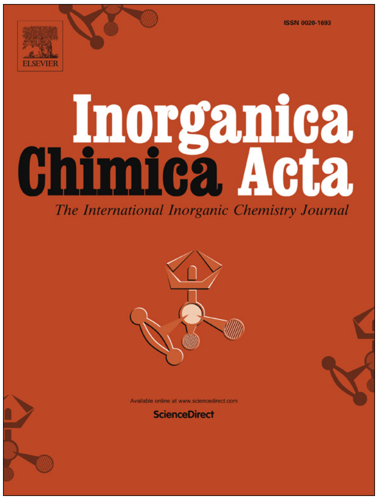

Research paper

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PII: S0020-1693(16)30439-X
DOI: http://dx.doi.org/10.1016/j.ica.2016.07.058
Reference: ICA 17193

To appear in: *Inorganica Chimica Acta*

Received Date: 4 April 2016
Revised Date: 28 June 2016
Accepted Date: 29 July 2016

Please cite this article as: R. Bikas, M. Ghorbanloo, S. Jafari, V. Eigner, M. Dusek, Catalytic oxidation of olefins and sulfides in the presence of hydrazone-oxidovanadium(V) complex containing $VOCl_2^+$ core, *Inorganica Chimica Acta* (2016), doi: http://dx.doi.org/10.1016/j.ica.2016.07.058

Catalytic oxidation of olefins and sulfides in the presence of hydrazone-oxidovanadium(V) complex containing $VOCl_2^+$ core

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Abstract

A new oxidovanadium(V) complex, [VO(L)Cl_2] (**1**), is synthesized by the reaction of $VOCl_3$ with (*E*)-*N'*-(phenyl(pyridin-2-yl)methylene)isonicotinhydrazide (HL) in chloroform as a solvent. The complex is characterized by elemental analysis, spectroscopic methods (FT-IR, UV-Vis), and its structure is determined by single crystal X-ray diffraction analysis. X-ray studies reveal a mononuclear complex of V(V) with the hydrazone ligand coordinated to the V(V) center as a tridentate mononegative ligand. This complex is used as a catalyst precursor for oxidation of olefins and sulfides in the presence of hydrogenperoxide (H_2O_2) as a green oxidant. The effect of various parameters is studied including the amount of the catalyst, temperature and solvent. The results show the system corresponds to an active and selective catalyst for oxidation of cyclooctene and thioanisole.

Keywords: Oxidovanadium(V), Catalytic oxidation, Hydrazone ligand, Crystal structure, $VOCl_2^+$

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Introduction

The coordination chemistry of vanadium is of interest for number of biological and therapeutic reasons. Vanadium complexes have many attractive features that constitute the basis for their utility as insulin-mimetic drugs stimulating the glucose uptake [1], potential anti-tumor agents exerting preventive effects against carcinogenesis [2], or promising agents against some of parasitic diseases [3]. Moreover, vanadium complexes in high-oxidation states have a high relevance in oxidation catalysis [4]. Hydrazone ligands have a tendency to stabilize the vanadium in its highest oxidation state [5]. Vanadium complexes with hydrazone ligands are good candidates for catalytic oxidation studies because of their stability in oxidizing conditions. They have been widely used as homogeneous or heterogeneous catalysts in oxidation processes in the presence of a suitable oxidant, *e.g.*, alkyl hydroperoxides, H_2O_2 or O_2, under mild conditions [6]. The use of high valent vanadium complexes in oxidation catalysis is encouraged by the easily interconvertible vanadium oxidation states (where +4 and +5 are the most stable ones under aerobic conditions), various possible coordination numbers, high affinity of vanadium toward oxygen and Lewis acid character of the vanadium centers [7]. In most cases, the active site contains either of the two motifs, VO^{3+} or VO^{2+}, coordinated by oxygen/nitrogen atoms provided by the ligands or solvents. In most vanadium complexes prepared in alcoholic solvents (like methanol or ethanol), the solvent is usually coordinated to the vanadium core as a neutral or mononegative alkoxide ligand [8]. In addition, in some cases the oxidovanadium core changes to dioxidovanadium [9]. Due to the high affinity of vanadium towards oxygen, the vanadium complexes containing “$VOCl_2$” are not frequently isolated, nevertheless some of them are reported in the scientific literature: $(CH_3C_5H_5O)_2VOCl_2$ [10], bpa($VOCl_2$), (where bpa = bis(2-methypyridyl)amine) [11], [$VOCl_2$(dpi)(THF)] (dpi = di-2-pyridylimine), [$VOCl_2$(adpe)] (adpe =

aminodi-2-pyridyl-methyl ethyl ether), [$VOCl_2$(adpm-/NH_2)] and [$VOCl_2$(adpm-/OMe)]•/MeOH (adpm = amino-di-2-pyridyl-methyl methyl ether) [12].

