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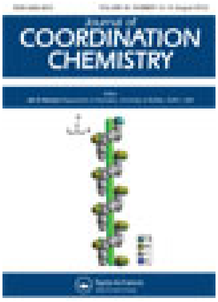

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Synthesis, crystal structure, and spectroscopic behavior of 8-hydroxyquinolato oxoalkoxo vanadium(V) complexes

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Synthesis, crystal structure, and spectroscopic behavior of 8-hydroxyquinolato oxoalkoxo vanadium(V) complexes

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Four oxoalkoxo vanadium(V) complexes, $[OV(OCH_3)_2Q]_2$ (**1**), $[OV(OC_2H_5)Q_2]$ (**2**), $[OV(O^iPr)Q_2]$ (**3**), and $[OV(O^tBu)Q_2]$ (**4**), were synthesized by reaction of $[OV(O^tBu)_3]$ and 8-hydroxyquinoline in a facile process. The complexes were characterized by elemental analysis, UV-Vis and infrared spectroscopies, as well as ^1H, ^{13}C, and ^{51}V NMR. The crystal and molecular structure of **1**, the first binuclear alkoxo-bridged oxoalkoxo vanadium(V) complex, and **2** were determined by X-ray diffraction from single crystals. Complex **1** is a dimer with distorted octahedral geometry, while **2** is monomeric with distorted octahedral geometry. ^1H NMR data revealed that alkoxy signal of **1**–**3** (OCH_3, OCH_2R and $OCHR_2$) are deshielded with the trend 5.68, 6.14, and 6.84 ppm, respectively. ^{51}V NMR data of these complexes are in the range of reported chemical shifts of complexes of the type $[VO_{6-n}N_n]$ ($n = 0$–2).

Keywords: Vanadium; Alkoxide; 8-Hydroxyquinoline; Crystal structure

1. Introduction

Vanadium chemistry is represented by oxo vanadium compounds, including a large number of vanadium oxo-alkoxides [1, 2]. Oxo- and alkoxo-bridged V(V) species are rare compared to Ti(IV), Mo(V), and Mo(IV) [3–5], but are valuable molecular precursors for sol-gel processing, electronic and ceramic materials, and attractive precursors for metal oxide preparation using chemical vapor deposition [6–10]. Coordination chemistry of oxo vanadium(V) receives interest due to the discovery of vanadium-containing enzymes such as bromoperoxidases and nitrogenases [11–14]. EXAFS and other spectroscopic investigations of vanadium active sites in haloperoxidases have shown that coordination environments of the metal center consist of N- and/or O-donor moieties [15–19]. These results have drawn the attention of researchers to coordination chemistry of vanadium involving N–O donor ligands.

8-Hydroxyquiniline (HQ) is a well-known N–O bidentate ligand and an analytical reagent. Synthesis and characterization of large numbers of metal complexes of HQ and its derivatives have been reported [3, 20–29] with remarkable antimicrobial, fungicidal,

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and antitumor activity of some of these complexes [30–33]. These findings motivate structural investigations on these types of ligands and their vanadium compounds, due to their therapeutic significance [34–36].

Herein, we report the synthesis, characterization, and molecular structure of the first binuclear alkoxo-bridged oxoalkoxo vanadium(V) complex along with mononuclear derivatives by using alkoxide precursor and a N–O bidentate ligand.

2. Experimental

2.1. *Materials and methods*

All manipulations were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Reagent grade chemicals are used as received. Oxovanadium *tert*-butoxide was synthesized from V_2O_5 based on reported procedure and purified by sublimation [37]. All solvents were purchased from Merck and dried with appropriate reagents prior to use.

Infrared spectra were recorded on a Shimadzu 470 instrument at 4 cm^{-1} resolution using KBr pellets. ^{1}H, ^{13}C, and ^{51}V NMR spectra were recorded at room temperature in C_6D_6 on a Bruker AVANCE 300 MHz instrument. UV-Vis spectra were recorded on a Shimadzu 2100 spectrophotometer.

2.2. *Syntheses*

2.2.1. General procedure. All complexes were synthesized according to the following procedure. HQ (5 mmol, 0.73 g) was added to a solution of $OV(^tOBu)_3$ (5 mmol, 1.43 g) in benzene (15 mL) and stirred for 1 h at room temperature. Addition of HQ led to an immediate color change from colorless to dark red. Thereafter, 40 mL of an appropriate alcohol was added and heated for 0.5 h at 50°C. Suitable crystals of **1** and **2** for X-ray crystallography were obtained at 5°C.

