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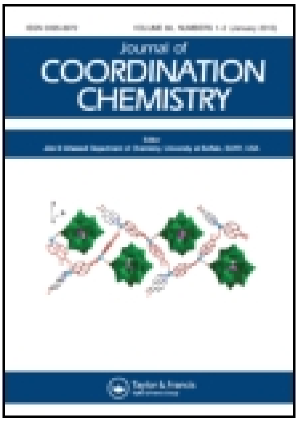

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Synthesis, X-ray structure, DFT studies, and catalytic activity of a vanadium(V) complex containing a tridentate Schiff base

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Synthesis, X-ray structure, DFT studies, and catalytic activity of a vanadium(V) complex containing a tridentate Schiff base

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Reactions of a solution of NH_4VO_3 in H_2O_2 and water and salicylidene benzoyl hydrazine as a tridentate Schiff base (ONO) afford a six-coordinate V(V) complex $[VO(ONO)(OCH_3)(CH_3OH)]$ with a distorted octahedral configuration. The complexes $[VO(ONO)(OCH_3)(CH_3OH)]$ were isolated as air-stable crystalline solids and fully characterized, including by single-crystal X-ray structure analysis. DFT calculations have been performed to understand the electronic structure of the complex. Vibrational frequencies and maximum absorption wavelengths of the complex theoretically calculated are in good agreement with experimental values. $[VO(ONO)(OCH_3)(CH_3OH)]$ shows efficient oxidation of sulfides to their corresponding sulfoxides using urea hydrogen peroxide as the oxidant at room temperature under air.

Keywords: Vanadium(V) complex; Schiff base; Crystal structure; Sulfide oxidation; DFT calculations

1. Introduction

Selective oxidation of sulfides to sulfoxides is an attractive method for production of sulfoxides, which are useful building blocks as chiral auxiliaries in organic synthesis and as bioactive ingredients in the pharmaceutical industry [1–4]. A number of methods and procedures have been devoted to the development of effective catalysts for oxidation of sulfides [5–7]. Transition metal complexes as catalytic systems based on readily available, inexpensive, and environmentally benign "green oxidants" like hydrogen peroxide is very attractive [8–10].

Metal complexes with Schiff bases have played an important part in the development of coordination chemistry with many reports on their applications in homogeneous and heterogeneous catalysis [11, 12]. Among various transition metal complexes, Schiff base oxovanadium(V) complexes are the most efficient catalysts for oxidation reactions [13–16].

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Density functional theory (DFT) has been accepted as a powerful tool in prediction of molecular properties of inorganic compounds [17, 18]. There is a lot of information in the literature about structures, electronic properties, chemical reaction kinetics and mechanism, thermodynamic properties, vibrational, absorption, Raman, and NMR spectra of metallic complexes predicted by DFT [19–25]. Vanadium complexes are also the subject of many theoretical studies [23–25]. For example, DFT computations were used to investigate nucleophilic and electrophilic centers of some vanadium complexes by calculating global hardness and global softness [23]. Another DFT study [24], investigated the correlation between catalytic activities of vanadium complexes toward sulfide oxidation and the electronic character of the vanadium center.

Herein, we describe the synthesis, X-ray analysis, and DFT results of a new V(V) complex [VO(ONO)(OCH_3)(CH_3OH)] (ONO = salicylidene benzoyl hydrazine). The use of this complex as a catalyst in the oxidation of sulfides in the presence of urea hydrogen peroxide (UHP) as an oxidant under air at room temperature was also studied (scheme 1).

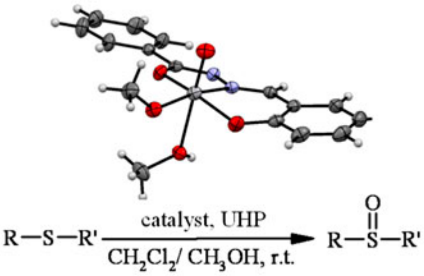
2. Experimental

Chemicals and solvents were purchased from Fluka and Merck Chemical companies. Salicylidene benzoyl hydrazine (ONO) was synthesized according to a published procedure [26].