Although the crystal structures of more than 300 oxidovanadium complexes with tridentate hydrazone ligands have been reported until now, searching the literature and Cambridge Structural Database (CSD) [13] indicates that surprisingly there is no report onvanadium complexes of hydrazone ligand containing V−X (X = Halogen) group. In all of the reported hydrazone-vanadium complexes available in CSD, the coordination environment around the vanadium ion contains five or six atoms. Most of hydrazone ligands act as tridentate ligands [14] and due to the presence of the V=O moiety, four equatorial coordination sites around the vanadium are available for these ligands. Thus, by considering octahedral geometry around the vanadyl ion, two vacant coordination sites are available (Scheme 1). In crystal structures of previously reported hydrazone-vanadium complexes these two coordination sites are occupied by N or O donors, and no other atom coordinated to these positions has been reported so far.

Selective oxidation of sulfides to sulfoxides is very important since sulfoxides are useful building blocks as chiral auxiliaries in organic synthesis [15]. Sulfoxides possess a wide range of biological activities, e.g. antimicrobial properties [16], ability to inhibit the biosynthesis of the uric acid and gastric acid secretion [17] or to regulate the cholesterol catabolism [18]. Vanadium complexes are efficient catalyst precursors for oxidation of sulfides to sulfoxides [19]. Additionally, vanadium complexes are useful compounds in oxidation of olefins [20]. Epoxides are the key starting materials for a wide variety of products, and the epoxidation of alkenes is one of the most widely studied reactions in organic chemistry. The importance of epoxides arises mainly from their ring opening reactions. Some review articles that focus on the vanadium catalysts (also in the form of complexes with Schiff base ligands) in epoxidation of olefinic compounds have been published recently [6a,21].

To continue our studies on the coordination complexes of hydrazone ligands and their applications in oxidation reactions [22], we aimed to prepare a vanadium-hydrazone complex containing V–X moiety. Comparing with V–O and V–N bonds, the V–Cl bond can be easily broken by attacking with the oxygen atom of oxidants like H_2O_2 or *tBut*-COOH. A variety of oxo- and/or peroxovanadium complexes, containing V−Cl bond, such as [LV(O)X] [X = Cl; R = H, L = $Me_2NCH_2CH(R)N(CH_2$-2-O-3,5-$C_6H_2tBu_2)_2$] [23], Bis[µ-chloro-chloro(η^2-2-*iso*-propoxyethanolato)-oxovanadium(V)], Bis[µ-chloro-chloro(η^2 -1-methoxy-2-methyl-2-propanolato)-oxovanadium(V)] and Bis[µ-chloro-chloro-oxo(η^2-2-tetrahydrofuranylmethanolato)-vanadium(V)] [24] have been used as catalyst precursors for oxidation reactions in the presence of various oxidants. Thus, it was predictable that the catalytic activity of hydrazone-vanadium complexes containing V–Cl moiety might be higher than for other hydrazone-vanadium complexes. In the present work, we report synthesis, characterization, crystal structure and catalytic activity of a new oxidovanadium-hydrazone complex containing $VOCl_2^+$ moiety.

Scheme 1.

2. Experimental

2.1. *Materials and instruments*

All chemicals and solvents were purchased from Merck and used as received without further purification. The ligand (*E*)-*N'*-(phenyl(pyridin-2-yl)methylene)isonicotinhydrazide (HL) was synthesized by the reaction of 4-pyridinecarboxylic acid hydrazide with 2-benzoylpyridine in methanol according to our previous reports [25]. IR spectra were recorded in KBr disks with the

Bruker FT–IR spectrophotometer. The elemental analyses (carbon, hydrogen and nitrogen) were obtained from the Carlo ERBA Model EA 1108 analyzer. The atomic absorption analysis was carried out using the Varian Spectra AA 220 equipment. ^{1}H and ^{13}C NMR spectra of the ligand and complex in DMSO-d_6 solution were recorded on a Bruker 250 MHz spectrometer and chemical shifts were indicated in ppm relative to tetramethylsilane (TMS). The reaction products of oxidation were determined and analyzed using the HP Agilent 6890 gas chromatograph equipped with the HP-5 capillary column (phenyl methyl siloxane 30 m × 320 µm × 0.25 µm) and the gas chromatograph-mass spectrometry (the Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector).

