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Synthesis, structural characterization and catalytic potential of oxidovanadium(IV) and dioxidovanadium(V) complexes with thiazole-derived NNN-donor ligand

Massomeh Ghorbanloo^a, Rahman Bikas^b, Solmaz Jafari^a, Marta S. Krawczyk^c and Tadeusz Lis^d

^aDepartment of Chemistry, University of Zanjan, Zanjan, Iran; ^bFaculty of Science, Department of Chemistry, Imam Khomeini International University, Qazvin, Iran; ^cFaculty of Pharmacy, Department of Analytical Chemistry, Wroclaw Medical University, Wroclaw, Poland; ^dFaculty of Chemistry, University of Wroclaw, Wroclaw, Poland

ABSTRACT

Reaction between the tridentate NNN donor ligand, (*E*)-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)benzo[*d*]thiazole (HL), and V₂O₅ in ethanol gave a new vanadium(V) complex, [VO₂L] (**1**), while the similar reaction by using [V^{IV}O(acac)₂] as the metal source gave two different types of crystals related to compounds [VO₂L] (**1**) and [V^{IV}O(acac)L] (**2**). The molecular structures of the complexes were determined by single-crystal X-ray diffraction and spectroscopic characterization was carried out by means of FT-IR, UV–vis and NMR experiments as well as elemental analysis. The oxidovanadium(IV) and dioxidovanadium(V) species were used as catalyst precursors for olefin oxidation in the presence of hydrogen peroxide (H₂O₂) as an oxidant. Under similar experimental conditions, the presence of **1** resulted in higher oxidation conversion than **2**.

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CONTACT Massomeh Ghorbanloo 🖾 m_ghorbanloo@yahoo.com

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1. Introduction

Vanadium is a versatile metal ion which has been widely used in coordination chemistry in a variety of oxidation states, from -3 to +5. The +4 and +5 oxidation states are the most stable ones under aerobic conditions [1]. The +5 oxidation state of vanadium has received considerable attention, not only due to its interesting chemistry associated with its ability to exist in three different motifs *viz.*, VO³⁺, V₂O₃⁴⁺ and VO₂⁺ but also due to its involvement in many catalytic processes [2]. The chemistry of vanadium compounds in the +4 oxidation state, also, has attracted particular attention for their interesting spectroscopic [3], biological [4], mechanochemical [5] and many other activities and characteristics [6]. High-valent vanadium complexes have been considered as new versatile catalytic reagents for a wide range of oxidation reactions, such as oxidation of olefins and alcohols [7], benzene alkylaromatic compounds [8] and sulfides [9].

Vanadium easily switches between +4 and +5 oxidation states and the relative stability of its species depends upon the basicity of the ligands and the pH of the reaction medium [10]. Our work in this area led us to design monobasic tridentate NNN donor ligands to prepare the respective both vanadium(IV) and vanadium(V) at ambient condition.

In general, N, O donor ligands (such as hydrazones) promote the aerial oxidation of oxidovanadium(IV) complexes to highly stable oxidovanadium(V) compounds. Hydrazones have a tendency to stabilize the vanadium in its highest oxidation state [11, 12] and, for that reason, they seem to be good candidates for catalytic oxidation studies because of their ability to resist oxidation [13]. Thiazoles are the significant class among heterocyclic compounds containing both S and N atoms. Metal complexes of these ligands have attracted much attention due to their appealing physico-chemical properties [14–16]. The combination of the thiazole moiety with hydrazides provides intriguing chemical properties and catalytic activity for the resulting condensation products [17]. Herein, we report the syntheses, crystal structures, spectroscopic properties and catalytic activity of two new vanadium complexes of the tridentate Schiff base ligand, (*E*)-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)-benzo[*d*]thiazole (HL).

2. Experimental

2.1. Materials and instruments

All chemicals and solvents were purchased in the highest possible purity from Merck or Sigma and used as received without further purification. FT-IR spectra were recorded in KBr disks with a Bruker FT–IR spectrophotometer. The elemental analyses (carbon, hydrogen and nitrogen) were obtained from a Carlo ERBA Model EA 1108 analyzer. The atomic absorption analysis was carried out using Varian Spectra AA 220 equipment. ¹H and ¹³C NMR spectra of the ligand in DMSO-d₆ solution were recorded on a Bruker 250 and 62.9 MHz spectrometer, respectively, and chemical shifts are indicated in ppm relative to tetramethylsilane (TMS). The reaction products of oxidation were determined and analyzed using an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m \times 320 µm \times 0.25 µm).