Elemental analysis (carbon, hydrogen, and nitrogen) of the compound was obtained from a Carlo ERBA Model EA 1108 analyzer. Molar conductance of the complex was determined in methanol (ca. 10^{-3} M) at room temperature using a Toa CM 405 conductivity meter. FT-IR spectrum was obtained by using an Unicam Matson 1000 FT-IR spectrophotometer using KBr disks at room temperature. The products of oxidation reactions were determined and analyzed by an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m 320 lm 0.25 lm), and a flame ionization detector.

2.1. *Synthesis of [VO(ONO)(OCH_3)(CH_3OH)]*

2.0 mM of H_2O_2 (*w* = 30%) was added to 1.0 mM of NH_4VO_3, dissolved in H_2O (2 mL), and then an ethanolic solution of salicylidene benzoyl hydrazine (1.0 mM) was added. After 2 h of stirring at room temperature, the solution was filtered, and evaporated under reduced



Scheme 1. Oxidation of sulfides in the presence of [VO(ONO)(OCH_3)(CH_3OH)].

pressure to give the complex. Recrystallization from methanol yielded the complex as red-brown crystals. Yield: 0.289 g, 79%. Anal. Calcd for $C_{18}H_{16}N_2O_5V$: C, 54.97; H, 4.61; N, 7.12. Found: C, 54.89; H, 4.57; N, 7.21. Selected IR frequency (KBr disk, cm^{-1}): 1612 ($\nu_{C=N}$); ^1H NMR(d^6-DMSO): δ 3.18 (s, 3 H), 4.09 (s, 1 H), 5.29 (s, 3 H), 6.90 (d, 1H), 7.04 (dt, 1H), 7.44 (t, 1H), 7.51 (t, 2H), 7.57 (t, 1H), 7.72 (dd, 1H), 8.06 (t, 2H), 9.01 (s, 1H).

2.2. *General procedure for sulfide oxidation*

To a solution of sulfide (0.2 mM), chlorobenzene (0.2 mM) as internal standard, and [VO (ONO)(OCH_3)(CH_3OH)] (0.01 mM) in a 1 : 1 mixture of CH_3OH/CH_2Cl_2 (1 mL) was added 0.4 mM UHP as oxidant. The mixture was stirred at room temperature and the reaction progress was monitored by GC. Assignments of products were made by comparison with authentic samples.

2.3. Computational details

The ground-state structure of the complex was optimized by B3LYP hybrid density functional method using the 6-31G* basis set. This hybrid functional exploits a combination of B3 exchange functional [27] and LYP correlation functional [28]. B3LYP functional is accepted as a reliable method for investigation of metal complexes and there is abundant evidence in the literature that persuaded us to use this method. Back *et al*. [23] used the B3LYP functional to calculate the HOMO-LUMO gap, electron affinity, ionization potential, global hardness, and global softness of vanadium complexes. The mechanistic aspects of sulfide oxidation on different complexes of vanadium were also investigated by B3LYP functional [24]. Magnetic properties of vanadium-based complexes were studied by B3LYP functional too [29]. Frequency calculations are also performed on the optimized structure to confirm that the structure belongs to the local minima on the potential energy surface.

3. Results and discussion

3.1. *Complex characterization*

[VO(ONO)(OCH_3)(CH_3OH)] was obtained by reaction of an ethanolic solution of salicylidene benzoyl hydrazine (ONO) with NH_4VO_3 and H_2O_2.

The molar conductance of the complex is 4 Ohm^{-1} cm^2 M^{-1}, indicating that the complex is a nonelectrolyte. The C=N stretching frequency for the ligand occurs at 1639 cm^{-1} and for the complex it is expected to appear at lower frequencies (1612 cm^{-1}). This shift by at least 29 cm^{-1} to lower frequency compared to that of free ligand indicates a decrease in the bond order due to coordination of the metal with the azomethine nitrogen of ligand [30, 31]. The characteristic V=O stretch of the complex is at 960 cm^{-1}, i.e. within the range 950–1000 cm^{-1} reported for similar oxovanadium complexes [32, 33].