2.2.2. Oxobis(methoxo)-8-hydroxyquinolato vanadium(V) $[OV(OCH_3)_2Q]_2$ (1). Yield: 86%. $C_{22}H_{24}N_2O_8V_2$ (546.31): Calcd (%) C 48.37, H 4.43, N 5.13; found: C 48.90, H 4.03, N 5.65. $T_{decomp.} = 130°C$. UV (C_6H_6, nm): 276, 378, 475. IR (KBr, cm^{-1}): 3058w (ν C–H arom.), 2906w and 2804w (ν C–H), 1601w (ν C=N), 1576m (ν C=C), 1498vs, 1469s, 1421w, 1377s, 1322s, 1271s, 1237m, 1173w, 1109s, and 1054s (ν C–O), 1022m (ν C–O), 961s (ν V=O), 824 m, 779w, 752s, 633w, 611s, 537s (ν V–O), 499w (ν V–O). ^{1}H NMR (300 MHz, benzene-d_6, 25°C, ppm): $\delta = 5.68$ (s, 3H, OCH_3), 6.10–6.40 (m, 1H, H-7), 6.70–6.90 (m, 1H, H-6), 7.10–7.30 (m, 1H, H-5), 7.30–7.50 (m, 2H, H-3 and H-4), 8.60, and 8.68 (2d, $^{3}J_d = 4.1$ Hz, 1H, H-2). ^{13}C NMR (75 MHz, benzene-d_6, 25°C, ppm): $\delta = 77.1$ (OCH_3), 110.0 and 111.4 (C-7), 114.1 and 116.9 (C-5), 121.5 (C-3), 128.8 and 129.3 (C-6), 129.8 and 130.0 (C-10), 136.7 and 137.6 (C-9), 141.0 (C-4), 145.6 and 145.8 (C-2), 164.3 and 165.6 (C-8). ^{51}V NMR (79 MHz, benzene-d_6, 25°C) $\delta = -478$ ppm.

2.2.3. Oxoethoxo-bis(8-hydroxyquinolato)vanadium(V) $[OV(OCH_2CH_3)Q_2]$ (2). Yield: 80%. $C_{20}H_{17}N_2O_4V$ (400.30): Calcd (%) C 60.01, H 4.28, N 7.00; found: C 60.45, H 4.12, N 7.15. UV (C_6H_6, nm): 278, 377, 477. IR (KBr, cm^{-1}): 3058w (ν C–H arom.), 2970w, 2928w, and 2876w (ν C–H), 1601m (ν C=N), 1588m (ν C=C), 1574s, 1497vs, 1467vs, 1421m, 1396m, 1376s, 1321s, 1272s, 1236m, 1174m, 1104vs (ν C–O), 1051w, 1028m (ν C–O), 948vs (ν V=O), 846s, 824s, 808(m), 787s, 775w, 745vs, 715w, 652s, 638vs, 624w, 588w, 564m, 536s (ν V–O), 499m (ν V–O), 462m, 452m, 403m, 362m, 334w. ^{1}H NMR (300 MHz, benzene-d_6, 25°C, ppm): $\delta = 1.59$ (t, $^3J_t = 7.0$ Hz, 3H, CH_3), 6.14 (q, $^3J_q = 7.0$ Hz, 2H, OCH_2), 6.25–6.40 (m, 1H, H-7), 6.70–6.90 (m, 1H, H-6), 7.05–7.25 (m, 1H, H-5), 7.30–7.50 (m, 2H, H-3, and H-4), 8.70 and 8.64 (2d, $^3J_d = 3.7$ Hz, 1H, H-2). ^{13}C NMR (75 MHz, benzene-d_6, 25°C, ppm): $\delta = 18.6$ (CH_3), 85.1 (OCH_2), 110.0 and 111.3 (C-7), 114.1 and 116.8 (C-5), 121.5 (C-3), 128.8 and 129.3 (C-6), 129.8 and 130.0 (C-10), 136.7 and 137.6 (C-9), 139.9 and 141.5 (C-4), 145.6 and 145.7 (C-2), 164.0 and 165.3 (C-8). ^{51}V NMR (79 MHz, benzene-d_6, 25°C) $\delta = -482$ ppm.