2.2. Synthesis of (E)-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)benzo[d]thiazole (HL)

(*E*)-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)benzo[*d*]thiazole (HL) was synthesized by the reaction of 2-acetylpyridine (0.121 g, 1.00 mmol) with 2-hydrazinolbenzothiazole (0.165 g, 1.00 mmol) in methanol (30 mL). The mixture of mentioned compounds was refluxed for 6 h. The solution was then evaporated on a steam bath and cooled to room temperature. The resulting precipitate was separated and filtered off, washed with 3 mL of cooled methanol and recrystallized from ethanol. Yield: 80% (0.21 g). Anal. Calcd for $C_{14}H_{12}N_4S$ (MW = 268.34 g mol⁻¹): C, 62.66; H, 4.51; N, 20.88%. Found: C, 62.63; H, 4.69; N, 20.86%. Selected FT-IR (KBr, cm⁻¹): 3443 (br, w), 3066 (w), 2939 (w), 2860 (w), 1610 (vs), 1565 (s), 1450 (s), 1375 (w), 1277 (m), 1127 (s), 1050 (m), 991 (m), 878 (s), 755 (s), 735 (m), 676 (m), 565 (m), 497 (w). ¹H NMR (250.13 MHz, DMSO-d₆, 25°C, TMS, ppm): δ = 2.3 (3H, s), 4.11 (1H, NH), 7.09 (2H, m), 7.28 (2H, m), 7.83 (2H, d, *J* = 7.25), 8.04 (1H, d, *J* = 7.5), 8.57 (1H, d, *J* = 5.50). ¹³C NMR (62.9 MHz, DMSO-d₆, 25 °C, TMS, ppm): δ = 13.50, 116.53, 120.12, 122.78, 125.26, 126.02, 127.32, 128.76, 138.17, 143.64, 147.86, 153.28, 154.91, 167.16 ppm. UV-vis in MeOH, $\lambda_{max'}$ nm (ϵ , M⁻¹ cm⁻¹): 226 (3290), 339 (1780), 431 (640).

2.3. Synthesis of dioxido-(2-((1-(pyridin-2-yl)ethylidene)hydrazono)-2,3-dihydro-1,3-benzothiazolato)-vanadium(V); [VO₂L] (1)

Complex **1** was synthesized by the reaction of thiazole-hydrazone ligand, HL (0.268 g, 1.00 mmol), and V₂O₅ (0.091 g, 0.50 mmol) in ethanol solvent. Mentioned amounts of materials were placed in the main arm of a branched tube. Ethanol was carefully added to fill the arms, the tube was sealed and the reagents containing arm immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After a week, block-red crystals of **1** were deposited in the cooler arm. Yield based on V₂O₅: 60% (0.21 g). Anal. Calcd for C₁₄H₁₁N₄O₂SV (MW = 350.27 g mol⁻¹): C, 48.01; H, 3.17; N, 16.00; V, 14.54%. Found: C, 48.03; H, 3.21; N, 15.97; V, 14.47%. Selected FT-IR (KBr, cm⁻¹): 3446 (br), 2927 (w), 2856 (w), 1600 (s), 1560 (w), 1506 (w), 1428 (s), 1328 (w), 1281 (m), 1237 (m), 1152 (m), 1078 (w), 945 (m), 872 (w), 747 (m), 695 (w), 660 (w), 554 (w), 443 (w). ¹H NMR (250.13 MHz, DMSO-d₆, 25 °C, TMS, ppm): δ = 2.57 (3H, s), 7.07 (1H, d), 7.30 (2H, m), 7.67 (2H, m), 8.07 (1H, d), 8.28 (1H, d), 8.73 (1H, d). UV-vis in MeOH, λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 227 (16,140), 284 (10,080), 471 (7550).

2.4. Synthesis of (acetylacetonato)-oxido-(2-((1-(pyridin-2-yl)ethylidene)hydrazono)-2,3-dihydro-1,3-benzothiazolato)-vanadium(IV); [VO(acac)L] (2)

Complex **2** was synthesized by a similar method to that described for **1**, but, in this case VO(acac)₂ was used instead of V_2O_5 as the vanadium source. In fact, thiazole-hydrazone ligand, HL (0.268 g, 1.00 mmol), and VO(acac)₂ (0.133 g, 0.50 mmol) were used. The reaction was done in ethanol and the red plate-shaped crystals of **2** together with some pieces of red block-shaped crystals were collected in the cooler arm after about one week. In this reaction, two kinds of crystals (block and plate red) were obtained which various analyses (like FT-IR, NMR, UV–vis and single crystal X-ray analysis) indicated that the block-red crystals are the same as the crystals of **1**. The reaction was repeated several times in various purity of ethanol solvent. The results of reaction indicated that the crystals of both **1** and **2**