The coordination of the ligand was confirmed by comparing ^1H NMR patterns of the ligands and the complex. The signal at δ = 12.11 ppm, due to phenolic OH, disappears in spectra of the complex [3, 30]. A significant downfield shift ($\Delta\delta = 1.94$ ppm) of the signal for the azomethine (–CH=N–) proton in the complex relative to the corresponding ligand demonstrates coordination of azomethine nitrogen. Aromatic protons appear in the expected regions with minor variations in their positions ($\delta = 6.90$–8.06 ppm). The methyl protons of methoxy resonate at $\delta = 5.29$ ppm and two signals appear at $\delta = 3.18$ and 4.09 ppm due to coordinated methanol [3, 30].

To confirm coordination of salicylidene benzoyl hydrazine in this complex as well as the stereochemistry of the complex, the structure of complex has been determined by X-ray crystallography, and an ORTEP view of the complex is shown in figure 1.

The complex crystallizes in the monoclinic crystal system, space group $P2_1/c$. The crystal data are given in table 1. The molecular view of complex containing [VO(ONO)(OCH_3)(CH_3OH)] is shown in figure 1. The structure of the complex is mononuclear, consisting of discrete monomeric units of [VO(ONO)(OCH_3)(CH_3OH)], in which V is surrounded by two O and one N of the tridentate Schiff base in a distorted octahedral configuration. The V–O distances of the oxo (O5) are significantly shorter [1.5936(14) Å] than the corresponding distances to O of the tridentate ligands (O1 and O2) [1.9610(13), 1.8544(14) Å]. The V–N distance is longer [2.1284(15) Å]. The V–O3 and V–O4 distances are 2.334(13) and 1.769(13) Å, respectively, which are typical for the methanol and the methoxy group, respectively.

The crystal lattice is stabilized by intermolecular hydrogen bonds O–H···N between hydrogen of coordinated methanol and N of the Schiff base belonging to two neighboring complexes to form an infinite one-dimensional polymeric array along the *a*-axis (figure 2).

3.2. *DFT computations*

The structure of the vanadium complex was optimized by B3LYP level of theory using the 6-31G* basis set. The calculation involves determination of vibrational frequencies for validation of the local energy minima of the optimized structure. The optimized structure of the complex has a distorted octahedral configuration as predicted by X-ray analysis. Table 2 presents some selected optimized and X-ray experimental values of bond lengths and bond angles around vanadium. The difference between experimental and optimized values

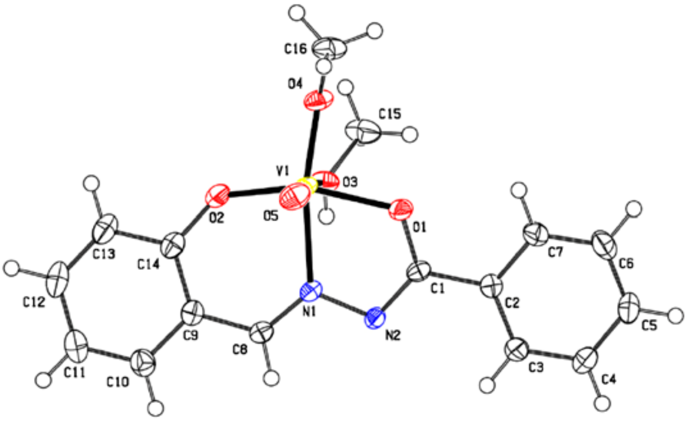


Figure 1. ORTEP diagram of [VO(ONO)(OCH_3)(CH_3OH)] with thermal ellipsoids drawn at 50% probability.

Table 1. Crystal data and structure refinement for [VO(ONO)(OCH$_3$)(CH$_3$OH)].