2.2.4. Oxo-*iso*-propoxo-bis(8-hydroxyquinolato)vanadium(V) [OV(O^{i}Pr)Q$_2$] (3). Yield: 84%. $C_{21}H_{19}N_2O_4V$ (414.33): Calcd (%) C 60.88, H 4.62, N 6.76; found: C 61.22, H 4.33, N 6.85. UV (C_6H_6, nm): 278, 376, 470. IR (KBr, cm^{-1}): 3059w (ν C–H arom.), 2962w and 2852w (ν C–H), 1601m (ν C=N), 1588w (ν C=C), 1574s, 1497vs, 1467vs, 1422m, 1396m, 1373s,1350w, 1322s, 1271s, 1237m, 1175m, 1134m, 1105s, 1087s and 1030 (ν C–O), 956s, 947s (ν V=O), 899s, 823s, 808(m), 785s, 746vs, 640s, 606s, 565m, 537s and 529 (ν V–O), 498m (ν V–O), 438m, 404m, 376w, 360m. ^{1}H NMR (300 MHz, benzene-d_6, 25°C, ppm): $\delta = 1.60$ and 1.70 (2d, $^3J_d = 6.0$ Hz, 3H, CH_3), 6.20–6.40 (m, 1H, H-7), 6.75–6.95 (m, 2H, H-5, and OCH), 7.10–7.30 (m, 1H, H-5), 7.35–7.50 (m, 2H, H-3, and H-4), 8.71 and 8.64 (2d, $^3J_d = 4.0$ Hz, 1H, H-2). ^{13}C NMR (75 MHz, benzene-d_6, 25°C, ppm): $\delta = 24.9$ and 25.2 (CH_3), 91.4 (OCH), 109.0 and 111.1 (C-7), 114.1 and 116.8 (C-5), 121.5 (C-3), 128.8 and 129.3 (C-6), 129.8 and 129.9 (C-10), 136.6 and 137.5 (C-9), 141.2 (C-4), 145.5 and 145.6 (C-2), 164.2 and 165.4 (C-8). ^{51}V NMR (79 MHz, benzene-d_6, 25°C) $\delta = -494$ ppm.

2.2.5. Oxo-*tert*-butoxo-bis(8-hydroxyquinolato)vanadium(V) [OV(O^{t}Bu)Q$_2$] (4). Yield: 65%. $C_{22}H_{21}N_2O_4V$ (428.35): Calcd (%) C 61.69, H 4.94, N 6.54; found: C 60.15, H 4.45, N 6.72. UV (C_6H_6, nm): 277, 373, 470. IR (KBr, cm^{-1}): 3053w (ν C–H arom.), 2970w (ν C–H), 1602w (ν C=N), 1590w (ν C=C), 1574m, 1497vs, 1467vs, 1422w, 1396w, 1375s, 1321s, 1270m, 1235w, 1173w, 1136w, 1104s (ν C–O), 1050w, 1026w, 952vs (ν V=O), 824m, 809w, 780s, 746s, 710vs, 639m, 618m, 565m, 537m and 519m (ν V–O), 500m (ν V–O), 438w, 404m, 373m, 341w. ^{1}H NMR (300 MHz, benzene-d_6, 25°C, ppm): $\delta = 1.90$ (s, 9H, CH_3), 6.10–6.50 (m, 1H, H-7), 6.60–7.00 (m, 1H, H-6), 7.10–7.30 (m, 1H, H-5), 7.30–7.50 (m, 2H, H-3, and H-4), 8.76 and 8.64 (2 s, 1H, H-2). ^{13}C NMR (75 MHz, benzene-d_6, 25°C, ppm): $\delta = 32.6$ (CH_3), 95.4 (OC), 110.1 and 111.4 (C-7), 114.0 and 116.7 (C-5), 121.4 (C-3), 128.9 and 129.2 (C-6), 129.7 and 130.1 (C-10), 136.6 and 137.4 (C-9), 139.8 and 141.4 (C-4), 145.5 and 145.6 (C-2), 164.2 and 165.5 (C-8). ^{51}V NMR (79 MHz, benzene-d_6, 25°C) $\delta = -542$ ppm.

2.3. *X-ray crystallography*

X-ray diffraction measurements were conducted on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. For **1**, a violet crystal with the

Table 1. Crystallographic data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{22}H_{24}N_2O_8V_2$	$C_{20}H_{17}N_2O_4V$
Formula weight	546.31	400.97
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	15.3295(12)	9.0226
b	9.9332(5)	9.5302(8)
c	15.9469(12)	12.5512(10)
α		108.720(6)
β	108.853(6)	95.537(6)
γ		112.312(6)
Volume (Å^3), Z	2298.0(3), 4	915.79(15), 2
Absorption coefficient (mm^{-1})	0.865	0.570
$F(000)$	1120	412
Crystal size (mm^3)	$0.12 \times 0.10 \times 0.07$	$0.50 \times 0.40 \times 0.35$
Calculated density (g cm^{-3})	1.579	1.452
θ range for data collection (°)	2.45–29.30	1.77–29.18
Reflections collected	17,828	10,862
Independent reflections	6195 [R(int) = 0.1063]	4893 [R(int) = 0.0360]
Data/restraints/parameters	6195/0/307	4893/0/244
Goodness-of-fit on F^2	1.193	1.085
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0820$, $wR_2 = 0.1443$	$R_1 = 0.0387$, $wR_2 = 0.0931$
R indices (all data)	$R_1 = 0.1229$, $wR_2 = 0.1590$	$R_1 = 0.0454$, $wR_2 = 0.0965$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