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simultaneously form in the branched tube; however, their ratio is controlled by the purity of solvent. Complex **2** is the sole product in absolute ethanol (Merck) while in ethanol with higher amount of water (ethanol 96%), **1** is the main product of this reaction. Anal. Calcd for $C_{19}H_{18}N_4O_3SV$ (MW = 433.37 g mol⁻¹): C, 52.66; H, 4.19; N, 12.93; V, 11.75%. Found: C, 52.36; H, 4.31; N, 12.99; V, 11.74%. Selected FT-IR (KBr, cm⁻¹): 3439 (br), 2927 (w), 2858 (w), 1750 (w), 1600 (s), 1564 (w), 1517 (m), 1428 (s), 1399 (w), 1331 (w), 1279 (w), 1238 (m), 1149 (s), 1081 (m), 1005 (w), 952 (m), 776 (m), 750 (m), 660 (w), 553 (w), 432 (w). UV–vis (MeOH): $\lambda_{max'}$ nm (ϵ , M⁻¹ cm⁻¹): 227 (15,550), 288 (7800), 493 (6500).

2.5. General oxidation procedure

Oxidation reactions were performed under air atmosphere in 2 mL of solvent and aqueous H_2O_2 (30%) was used as oxidant. In a typical experiment, a mixture of catalyst precursor (**1** or **2**), 2.0 mL solvent and 0.5 mmol of substrate were placed in a 25 mL round bottomed glass flask. The mixture was heated to the desired temperature and after addition of H_2O_2 , the solution was placed to continue the reaction in the stable temperature. At appropriate intervals, aliquots were removed and analyzed immediately by GC. The oxidation products were identified by comparison of their retention times with those of authentic samples.

2.6. X-ray crystallography

X-ray diffraction data for **1** and **2** were collected at 120 and 150 K, respectively, by the ω -scan technique on Kuma KM4 CCD diffractometers with a Sapphire 2 CCD detector using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Data collection, cell refinement, and data reduction and analysis were carried out with CrysAlis CCD and CrysAlis RED, respectively (Table 1) [18]. Analytical absorption corrections were applied to the data with the use of CrysAlis RED. The structures were solved by direct methods using SHELXS-97 and refined by a full-matrix least squares technique on F^2 with SHELXL-2014 with anisotropic thermal parameters for all non-H atoms [19]. All H atoms were found in difference Fourier maps, and in the final refinement cycles the C-bonded H atoms were repositioned in their calculated positions and refined using a riding model, with C–H = 0.95 Å, and with U_{iso}(H) = 1.2Ueq(C) for aromatic CH. The structure plots were prepared with DIAMOND [20].

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, No. 1573423 and 1573424 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44 1223 336 033, deposit@ccdc.cam.ac.uk, or www: www. ccdc.cam.ac.uk.

3. Results and discussion

3.1. Synthesis and characterization

The tridentate Schiff base ligand, HL, was derived from the reaction of 2-hydrazinylbenzo[*d*]-thiazole with 2-acetylpyridine in methanol under refluxing condition. ¹H and ¹³C NMR spectra of HL in DMSO-d₆ confirmed the proposed structure for the ligand. In the ¹H NMR spectrum of HL, signals at δ 2.3 and 4.11 ppm are assigned to the –CH₃ and NH– groups,

Identification code	1	2
Net formula	C ₁₄ H ₁₁ N ₄ O ₂ SV	C ₁₀ H ₁₀ N₄O₂SV
Formula weight	350.27	433.37
Radiation	ΜοΚα	ΜοΚα
Т (К)	120	150
Crystal size (mm)	$0.55 \times 0.30 \times 0.18$	$0.40 \times 0.16 \times 0.08$
Crystal shape (color)	Block, red	Plate, red
Crystal system	Monoclinic	Orthorhombic
Space group	P2,/c	Pbca
a (Å)	15.230(4)	8.003(2)
b (Å)	13.414(3)	15.350(6)
<i>c</i> (Å)	13.611(3)	32.120(12)
β (°)	96.09(2)	90
Volume (ų)	2765.0(11)	3946(2)
Ζ	4	8
Density (mg m ⁻³)	1.683	1.459
Absorption coefficient (mm ⁻¹)	0.88	0.64
Absorption correction	Analytical	Analytical
F(0 0 0)	1424	1784
Θrange (°)	3.0-28.5	2.8–26.5
Independent reflections	6998	4079
Measured reflections	36,407	25,068
Reflections with $l > 2\sigma(l)$	5383	2465
Index ranges (<i>hkl</i>)	−20 < h < 20; −10 < k < 17; −18 < l < 18	-9 < h < 10; -18 < k < 18; -40 < l < 34
R _{int}	0.058	0.153
Restraints; parameters	0; 399	0; 256
Goodness of fit on F ²	1.032	1.002
$R[F^2 > 2\sigma(F^2)]$	0.043	0.061
$wR(F^2)$	0.117	0.150
Max. electron density (e·Å ⁻³)	0.67	0.36
Min. electron density (e·Å ⁻³)	-0.52	-0.50