Empirical formula	$C_{16}H_{16}N_2O_5V$
Formula weight	367.25
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P\ 1\ 21/c\ 1$
Unit cell dimensions	$a = 8.0974(6)$ Å
	$\alpha = 90°$
	$b = 16.9355(12)$ Å
	$\beta = 103.7170(10)°$
	$c = 12.1217(9)$ Å
	$\gamma = 90°$
Volume	1614.9(2) Å^3
Z	4
Density (Calcd)	1.511 Mg/cm^3
Absorption coefficient	0.643 mm^{-1}
F (0 0 0)	756
Crystal size	0.13 × 0.22 × 0.26 mm^3
Theta range for data collection	2.11–28.79°
Index ranges	$-10<=h<=10$, $-22<=k<=22$, $-16<=l<=16$
Reflections collected	16,826
Independent reflections	4177 [R(int) = 0.0352]
Completeness to theta = 28.70°	99.4%
Absorption correction	Multi-scan
Max. and min. transmission	0.9211 and 0.8506
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4177/0/219
Goodness-of-fit on F^2	1.045
Final R indices [I>2 sigma(I)]	$R_1 = 0.0363$, $wR_2 = 0.0890$
R indices (all data)	$R_1 = 0.0519$, $wR_2 = 0.0976$
Largest diff. peak and hole	0.770 and −0.389 eÅ^{-3}

$R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$.
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
$\text{GOOF} = S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
$w = 1/[\sigma(F_o^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

(Error %) are also reported in table 2. Very good agreement between optimized and experimental values is observed and the error % values are acceptable because we note that the experimental results are for the solid phase while the computational results are for the gas phase. The optimized values of V–N and V–O bond lengths are acceptable according to data in the literature [34]. Among the optimized V–O bonds (see table 2 and figure 1), the V1–O5 (double bond character) bond length is shorter than the others, in accord with the experimental results. The V1–O3 bond length as obtained by both computational and experimental methods is longer than the other V1–O bond lengths. As can be seen in table 2, the optimized angles are in very good agreement with the experimental values. The highest error (3.97%) is for O1–V1–O3. The other bond lengths and angles of the complex (not shown in table 2) differed from the X-ray values with lower than 3% error.

The calculated Mulliken atomic charges of V1, O1, O2, O3, O4, O5, N1, and N2 (see figure 1) are +1.32, −0.63, −0.65, −0.61, −0.54, −0.42, −0.40, and −0.37, respectively. The charge on vanadium (+1.32) is significantly lower than the formal charge of +5, which indicates charge donation from the ligands to the metal center. The charge on C15 (carbon of methanol group) and C16 (carbon of methoxy) is negative (−0.23 and −0.20,

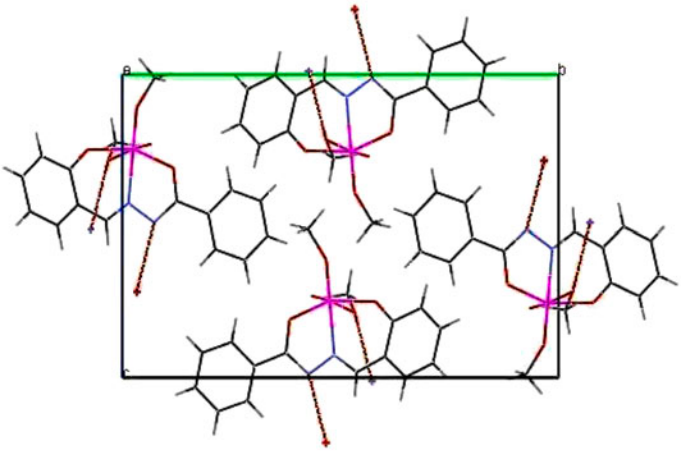


Figure 2. Depicting intermolecular hydrogen bonded 1D polymeric array along the *a* axis for [VO(ONO)(OCH$_3$)(CH$_3$OH)].

Table 2. Experimental X-ray and optimized geometrical parameters of the vanadium complex.

Selected bond	Optimized (Å)	X-ray (Å)	Error (%)	Selected angle	Optimized (°)	X-ray (°)	Error (%)
V1–O1	1.9523	1.9610(13)	0.45	N1–V1–O5	97.22	96.08(6)	1.18
V1–O2	1.8491	1.8544(14)	0.29	N1–V1–O1	73.44	73.91(5)	0.64
V1–O3	2.5321	2.3441(13)	8.02	N1–V1–O3	77.18	79.44(5)	2.84
V1–O4	1.7678	1.7691(13)	0.07	N1–V1–O2	82.55	83.58(5)	1.23
V1–O5	1.5656	1.5936(14)	1.76	O5–V1–O4	104.24	103.25(7)	0.95
V1–N1	2.1585	2.1284(15)	1.41	O1–V1–O4	93.25	94.44(6)	1.26
				O3–V1–O4	81.00	80.91(5)	0.11
				O2–V1–O4	102.08	101.85(6)	0.22
				O5–V1–O1	99.67	96.93(7)	2.83
				O1–V1–O3	77.11	80.30(5)	3.97
				O3–V1–O2	79.35	81.38(6)	2.49
				O2–V1–O5	101.91	99.86(7)	2.05
				O4–V1–N1	156.46	158.58(6)	1.34