dimensions of 0.12 mm × 0.10 mm × 0.07 mm and for **2**, a violet crystal with the dimensions of 0.50 mm × 0.40 mm × 0.35 mm, were mounted on a glass fiber and used for data collection. The cell constants and an orientation matrix for the data collection were obtained by least-squares refinement of diffraction data from 6195 and 4893 unique reflections for **1** and **2**, respectively. Data were collected at 120 K in a series of ω scans in 1° oscillations to a maximum 2θ value of 29.30 and 29.18 for **1** and **2**, respectively. Data were integrated using the Stoe X-AREA software package [38]. A numerical absorption correction was applied in each case using X-RED [39] and the X-SHAPE software [40]. The structures were solved by direct and subsequent difference Fourier maps, and then refined on F^2 by a full-matrix least-squares using anisotropic displacement parameters [41]. Atomic factors were obtained from the International Tables for X-ray Crystallography [42]. All refinements were performed using the X-STEP32 crystallographic software package [43]. Crystal data and refinement details are listed in table 1.

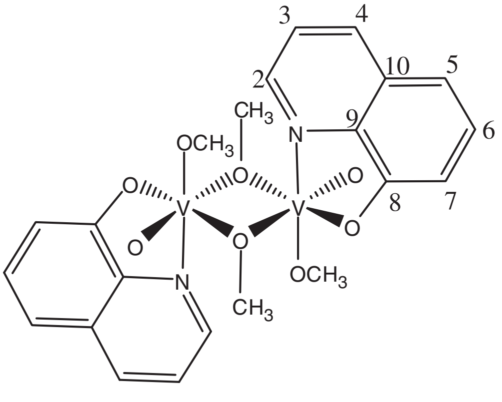
3. Results and discussion

3.1. *Synthesis*

For the syntheses, vanadium alkoxides were used as a vanadium source, because alkoxides have several advantages over other metal salts used for preparation of metal complexes. They are accessible as very pure materials, with good solubility in organic solvents, and their reactivity leads to neutral complexes in shorter time and milder condition. All reactions proceeded by equimolar addition of HQ to a solution of $OV(^{t}OBu)_3$ in benzene led to an immediate color change from colorless to dark red. These observations showed an immediate reaction and consequently there is no need for more stringent reaction conditions. Afterward, addition of methanol, ethanol, *iso*-propanol, and *tert*-butanol in excess led to formation of **1**–**4**. Although the synthesis and crystal structure of $[OV(O^{i}Pr)Q]$ was previously reported [20], spectroscopic data of this complex were necessary for comparison to other derivatives. Formation of all the complexes has been established by NMR spectroscopy and elemental analysis as well as UV-Vis and infrared spectroscopies. The crystal structures of **1** and **2** were determined by X-ray diffraction from single crystals.

3.2. *Structural descriptions of 1 and 2*

Crystal structures of nearly all the previously reported complexes of oxoalkoxo vanadium(V) with HQ and its derivatives have shown mononuclear oxoalkoxo vanadium complexes, $[OV(OR)Q_2]$ [20, 21, 23, 24]. Mononuclear complexes can dimerize giving oxo-bridged dinuclear vanadium(V) species in which two VQ_2 moieties are linked by oxo groups [3]. Using 1 : 1 ratio of vanadium precursor to HQ or an attempt to synthesize mixed ligand complexes usually leads to chelation of two Q to one vanadium center [24]. These results reflect the formation of thermodynamically more favorable VQ_2 moieties. We isolated the first alkoxo-bridged binuclear complex of this family by using vanadium alkoxide as precursor. Complex **1** (scheme 1) crystallizes in the monoclinic system with the space group *P2₁/a*. The molecular structure and packing diagram of $[OV(OCH_3)_2Q]_2$ (**1**) are shown in figures 1 and 2, respectively. Selected bond lengths and angles as well as interatomic distances are summarized in table 2. Distorted octahedral geometry around V(V) is formed by an overall $[NO_5]$ coordination environment (figure 3). Three different methoxy groups are coordinated to each vanadium, one terminal and two bridging. Nitrogen is *trans* to terminal methoxy while the other two bridged methoxy groups are *trans* to oxo and oxygen from Q.



Scheme 1. Molecular representation of $[OV(OCH_3)_2Q]_2$ (**1**).