 Table 1. Crystal data and structure refinement parameters for 1 and 2.

respectively. The reaction of V_2O_5 and $VO(acac)_2$ with HL in ethanol afforded $[VO_2L]$ (1) and [VO(acac)L] (2) as red block-shaped and red plate-shaped crystalline compounds, respectively (see Equations 1 and 2). Complex 1 was obtained as the sole product by the reaction of HL and V_2O_5 . In the case of $VO(acac)_2$, 2 was not the sole product because some crystals of 1 were formed beside the crystals of 2; their amount was dependent to the nature of the solvent. It is seen that the amount of 1 in this reaction is dependent upon the purity of ethanol and the presence of water in the solvent. However, in absolute ethanol it is possible to obtain 2 as the sole product. In this reaction the formation of the dioxidovanadium(V) core conceivably takes place according to the overall Equation (3). In this reaction the V(IV) is oxidized to V(V) by aerial oxygen and the presence of aerial oxygen is also an effective parameter in controlling the formation of 2 as sole product.

$$V_2O_5 + 2HL \rightarrow 2[VO_2L] + H_2O \tag{1}$$

$$VO(acac)_2 + HL \rightarrow [VO(acac)L] + Hacac$$
 (2)

$$2VO(acac)_2 + 2HL + \frac{1}{2}O_2 + H_2O \rightarrow 2|VO_2L| + 4Hacac$$
 (3)

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Figure 1. UV–vis spectra of HL (black), 1 (0.57×10^{-5} M) (blue) and 2 (0.57×10^{-5} M) (red).

Spectroscopic studies confirmed that both red, block-shaped crystals obtained from two different metal sources (V₂O₅ and VO(acac)₂) are the same. Checking the unit cell parameters of these crystals was another tool which confirmed this finding, since the unit cell parameters of the crystals obtained from two methods were the same. In the ⁵¹V NMR spectra of **1** and 2 a single signal related to the vanadium ions is observed at 533.8 and 535.8 ppm, respectively [21]. In the case of 1, due to the presence of two independent V(V) molecules in the crystal structure, two peaks were expected. However, as mentioned in section 3.2., the coordination spheres around the V(V) ions in these molecules are almost the same and there are not considerable differences in the electronic properties of vanadium ions in these molecules.

A comparison of the FT-IR spectra of the complexes (Figure S1) with the ligand provides some evidences for the coordination of the ligand to the vanadium core. On complexation, the absence of the $v_{\rm NH}$ band of the ligand shows coordination of the ligand as a mono-anionic ligand, (L)⁻¹. The infrared spectra of the complexes display an absorption band at 1600 cm⁻¹ which can be assigned to the C=N stretching frequency of the coordinated ligand [22]. The red shift of the strong C=N stretch in the FT-IR spectra of complexes indicates the C=N group of the Schiff base ligand is coordinated to the metal ion [23]. The FT-IR spectrum of **2** exhibits one sharp band at 952 cm⁻¹ due to the v(V=O) mode [24]. Complex 1 exhibits one sharp band at 945 cm⁻¹ due to v(V=O) and a band at *ca*. 872 cm⁻¹ due to the $v[V-(\mu-O)-V]$ vibrations [25].

The electronic absorption bands of the ligand and complexes were recorded in methanol solution (Figure 1). Bands at 431 and 339 nm are attributed to the $n \rightarrow \pi^*$ and the band at 226 nm is due to $\pi \rightarrow \pi^*$ transitions. These bands are shifted in the UV-vis spectrum of the complexes which confirm the coordination of hydrazone ligand to the vanadium ion. For 1 and 2, high energy bands in the range 471 and 493 nm are assigned to the ligand to metal charge transfer (LMCT) transitions (ligand to an empty d orbital of the vanadium ion).



Figure 2. (a) Molecular structure of components in the asymmetirc unit of the crystal 1; (b) overlay of two molecules. Thermal ellipsoids are drawn in 30% probability level.