respectively) while the charge on C1, C8, and C14 (carbons of Schiff base) is positive (+0.55, +0.07, and +0.40, respectively). Such a charge distribution produces a total dipole moment of 2.39 Debye for the complex that is directed toward the coordinated methoxy and methanol. The charge on hydrogen (H–OCH$_3$) of the coordinated methanol is +0.43. Therefore, an intermolecular hydrogen bond can easily form between this positive hydrogen of one complex and negative nitrogens (charges −0.40, −0.37) of another complex.

Frontier molecular orbitals are very important to clarify optical properties and chemical activity. Figure 3 shows HOMO-1 (−6.31 eV), HOMO (−5.72 eV), LUMO (−2.48 eV), and LUMO + 1 (−2.03 eV) molecular orbitals of the vanadium complex computed at the B3LYP/6-31G* level of theory. While the HOMO-1 and HOMO show greater contributions at the benzene rings (π-like orbitals) at both sides of the complex center, the LUMO and LUMO + 1 show greater contributions in the center of the complex on the vanadium, oxygen, and nitrogen. The calculated HOMO-LUMO and HOMO-1–LUMO + 1 energy gaps are 3.24 and 4.28 eV, respectively. These large energy gaps indicate high excitation

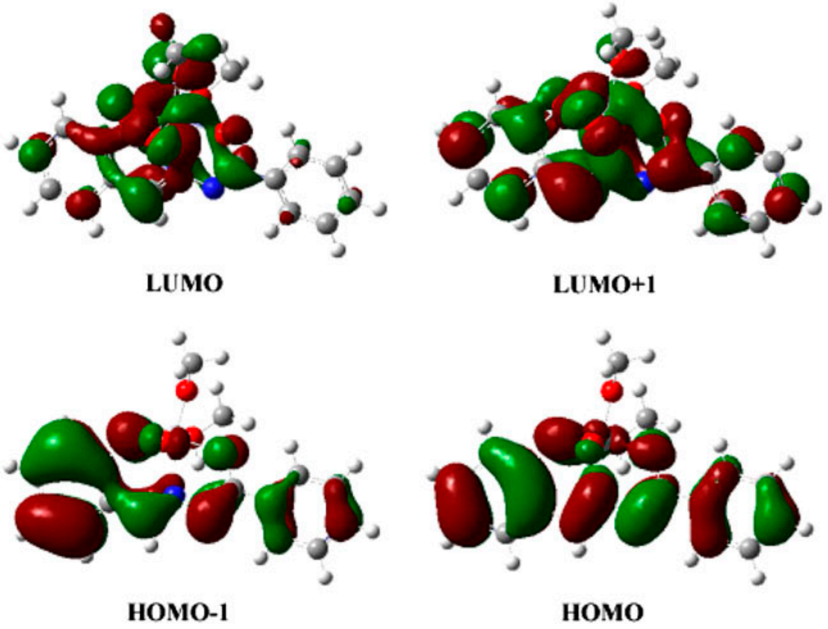


Figure 3. Presentation of HOMO-1, HOMO, LUMO, and LUMO + 1 molecular orbitals of the vanadium complex.

energies (in the UV region), good stability, and chemical hardness. Ultraviolet spectrum of vanadium complex in the gas phase has been calculated. Time-dependent DFT (TD-DFT) through B3LYP functional and 6-31G* basis set was employed to predict the electronic excitation of the vanadium complex. The calculated maximum absorption wavelengths obtained, *viz*. 383, 323, and 270 nm, are in good agreement with the experimental values of 393, 320, and 260 nm, attributed to the excitation from HOMO to LUMO, HOMO-1 to LUMO, and HOMO-1 to LUMO + 1 or LUMO + 2 (not shown in figure 3), respectively.