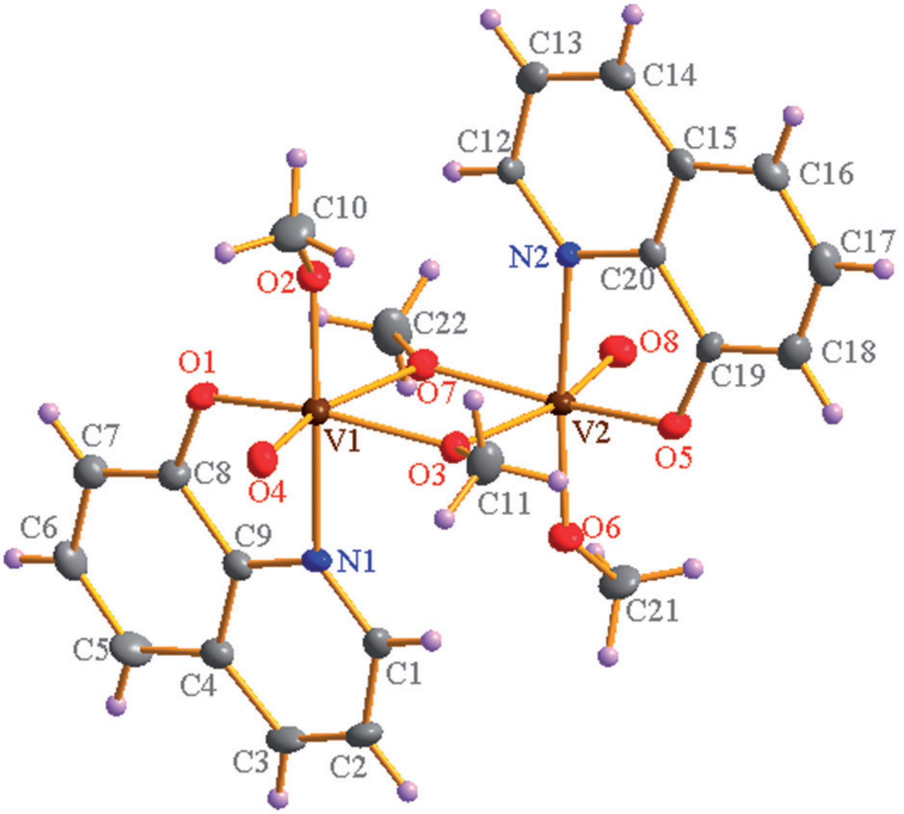


Figure 1. The structure of **1** in the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

The two V–O bond lengths of bridging methoxy are longer than the terminal ones. The two bridging methoxy groups have different V–O bond lengths as a result of structural *trans* effect exerted by oxo and unsymmetrical electron-donating properties in dimeric structures. The V–O bond lengths of **1** compared to monomer structures show similar values [24]. Also, π–π stacking interactions throughout the crystal structure, with an average distance between the aromatic parts of *ca* 3.7 Å, is observed.

Complex **2** (scheme 2) crystallizes in the triclinic system with the space group $P\bar{1}$. The molecular structure of [OV(OCH$_2$CH$_3$)Q$_2$] (**2**) is shown in figure 4 and selected bond lengths and angles as well as interatomic distances are summarized in table 3. Coordination sphere around the monoalkoxo vanadium(V) is distorted octahedral, formed by an overall [N$_2$O$_4$] coordination environment. Oxo (V=O) and ethoxo groups are *cis* with O(3)–V(1)–O(4) angle of 101.9(2)°, slightly smaller than [VO(QCl$_2$)$_2$OCH$_2$CH$_3$] (102.7°) [21]. An increase in the alcohol chain length from methoxo [24] to ethoxo (**2**) and *n*-propoxo [23] shows a small increase in this bond angle from 101.08° to 102.11°. Two Q are attached to V in a bidentate fashion and their nitrogen atoms are *cis* with significantly different bond lengths. The V(1)–N(1) bond *trans* to oxo is longer (2.302(3) Å) than that positioned *trans* to ethoxo (2.211(7) Å). This trend is also observed in previously reported structures as a result of the *trans*