3.2. Description of the crystal structure of [VO₂L] (1)

Single crystal X-ray analysis indicates that **1** is a molecular complex of dioxidovanadium(V). The molecular structure of **1** is shown in Figure 2(a) and selected bond lengths and angles are given in Table 2. The asymmetric part of the unit cell of **1** consists of two independent complex molecules (labeled as molecules A and B) in which one of them (A) may be considered as a dimeric species (similar to dioxidovanadium(V) complexes presented in our previous report [26]). Comparison of geometries of these two components is presented in Figure 2(b) indicating significant similarity between them, with the exception of some differences observed in the position of oxido ligands toward the vanadium(V) center. In the presented

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Bond	Length	Bond	Angle
V1A-02A	1.6116(17)	02A-V1A-01A	105.98(8)
V1A-O1A	1.6574(16)	O2A–V1A–N2A	98.26(7)
V1A–N2A	2.0384(18)	O1A-V1A-N2A	103.84(7)
V1A–N1A	2.0920(18)	O2A-V1A-N1A	94.26(8)
V1A–N3A	2.1405(19)	O1A-V1A-N1A	102.03(7)
V1A–O1A ⁱ	2.4218(17)	N2A–V1A–N1A	146.78(7)
S1A-C7A	1.751(2)	O2A–V1A–N3A	105.11(8)
S1A-C8A	1.753(2)	O1A-V1A-N3A	148.86(7)
O1A–V1A ⁱ	2.4219(17)	N2A–V1A–N3A	73.20(7)
V1B-O1B	1.6203(17)	N1A–V1A–N3A	73.86(7)
V1B-O2B	1.6213(17)	O2A–V1A–N1A ⁱ	175.30(7)
V1B–N2B	2.0222(18)	O1A–V1A–N1A ⁱ	77.44(7)
V1B-N1B	2.1109(18)	N2A–V1A–O1A ⁱ	83.87(6)
V1B-N3B	2.1495(19)	N1A–V1A–O1A ⁱ	81.77(6)
Bond	Angle	N3A–V1A–O1A ⁱ	71.42(6)
O2B-V1B-N1B	99.18(8)	O1B–V1B–O2B	109.09(10)
N2B-V1B-N1B	146.08(7)	O1B-V1B-N2B	102.04(8)
O1B-V1B-N3B	126.88(8)	O1B-V1B-N2B	99.66(8)
O2B-V1B-N3B	123.98(9)	O1B-V1B-N1B	98.08(8)
N1B-V1B-N3B	73.02(7)	N2B–V1B–N3B	73.06(7)

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

Symmetry codes: (i) 1 − *x*, 1 − *y*, 1 − *z*.

molecules, the vanadium(V) ions have a five coordinate $\{N_3O_2\}$ environment and the coordination geometry around them may be described as distorted trigonal-bipyramidal with equatorial angles in the range of 105–148° in molecule A and 109–126° in molecule B. In both species the coordination environments around the vanadium(V) ions are composed by three nitrogen atoms provided by tridentate thiazole-hydrazone Schiff base ligand, (L)⁻ and two oxygen atoms of oxido groups. In both molecules, the hydrogen atom of the NH moiety of thiazole-hydrazone ligand was eliminated during the complexation. Consequently, the ligand acts as tridentate mononegative NNN-donor ligand, (L^{1)–}. The crystal structure of **1** is stabilized by the network of C–H···O and C–H···N interactions (Table 3).

Despite a great resemblance between A and B components of 1, they exhibit quite different intermolecular contacts. As was noticed before, molecule A is involved in the $\pi \cdots \pi$ interactions with the neighboring molecule of A type, resulting in a centrosymmetric architecture of "dimer" [27], with the nearest distance between adjacent components (viz. centroid…centroid distance) of about 3.60 Å, between N1A/C1A/C2A/C3A/C4A/C5A and C8A/ C9A/C10A/C11A/C12A/C13A rings (see Figure S2). Moreover, the V^{5+} ions are combined by the dioxido bridge in this unit, with the V1A–O1A bond length of 1.6574(16) Å and V1A–O1Aⁱ of 2.4219(17) Å (i = -x + 1, -y + 1, -z + 1), forming a {V₂O₂} cyclic unit. The V···V distance through this bridge is 3.2185(10) Å and the V1A–O1A–V1Aⁱ angle is 102.56(7)°. By considering this V···O interaction a distorted octahedral geometry can also be described for the vanadium ion in this unit. In the case of molecule B in the crystal 1, $\pi \cdots \pi$ interactions between the adjacent species are also created (see Figure S3). The distance between V1B/N2B/C7B/ N4B/N3B ring and C8B/C9B/C10B/C11B/C12B/C13B ring from neighboring unit is about 3.66 Å. The plane of the ligand is approximately planar to the crystallographic plane (001). The molecules from adjacent layers are related to each other by inversion through a center of inversion whereby 5-membered S1B/C7B/N2B/C9B/C8B rings from these neighboring species are arranged one above the other (the centroid ··· centroid distance equals 3.70 Å). Unlike molecule A, there are no V…O interactions in the case of molecule B.

