1608 ν(C=N), 1254 ν(C–O)$_{enolic}$, 1111 ν(N–N), 991 ν(V=O).

*2.2.2.6. [VO(O^{t}Bu)L] (**6**).* Yield 74%. *Anal.* Calc. for $C_{18}H_{19}N_2O_5V$: C, 54.82; H, 4.82; N, 7.11; V, 12.94. Found: C, 54.76; H, 4.80; N, 7.13; V, 12.92%. ^{1}H NMR ($CDCl_3$, δ): 10.17 (s, 1H, OH), 8.56 (s, 1H, –CH=N), 7.92–6.96 (m, 8H, C_6H_4), 4.26 (s, 9H, CH_3, O^t*Bu*). IR (KBr; cm^{-1}): 2974 ν(OH), 1606 ν(C=N), 1247 ν(C–O)$_{enolic}$, 1063 ν(N–N), 940 ν(V=O).

*2.2.2.7. [VO(O^{n}Pen)L] (**7**).* Yield 68%. *Anal.* Calc. for $C_{19}H_{21}N_2O_5V$: C, 55.88; H, 5.14; N, 6.83; V, 12.60. Found: C, 55.84; H, 5.12; N, 6.83; V, 12.6%. ^{1}H NMR ($CDCl_3$, δ): 10.13 (s, 1H, OH), 8.57 (s, 1H, –CH=N), 7.96–6.88 (m, 8H, C_6H_4), 5.55 (t, 2H, CH_2, O^n*Pen*), 3.64 (m, 2H, O^n*Pen*), 2.08 (m, 2H, O^n*Pen*), 1.45 (m, 2H, CH_2, O^n*Pen*), 0.97 (t, 3H, CH_3, O^n*Pen*). IR (KBr; cm^{-1}): 2947 ν(OH), 1609 ν(C=N), 1254 ν(C–O)$_{enolic}$, 1042 ν(N–N), 985 ν(V=O).

*2.2.2.8. [VO(OCH$_2$CH$_2$OH)L] (**8**).* Yield 69%. *Anal.* Calc. for $C_{16}H_{15}N_2O_6V$: C, 50.26; H, 3.92; N, 7.32; V, 13.35. Found: C, 50.21; H, 3.72; N, 13.82; V, 12.55%. ^{1}H NMR ($CDCl_3$, δ): 10.18 (s, 1H, OH), 8.57 (s, 1H, –CH=N), 7.92–6.87 (m, 8H, C_6H_4), 5.54 (t, 2H, CH_2, OCH_2CH_2OH), 5.12 (m, 2H, OCH_2CH_2OH). IR (KBr; cm^{-1}): 3359 ν(OH), 1607 ν(C=N), 1251 ν(C–O)$_{enolic}$, 1059 ν(N–N), 988 ν(V=O).

*2.2.2.9. $[NH_3CH_2CH_2OH]^+[VO_2L]^-$ (**9**).* Yield 68%. *Anal.* Calc. for $C_{16}H_{18}N_3O_6V$: C, 48.12; H, 4.51; N, 10.52; V, 12.78. Found: C, 48.08; H, 4.54; N, 140.47; V, 12.75%. ^{1}H NMR (D_2O, δ): 8.58 (s, 1H, –CH=N), 7.89–6.92 (m, 8H, C_6H_4), 5.56 (m, 3H, CH_2, $H_3N^+CH_2CH_2OH$), 5.21 (m, 2H, $H_3N^+CH_2CH_2OH$). IR (KBr; cm^{-1}): 3022 ν(OH), 1611 ν(C=N), 1256 ν(C–O)$_{enolic}$, 1070 ν(N–N), 944 ν(V=O)$_{asym}$, 910 ν(V=O)$_{sym}$.

2.3. Physical measurements

Elemental analyses (C, H and N) were performed with a Perkin–Elmer 2400 CHNS/O analyser and the vanadium contents (%) of the complexes were determined gravimetrically as V_2O_5 [70]. Electronic spectra of the complexes in acetonitrile were recorded on a Hitachi U-3501 spectrophotometer and IR spectra (as KBr pellets) were recorded using a Perkin Elmer RXI FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Model Advance DPX300 spectrometer. Electrochemical experiments were performed with a PAR model 362 scanning potentiostat and cyclic voltammograms were recorded at 25 °C in the designated solvent under dry dinitrogen with the electroactive component at ca. 10^{-3} M. Tetraethyl ammonium perchlorate (NEt_4ClO_4, 0.1 M) was used as the supporting electrolyte. A three-electrode configuration was employed with a platinum working electrode, a calomel reference electrode, and a platinum auxiliary electrode. Room temperature magnetic susceptibilities of the complexes were measured in the polycrystalline state on a PAR 155 vibrating sample magnetometer using Hg[Co(SCN)$_4$] as the calibrant.