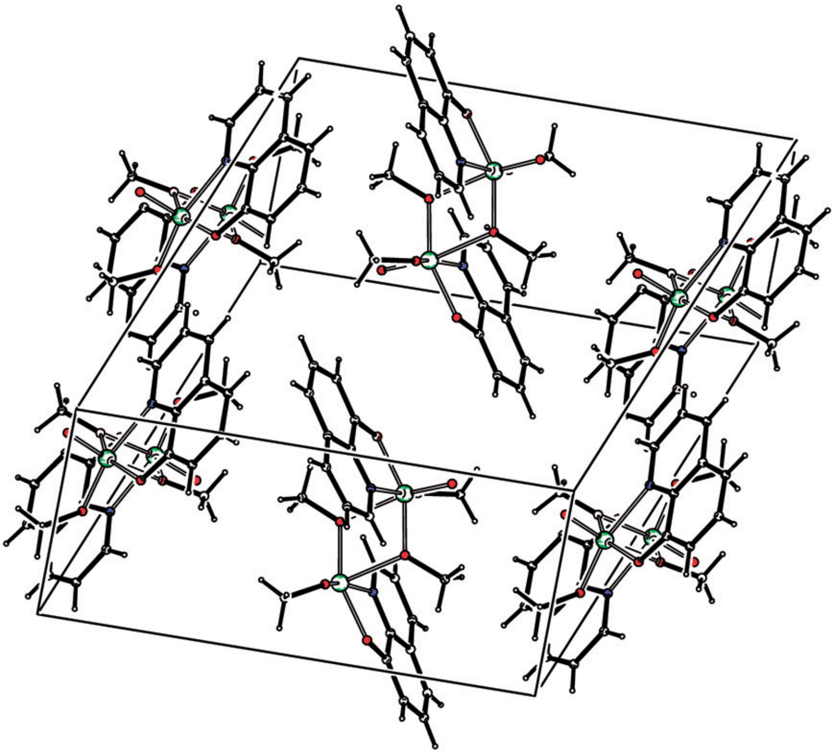


Figure 2. Packing diagram of the unit cell of **1**.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

V(1)–O(1)	1.929(3)	V(2)–O(5)	1.937(3)
V(1)–O(2)	1.783(3)	V(2)–O(6)	1.780(3)
V(1)–O(3)	1.901(3)	V(2)–O(7)	1.894(3)
V(1)–O(4)	1.601(3)	V(2)–O(8)	1.595(3)
V(1)–O(7)	2.219(3)	V(2)–O(3)	2.222(3)
V(1)–N(1)	2.206(4)	V(1)–N(2)	2.202(3)
O(1)–C(8)	1.339(5)	O(5)–C(19)	1.332(5)
V(1)–O(3)–V(2)	108.52(13)	V(1)–O(7)–V(2)	108.87(14)
O(1)–V(1)–O(2)	92.84(14)	O(5)–V(2)–O(6)	90.12(15)
O(1)–V(1)–O(3)	153.52(13)	O(5)–V(2)–O(3)	86.67(12)
O(1)–V(1)–O(4)	103.59(15)	O(5)–V(2)–O(8)	102.42(16)
O(1)–V(1)–O(7)	87.50(13)	O(5)–V(2)–O(7)	154.11(13)
O(3)–V(1)–O(4)	96.07(15)	O(3)–V(2)–O(8)	167.19(14)
O(7)–V(1)–O(4)	166.87(14)	O(7)–V(2)–O(8)	97.53(16)
O(3)–V(1)–O(7)	71.27(12)	O(3)–V(2)–O(7)	71.33(12)
O(1)–V(1)–N(1)	76.52(13)	O(5)–V(2)–N(2)	76.84(13)
O(2)–V(1)–N(1)	164.72(14)	O(6)–V(2)–N(2)	164.92(15)
O(3)–V(1)–N(1)	84.81(13)	O(3)–V(2)–N(2)	82.78(12)
O(4)–V(1)–N(1)	93.56(15)	O(8)–V(2)–N(2)	90.44(15)
O(7)–V(1)–N(1)	82.07(12)	O(7)–V(2)–N(2)	86.76(13)
V(1)–O(1)–C(8)	121.6(3)	V(2)–O(5)–C(19)	120.7(3)
V(1)–O(2)–C(10)	127.5(3)	V(2)–O(6)–C(21)	128.5(3)
V(1)–N(1)–C(1)	130.3(3)	V(2)–N(2)–C(12)	129.8(3)
V(1)–N(1)–C(9)	111.5(3)	V(2)–N(2)–C(20)	111.1(3)

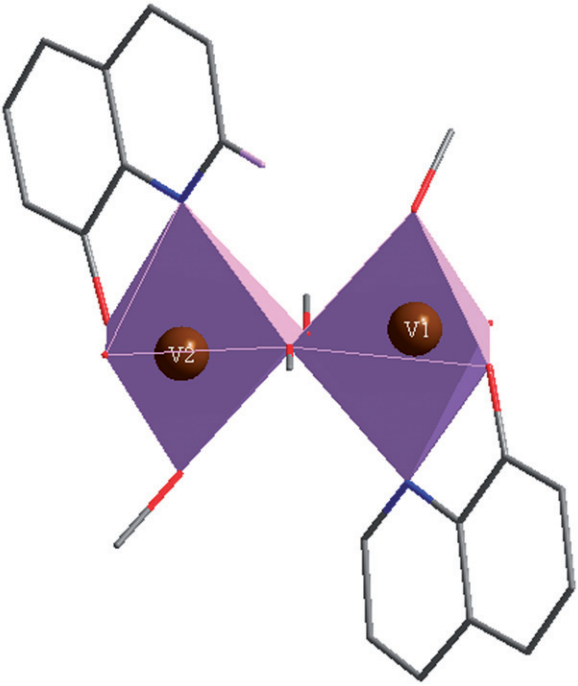
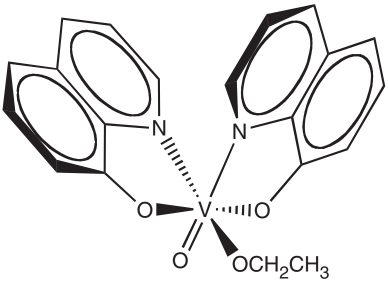


Figure 3. Polyhedral representation of **1**.