D–H···A	D–H	Н…А	D····A	D-H···A
Complex 1				
C4A—H4A···O2A ⁱⁱⁱ C61A—H61C···N4B ^{iv}	0.95 0.98	2.54 2.60	3.097(3) 3.455(3)	118 146
Complex 2				
C61–H61 <i>C</i> ···N4 ⁱ C14–H14 <i>B</i> ···O1 ⁱⁱ	0.98 0.98	2.55 2.38	3.522(5) 3.350(6)	171 169

Table 3. Hydrogen-bond geometry (Å, °) in 1 and 2.

Symmetry codes: (i) x + 1/2, $y_{-}z + 3/2$; (ii) x + 1, $y_{-}z$; (iii) -x + 1, y + 1/2, -z + 3/2; (iv) -x + 1, y - 1/2, -z + 3/2.





3.3. Description of the crystal structure of [VO(acac)L] (2)

The molecular structure of **2** is shown in Figure 3 and selected bond lengths and angles are given in Table 4. X-ray studies indicated that the obtained product is a molecular mononuclear oxidovanadium(IV) complex, [VO(acac)L] (**2**). The vanadium(IV) ion adopts a distorted octahedral geometry and its coordination environment is filled by three nitrogen atoms provided by the tridentate thiazole-hydrazone Schiff base ligand, (L)⁻, two oxygen atoms of an acetylacetonate ligand, (acac)⁻, and the oxygen atom of the oxido group. Three donor atoms of the Schiff base ligand (N1, N2, N3) and one oxygen atom of (acac)⁻ create the equatorial plane of the octahedral geometry. One axial position is occupied by the oxygen atom of (acac)⁻, (V–O3 = 2.168(3) Å). The metal center (V) is deviated by 0.275 Å from the mean plane defined by the equatorial donor atoms towards the V=O moiety. In **2**, the hydrogen of the NH moiety of thiazole-hydrazone ligand was eliminated during the complexation. Consequently, the ligand acts as a tridentate monon-egative N₃-donor ligand, (L¹)⁻. The crystal packing of **2** is stabilized by C–H…O and C–H…N interactions (see Figure **4** and Table 3).

According to our previous report on dioxidomolybdenum and dioxidovanadium complexes of thiazole-hydrazone ligands [17, 26], two resonance structures contribute to the thiazole part of ligand in the deprotonated form. These resonance contributors can be easily identified by comparing the C7–N2 and C7–N4 bond lengths. The C7–N2 (1.338(4) Å) and C7–N4

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Bond	Length	Bond	Angle
V-01	1.610(3)	01-V-04	97.50(13)
V-04	1.976(3)	01-V-N3	98.49(13)
V–N3	2.061(3)	04-V-N3	162.73(13)
V–N2	2.087(3)	01-V-N2	97.60(14)
V–N1	2.114(3)	04-V-N2	108.19(13)
V-03	2.168(3)	N3-V-N2	76.10(13)
S-C8	1.753(3)	01-V-N1	97.40(13)
S-C7	1.755(4)	04-V-N1	95.27(14)
N1-C5	1.341(5)	N3-V-N1	76.22(14)
N1-C1	1.357(5)	N2-V-N1	150.11(13)
		01-V-03	178.49(13)
		04-V-03	83.37(11)
		N3-V-O3	80.80(12)
		N2-V-O3	80.94(12)
		N1-V-O3	83.74(12)
		C5–N1–V	125.7(3)
		C1-N1-V	115.2(3)

Table 4. Selected bond lengths (Å) and angles (°) in 2.

(1.329(4) Å) bond lengths in complex **2** are different in comparison to the lengths reported for double C=N (\approx 1.30 Å) or single C–N (\approx 1.35 Å) bonds. These bond lengths are close to the delocalized C=N bond lengths (\approx 1.33 Å) and show that the negative charge is delocalized over N2, C7 and N4 atoms. A similar effect is also observed in the case of complex **1**.