Frequency calculation of the complex has been performed at the B3LYP/6-31G* level of theory, confirming that the optimized structure is a minimum on the potential energy surface. The experimental and theoretical FTIR spectra are presented in figure 4. Some of the experimental and corresponding calculated vibrational wavenumbers along with their intensities and assignments are reported in table 3. The vibrational wavenumbers of the complex were scaled by a scaling factor of 0.9613 [35] in order to correct the theoretical errors, such as electron correlation and basis set deficiencies. According to figure 4 and table 3, good agreement between experimental and calculated values in the main spectral features is observed.

The observed peaks with medium intensities between 3100–3000 cm^{-1} in the theoretical FTIR spectrum are related to aromatic C–H stretches [36]. The aromatic C–H in-plane bending and C–H out-of-plane bending modes of benzene and its derivatives are at 1300–1000 and 1000–675 cm^{-1}, respectively [37]. Our calculated wavenumbers of the aromatic C–H in-plane bending are 1235, 1147, and 1110 cm^{-1} and C–H out-of-plane bending are 966, 740, and 686 cm^{-1}, in agreement with reported values. Some of the aromatic C–H in-plane bending modes overlap with other vibrational modes. The expected

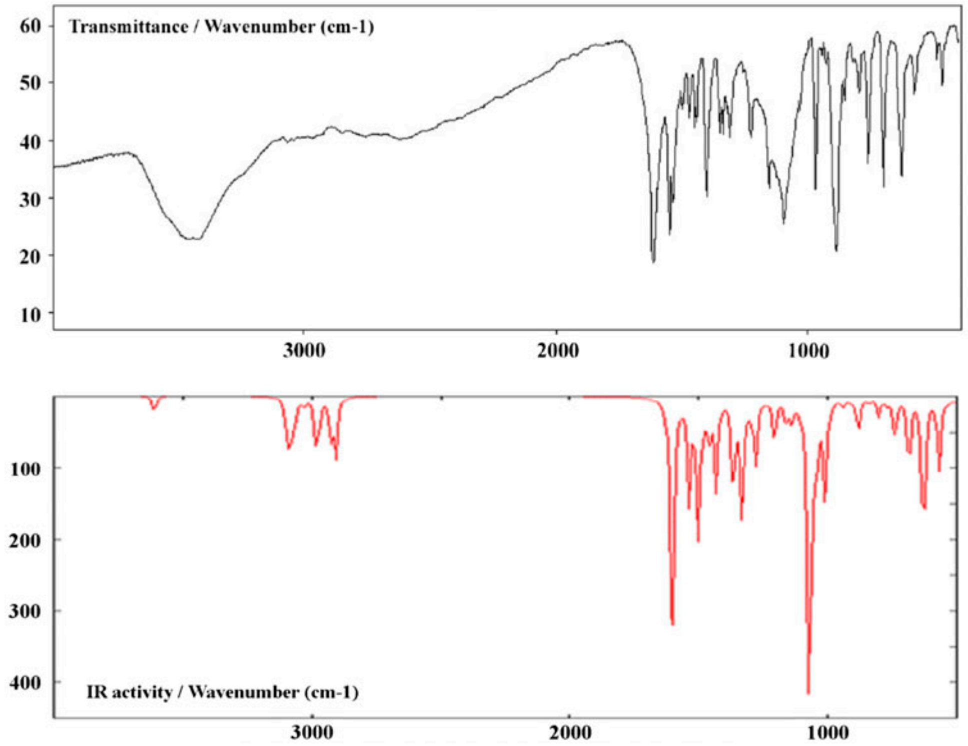


Figure 4. Experimental (top) and theoretical (bottom) FTIR spectra of the vanadium complex.

values of the C–C stretch of benzene and its derivatives are 1650–1200 cm^{-1} [38]. Our calculated values of 1605, 1537, and 1504 cm^{-1} for C–C stretches of benzene are in agreement. Our calculated value of the V=O stretching frequency is 982 cm^{-1}, i.e. within the 950–1000 cm^{-1} range reported for similar oxovanadium complexes [32, 33].