Scheme 2. Molecular representation of [OV(OCH_2CH_3)Q_2] (**2**).

influence [3, 20–24]. Due to markedly nonstandard bond angles summarized in table 3, V is positioned 0.289 Å above the basal plane. V–O bond distances of the two chelates have different values due to different values of V–N bonds and rigidity of the chelate. This rigidity implies nearly constant values for internal angle of chelate ring and leads to an increase in one of the bond lengths at the expense of the other.

3.3. *Spectroscopic characterization*

Solution chemistry and the nature of the metal ligand bonds for HQ complexes can be investigated by NMR spectroscopy. ^{51}V NMR is widely utilized to study the coordination geometry of vanadium complexes [44], but there is no report on

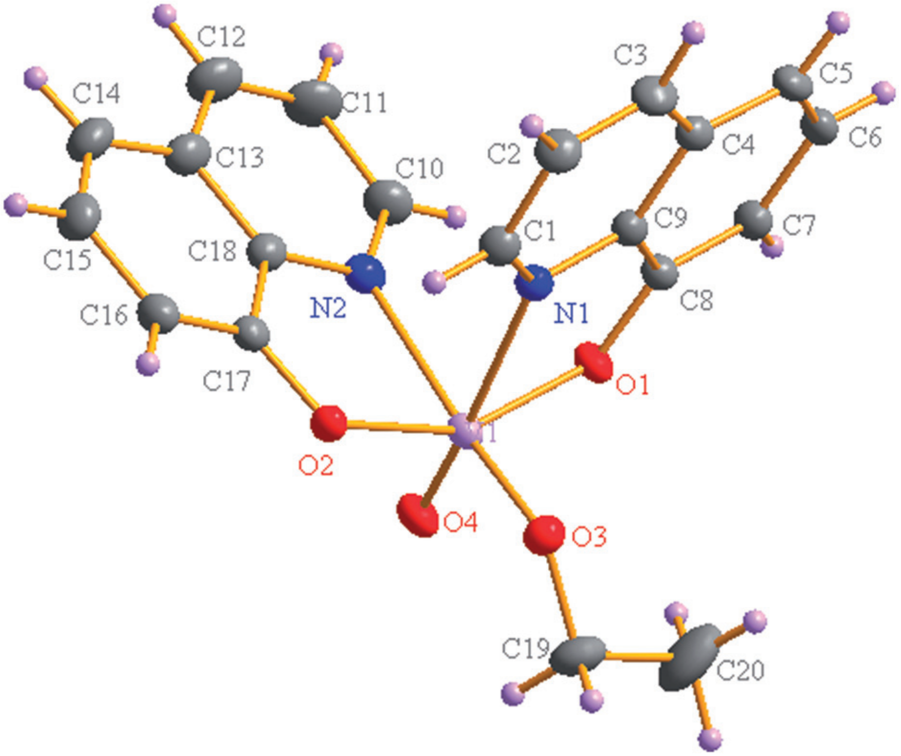


Figure 4. The structure of **2** in the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

V(1)–O(1)	1.849(3)	V(1)–N(1)	2.3023(13)
V(1)–O(2)	1.912(3)	V(1)–N(2)	2.2117(15)
V(1)–O(3)	2.202(4)	O(1)–C(8)	1.3421(18)
V(1)–O(4)	1.975(4)	O(3)–C(19)	1.437(2)
O(1)–V(1)–O(2)	153.32(5)	O(4)–V(1)–N(2)	92.70(6)
O(1)–V(1)–O(3)	100.39(6)	O(3)–V(1)–N(1)	87.25(5)
O(1)–V(1)–O(4)	95.85(6)	O(3)–V(1)–N(2)	164.33(6)
O(1)–V(1)–N(1)	76.57(5)	N(1)–V(1)–N(2)	78.86(5)
O(1)–V(1)–N(2)	83.52(5)	V(1)–O(1)–C(8)	122.20(10)
O(3)–V(1)–O(4)	101.91(6)	V(1)–O(2)–C(17)	120.69(10)
O(3)–V(1)–O(2)	94.00(5)	V(1)–O(3)–C(19)	127.44(12)
O(4)–V(1)–O(2)	103.05(6)	V(1)–N(1)–C(1)	132.79(11)
O(2)–V(1)–N(1)	81.86(5)	V(1)–N(1)–C(9)	108.62(10)
O(2)–V(1)–N(2)	77.01(5)	V(1)–N(2)–C(10)	130.26(13)
O(2)–V(1)–O(4)	103.05(6)	V(1)–N(2)–C(18)	130.26(13)
O(4)–V(1)–N(1)	169.14(6)		