3.4. Catalytic activity of 1 and 2

The catalytic oxidation of cyclooctene was carried in the presence of H₂O₂ by using 1 or 2 as a catalyst precursor. Complex 1 was used as a representative catalyst precursor for the optimization of different reaction parameters viz. amounts of catalyst, oxidant (30% aqueous H_2O_2), solvent, and temperature. It was observed that only one product, namely cyclooctene epoxide, was formed in these catalytic reactions. To optimize the amount of catalyst precursor, three different amounts of 1 (0.0005, 0.0010 and 0.0020 g equal to 1.43, 2.85 and 5.70×10^{-3} mmol, respectively) were taken while the amount of cyclooctene (0.5 mmol) and other reaction parameters were constant (aqueous 30% H₂O₂ (1 mmol), acetonitrile (2 mL) and temperature (60 °C)). By increasing the amount of **1** from 1.43×10^{-3} mmol to 2.85×10^{-3} mmol, the conversion increased from 47% to 94%, but there was no further improvement in conversion on increasing its amount up to 5.70×10^{-3} mmol. Therefore, 2.85×10^{-3} mmol of **1** was chosen as an appropriate amount for optimizing the remaining conditions. Considering 2.85×10^{-3} mmol of catalyst precursor for 0.5 mmol of cyclooctene, three different amounts of oxidant (30% H₂O₂) viz. 0.5, 1.0 and 1.5 mmol were tested. The lowest i.e. 49% conversion of epoxide was obtained with 0.5 mmol of oxidant under above reaction conditions, whereas maximum of 94% conversion was obtained using 1.0 mmol of oxidant (see Figure 5). Further increasing the amount of oxidant to 1.5 mmol did not improve the conversion (95%). Thus, 1.0 mmol of oxidant (cyclooctene : oxidant ratio is 1:2) was found to be suitable for the maximum conversion of cyclooctene.

The solvent also affects the oxidation of substrate (Figure 6). It was found that CH_3CN gave the highest conversion (94%). The difference is explained by the high solubility of catalyst in this solvent and also the high miscibility of CH_3CN with water in comparison with *n*-hexane (immiscible). The effect of temperature on oxidation of cyclooctene was also



Figure 4. Hydrogen bonding interactions in the crystal of 2.



Figure 5. Effect of different amount of H_2O_2 in the oxidation of cyclooctene by 1. *Reaction conditions*: 1 (2.85 × 10⁻³ mmol); temperature, 60 °C; cyclooctene, 0.5 mmol; CH₃CN (as solvent), 2 mL; time, 5 h.



Figure 6. Influence of solvent in the catalytic epoxidation of cyclooctene by 1.^a *Reaction conditions*: 1 (2.85 × 10⁻³ mmol); temperature, 60 °C; cyclooctene, 0.5 mmol; solvent, 2 mL; time, 5 h; H_2O_2 , 1 mmol.

studied. The reaction was monitored at four different temperatures *viz.* 40, 60 and 70 and 80 °C for 5 h. The conversion was lowest (61%) at 40 °C but improved to 97% at 70 °C. Increasing the temperature to 80 °C did not improve the conversion.

Thus, the optimized reaction conditions for the oxidation of 0.5 mmol of cyclooctene are: catalyst (2.85×10^{-3} mmol), 30% aqueous H₂O₂ (1 mmol), acetonitrile (2 mL) and temperature 70 °C. Blank reactions gave only *ca*. 5% conversion after 24 h [27]. Thus, the presence of **1** as a catalyst precursor in running the oxidation reactions is necessary.

To establish the scope for the activity of $[VO_2L]$, this study was further extended to the catalytic epoxidation of several linear and cyclic olefins, namely styrene, α -methyl styrene,



Table 5. Oxidation of alkenes with H₂O₂ catalyzed by 1.^a

^aReaction conditions: 1 (2.85 \times 10⁻³ mmol), substrate (0.5 mmol), CH₃CN (2 mL), H₂O₂ (1 mmol) and temperature 70 °C; Time 5 h.

^bConversions are based on the starting substrates.

"TON = (mmol of product)/(mmol of vanadium).

1-octene, 1-decene, cyclohexene and indene, using $[VO_2L]$ (Table 5). Generally, the present catalytic system was completely selective for the epoxidation of cyclooctene, indene, 1-octene and 1-decene while for styrene and α -methyl styrene, benzaldehyde and acetophenone were the byproducts, respectively (Table 5, entries 1–6).

In continuation, we studied catalytic oxidation of olefins using [VO(acac)L] as catalyst precursor. As same as catalyst **1**, we determined the optimized reaction conditions for **2**. Thus, the optimized reaction conditions for the oxidation of 0.5 mmol of cyclooctene are: **2** (2.85×10^{-3} mmol), 30% aqueous H₂O₂ (1 mmol), acetonitrile (2 mL) and temperature 70 °C. Details of experimental conditions are presented in Table 6 and Figures 7 and 8.

This study was further extended to the catalytic epoxidation of several linear and cyclic olefins, namely styrene, α -methyl styrene, 1-octene, 1-decene, cyclohexene and indene, by using **2** (Table 7).