3.3. *Catalytic reaction*

Figure 5 illustrates the effect of amount of catalyst on the conversion and the selectivity of methylphenyl sulfide oxidation, at room temperature for 60 min in a 1 : 1 mixture of CH_3OH/CH_2Cl_2 (1 mL). The conversion of methylphenyl sulfide increases with the addition of catalyst of 0.004–0.01 mM. When the amount of catalyst is increased to 0.012 mM, the selectivity of methylphenyl sulfide oxidation reduces from 83 to 69%. The reaction without catalyst proceeds very slightly. Hence, the amount of catalyst can enhance the reaction rate for selective oxidation of methylphenyl sulfide.

The amount of UHP could also significantly affect the conversion and methylphenyl sulfoxide selectivity (figure 6). When the amount of UHP was increased from 0.1 to 0.4 mM, the conversion of methylphenyl sulfide increased from 33 to 96%. With a further increase of UHP to 0.5 mM, the selectivity to sulfoxide decreases from 83 to 71%, where the conversion of methylphenyl sulfide increased from 96 to 100%.

A series of structurally diverse sulfides were subjected to oxidation using $[VO(ONO)(OCH_3)(CH_3OH)]$ as catalyst and UHP as oxidant (table 4). Arylalkyl (table 4, entries

Table 3. Comparison of the experimental and calculated vibrational frequencies of the vanadium complex.

		Theoretically calculated IR		
Assignment	Experimental IR wavenumber (cm^{-1})	Unscaled wavenumber (cm^{-1})	Scaled wavenumber (cm^{-1})	Intensity
α (O3–H)	3438	3756	3611	19.5
α (C8–N1) + α_{asymm} $(C–C)_{rings}$	1612	1670	1605	315.7
α_{asymm} $(C–C)_{rings}$	1548	1599	1537	141.7
α (C1–N2) + α_{asymm} $(C–C)_{rings}$	–	1565	1504	191.2
α (C1–C2) + β (C8–H) + β $(C–H)_{rings}$	1400	1421	1366	125.8
β (C15–O3–H) + β $(C–H)_{rings}$	1311	1386	1332	82.6
α_{asymm} [C16–O4, V1–O5]	1094	1118	1075	368.4
α (C15–O3)	–	1050	1009	137.1
α_{asymm} [C16–O4, V1–O5]	960	1022	982	147.2
β $(C–C–C)_{ring}$	888	917	882	48.9
γ $(C–H)_{rings}$	759	770	740	51.6
γ $(C–H)_{rings}$	701	714	686	47.2
α (V1–O4)	623	655	630	172.2
α (V1–O1) + β $(C–C–C)_{rings}$	578	592	569	100.1
γ (O3–H) + γ $(C–C–C)_{rings}$	466	480	461	56.7

α: stretching, β: in-plane bending, γ: out-of-plane bending.

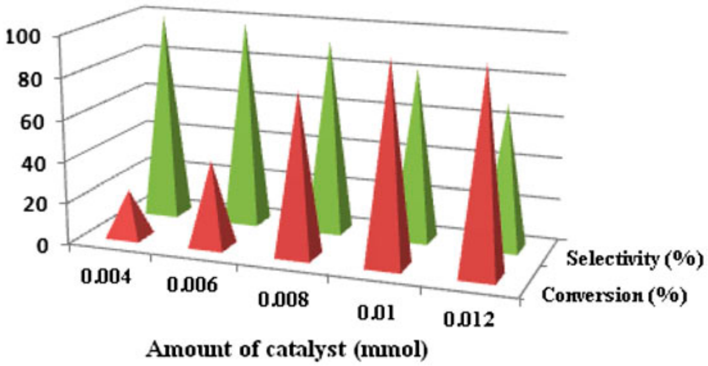


Figure 5. The effect of the amount of catalyst on the oxidation of methylphenyl sulfide by the $[VO(ONO)(OCH_3)(CH_3OH)]$/UHP catalytic system.