^{13}C NMR of HQ vanadium complexes, probably associated with the low solubility. ^{1}H NMR spectra of these complexes have been recorded at room temperature and exhibit expected aromatic and aliphatic protons. A comparison of spectra of free ligand with spectra of the corresponding complexes shows the absence of hydroxyl signal of

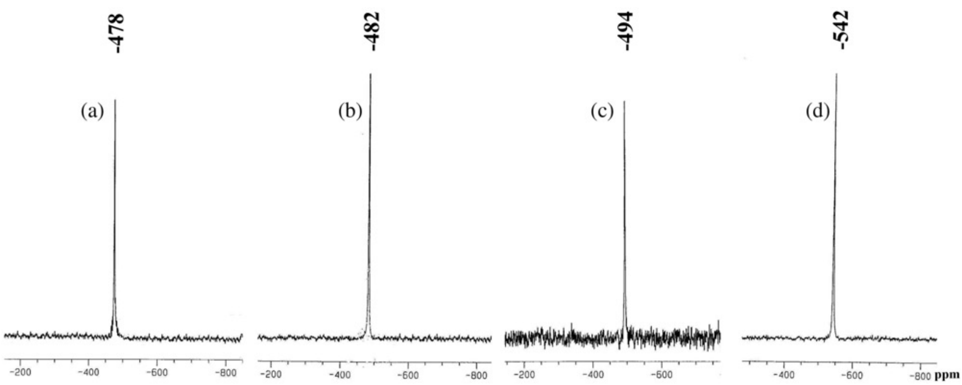


Figure 5. ^{51}V NMR spectra of (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

free HQ at δ9.32 ppm. Considerable deshielding of the proton bonded to the carbon adjacent to the nitrogen and shielding of the proton bonded to the carbon adjacent to the oxygen (phenolate ring) is observed. Such a shift has been reported previously in HQ complexes of vanadium and titanium [45, 46]. Two sets of signals were observed for 8-hydroxyquinolato moieties, with most of the protons signals overlapped except for H-2, which appears as two distinct doublets with similar coupling constants. Alkoxy signals of **1**–**3** (OCH_3, OCH_2R, and $OCHR_2$) show a deshielding trend from 5.68, 6.14, and 6.84 ppm, respectively. In ^{13}C NMR spectra two sets of signals are observed, in agreement with two non-equivalent bidentate quinoline moieties in solid-state structures. ^{51}V NMR data of these complexes are in the range of reported complexes of the type $[VO_{6-n}N_n]$ ($n = 0$–2) [44]. Complex **1** exhibits a signal at −478 ppm with lower shielding than **2**, −482 ppm (figure 5). In these complexes shielding increases in this order $OCH_3 < OCH_2R < OCHR_2 < OCR_3$ ($R = CH_3$), consistent with the reported trends for vanadium complexes [44].

The electronic absorption spectra of the complexes in C_6H_6 show three bands. An absorption at 280 nm has been assigned to intraligand transition (π–π^*) of 8-hydroxyquinolato and probably superimposed with the $O \rightarrow V$ charge transfer, involving the oxo double bond [21]. The other broad bands are associated with LMCT transitions involving internal (π–π^*) transition of the organic ligand. The band at 380 nm essentially involves oxygen to vanadium transition whereas the transition at 470 nm can be assigned to nitrogen to vanadium [21].

IR spectra of the complexes exhibit a characteristic spectral pattern; significant proposed assignments are absorptions at *ca* 950, *ca* 540, and *ca* 500 cm^{-1}, assigned to ν (V=O), ν (V–O), and ν (V–O), respectively [45]. 8-Hydroxyquinolato related bonds show a similar pattern to previously reported HQ coordination compounds [21, 45].

4. Conclusion

Using vanadium(V) oxoalkoxide, four different oxoalkoxo vanadium(V) complexes of HQ have been synthesized in a facile procedure. Spectroscopic behavior of the complexes and also crystal and molecular structures of **1** and **2** have been investigated. Methoxo complex (**1**) has a dimeric structure with a V to Q ratio of 1 : 1, while **2–4** have a monomeric structure with 1 : 2 ratios. NMR studies demonstrate that chemical shifts of vanadium and protons of alkoxy groups follow a regular trend.

Supplementary material

Crystallographic data of **1** and **2** has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 867510 and 867511. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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