The catalytic efficiency of **1** and **2** for hydrocarbon oxidation are not same (as shown in Tables 5 and 7) which can be attributed to their different coordination geometry and also different oxidation state of vanadium centers. Probably, the high oxidation state of vanadium

Entry	$[H_2O_2]/[C_8H_{12}]$ Molar ratio	Conversion (%) ^b	Catalyst amount (× 10 ⁻³ mmol)	Temperature (°C)	TON ^c
1	0.5	37	2.85	60	64.9
2	1	83	2.85	60	145.6
3	1.5	85	2.85	60	149.1
4	1	38	1.43	60	132.9
5	1	86	5.70	60	75.4
6	1	39	2.85	40	68.4
7	1	92	2.85	70	161.4
8	1	94	2.85	80	164.9

Table 6. Catalytic activity of 2 on cyclooctene oxidation.^a

^aReaction conditions: **2** (2.85 \times 10⁻³ mmol); cyclooctene, 0.5 mmol; CH₃CN, 2 mL; time, 5 h.

^bConversions are based on the starting substrate.

^cTON = (mmol of product)/(mmol of vanadium).



Figure 7. Effect of different amount of H_2O_2 in the oxidation of cyclooctene by **2**. *Reaction conditions*: **2** (2.85 × 10⁻³ mmol); temperature, 70 °C; cyclooctene, 0.5 mmol; CH₃CN (as solvent), 2 mL; time, 5 h.



Figure 8. Influence of solvent in the catalytic epoxidation of cyclooctene by **2**. *Reaction conditions*: **2** (2.85×10^{-3} mmol); temperature, 70 °C; cyclooctene, 0.5 mmol; solvent, 2 mL; time, 5 h; H₂O₂, 1 mmol.

Entry	Substrate	Conversion (%) ^b	Product(s)	Selectivity (%)	TON
1		86	o	78	150.9
2		71		22 84	124.6
3		47		16 >99	82.5
4		93	0	>99	163.2
5		32		>99	56.1
6	~~~~	18		>99	31.6

Table 7. Oxidation of alkenes with H₂O₂ catalyzed by 2.^a

^aReaction conditions: **2** (2.85 × 10⁻³ mmol), substrate (0.5 mmol), CH₃CN (2 mL), H₂O₂ (1 mmol) and temperature 70 °C. ^bConversions are based on the starting substrates. ^cTON = (mmol of product)/(mmol of vanadium).

in **1** makes it more active in hydrocarbon oxidation. Similar trends have been reported for $[V^{IV}O(sal-his)(acac)]$ and $[V^{V}O_2(sal-his)]$ [28] and for $V^{IV}OL^1$ ($L^1 = 2,2'-((1E,1'E)-((2-hydroxybutane-1,4-diyl)bis(azanylylidene))$ bis(methanylylidene))diphenol) and $V^{V}OL^2$ ($L^2 = 6,6'-((1E,1'E)-((2-hydroxybutane-1,4-diyl)bis(azanylylidene))$ bis(methanylylidene)) bis(2-methoxyphenol)) [29]. In comparison with the previously reported catalysts, both **1**

and **2** exhibited better activity for the oxidation of hydrocarbons. The previously reported *N*,*N*[']-bis(salicylaldiminato)oxidovanadium(IV) [30] complex showed lower catalytic activity than **1** and **2** for the oxidation of cyclooctene. Additionally, catalysts **1** and **2** showed higher catalytic activity than the VO(tmbmz)₂ (tmbmz = 2-thiomethylbenzimidazole) [31] and $V^{IV}O\{N,N'$ -salicyl-*R*,*R*-cyclohexanediaminium} [32] for the oxidation of cyclohexene and styrene. However, for the oxidation of cyclohexene and styrene, these catalytic systems are less effective than the [VO(acac)(R-1,2-bis{(Cl-phenyl)imino}acenaphthene)]Cl [33] system.

Although the details of the catalytic mechanism were not studied in the present work, on the basis of the electronic absorption spectroscopy studies (Figures S7 and S8) and also by considering the previous studies on catalytic oxidation by oxidovanadium complexes [13b, 14, 27, 34], it is predicted that the key step in this catalytic process is the oxidation of substrates by a peroxovanadium-hydrazone Schiff base species formed after addition of H₂O₂ to the solution of complex.

4. Conclusion

New oxidovanadium(IV) and dioxidovanadium(V) complexes with thiazole-hydrazone ligand have been synthesized and characterized by spectroscopic methods and single crystal X-ray analyses. The catalytic activity of these compounds has been tested in olefin epoxidation by H_2O_2 . The epoxide yields show that the catalytic activity of these complexes is strongly dependent on the temperature and nature of solvent. These compounds can be considered as active catalyst precursors for epoxidation reactions. Nevertheless, the results obtained with the V(V) complex provide a good basis for further optimization aiming at efficient catalytic activity.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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