1 and 2), arylbenzyl (table 4, entry 3), dibenzyl (table 4, entry 4), diaryl (table 4, entry 5), and dialkyl (table 4, entries 6–8) sulfides underwent clean and selective oxidation to the corresponding sulfoxide under air, with impressive selectivity (78–100%). Very good conversions of substrates depending on the nature of the sulfide, 62–100% (TON = 12.4–20), were obtained for all cases. Aromatic sulfides undergo oxidation reactions more easily than aliphatic substrates. The highest and lowest conversions were obtained for dibenzyl sulfide (100%) and dioctyl sulfide (62%), respectively (table 4, entries 4 and 8).

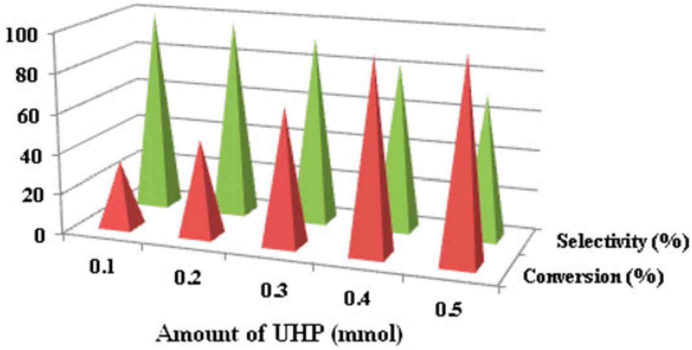
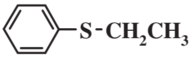
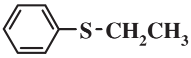
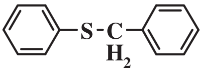
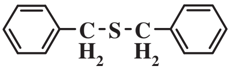
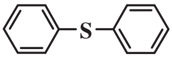


Figure 6. The effect of the amount of UHP on the oxidation of methylphenyl sulfide by the [VO(ONO)(OCH_3)(CH_3OH)]/UHP catalytic system.

Table 4. Oxidation of sulfides catalyzed by [VO(ONO)(OCH_3)(CH_3OH)]/UHP[a].

Entry	Substrate	Conversion (%)[b] (TON)[c]	Selectivity (%)[d]
1		96 (19.2)	83
2		91 (18.2)	85
3		99 (19.8)	85
4		100 (20)	78
5		94 (18.8)	81
6	$CH_3\ CH_2–S–CH_2\ CH_3$	73 (14.6)	99
7	$CH_3\ (CH_2)_2–S–(CH_2)_2\ CH_3$	68 (13.6)	100
8	$CH_3\ (CH_2)_7–S–(CH_2)_7\ CH_3$	62 (12.4)	100

[a] The molar ratios for [VO(ONO)(OCH_3)(CH_3OH)]: substrate: oxidant are 1 : 20 : 40. The reactions were performed in (1 : 1) mixture of CH_2Cl_2/CH_3OH (1 mL) under air at room temperature within 60 min.

[b] The GC yield (%) are measured relative to the starting sulfide.

[c] TON = (mM of sulfoxide + mM of sulfone)/mM of catalyst.

[d] Selectivity to sulfoxide = (sulfoxide %/(sulfoxide % + sulfone %)) × 100.

4. Conclusion

The six-coordinate V(V) complex [VO(ONO)(OCH_3)(CH_3OH)] has been synthesized and characterized. X-ray diffraction studies revealed coordination of the tridentate salicylidene benzoyl hydrazine to vanadium via two O and one N. The complex has distorted octahedral configuration around V. The complex has been theoretically analyzed through the B3LYP level of theory using the 6-31G* basis set. Very good agreement between the X-ray and optimized geometrical parameters has been observed. Distributions of electron density, dipole moment, and HOMO-LUMO energy gap of complex have been addressed. The IR spectrum of the complex was calculated and different modes of vibration assigned. We have demonstrated the effectiveness of this complex as a catalyst for oxidation of sulfides to their corresponding sulfoxides. Easy preparation, mild reaction condition, the use of UHP as a green oxidant, high yields of the products, short reaction time, high selectivity, and low cost make [VO(ONO)(OCH$_3$)(CH$_3$OH)]/UHP an useful catalytic system for oxidation of sulfides.

Supplementary material

The CIF file of crystal structure complex [VO(ONO)(OCH$_3$)(CH$_3$OH)] has been deposited with the CCDC, No. 940784. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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