*2.2. Synthesis of [VO(L)Cl$_2$] (**1**)*

Complex **1** was synthesized by the reaction of hydrazone ligand, HL, (0.302 g, 1.0 mmol) and VOCl$_3$·(0.173 g, 1.0 mmol) in chloroform solvent according to the previously reported method [26]. The above mentioned amounts of materials were placed in the main arm of a branched tube. Chloroform 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, dark brown crystals of complex **1** were deposited in the cooler arm. Yield: 88% (0.35 g). *Anal.* Calc. for $C_{18}H_{13}Cl_2N_4O_2V$ (MW = 439.2): C, 49.23; H, 2.98; N, 7.29; V, 11.60%. Found: C, 49.46; H, 3.01; N, 7.29; V, 11.54%. Selected FT-IR (KBr, cm^{-1}): 3418 (br, w), 3085 (w), 2925 (w), 2871 (w), 1632 (vs), 1598 (m), 1587 (m), 1561 (m), 1530 (vs), 1498 (s), 1453 (s), 1372 (s), 1362 (s), 1333 (m), 1297 (w), 1255 (w), 1247 (w), 1195 (w), 1155 (m), 1148 (m), 1088 (s), 1080 (s), 1045 (w), 1029 (w), 1023 (w), 969 (s), 950 (vs), 931 (m), 918 (m), 837 (s), 794 (s), 778 (m), 755 (s), 742 (m), 705 (vs), 689 (s), 685 (s), 659 (m), 647 (w), 606 (w), 489 (w), 472 (m), 454 (w), 432 (m). UV-Vis (H_2O): λ_{max} , nm (ε, $M^{-1}cm^{-1}$): 280 (13647), 400 (10000). ^1H NMR (250.13 MHz, DMSO-d_6, 25 °C, TMS, ppm): δ = 7.43 (3H, m), 7.54 (2H, d, *J* = 6.25 Hz), 7.64 (2H, d, *J* = 5.75 Hz), 7.81-7.96 (3H, m), 8.60 (3H, m). UV-Vis (H_2O): λ_{max} , nm (ε, $M^{-1}cm^{-1}$): 280 (13647), 400 (10000).

2.3. X-ray Crystallography

X-ray diffraction data for **1** were collected at 95 K by the ω-scan technique on the SuperNova diffractometer of Rigaku Oxford Diffraction equipped with the Atlas S2 CCD detector using mirror collimated Mo-Kα radiation (λ = 0.71073 Å). The data integration and numerical absorption corrections were carried out with the CrysAlis program [27]. Two crystal structures were obtained, the first one for the fresh sample containing the lattice water, and the second one for an aged sample without the lattice water. The form with the lattice water had a primitive unit cell while the other converted to a C-centered unit cell. Both solvatomorphs were solved by the charge flipping method using the Superflip program [28] and refined using Jana2006 software [29]. Symmetry analysis of the electron density maps resulting from the charge flipping clearly indicated the lack of the symmetry centre for both structures. The crystal data and refinement parameters are presented in Table 1.

Table 1

CCDC 1470224 and 1470225 contains the supplementary crystallographic data for both polymorphs of **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supporting information for this article is available on the DOI:

2.4. General oxidation procedure

Oxidation reactions were carried out under air in 3 mL of solvent, and aqueous H_2O_2 (30%) was used as an oxidant. In a typical experiment, a mixture of 2.3×10^{-3} mmol of the complex **1**, 3.0 mL of the solvent and 1.0 mmol of the substrate were placed in a 25 mL round bottomed glass flask. The mixture was heated to reach to the desired temperature and after addition of H_2O_2 the solution was placed in an oil bath to continue the reaction at the set 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 the authentic samples.

3. Results and Discussions

3.1. Synthesis and Characterization

The reaction of 2-benzoylpyridine with the equimolar amount of 4-pyridinecarboxylic acid hydrazide gave the desired tridentate Schiff base ligand (HL) in high yield and purity (Scheme 1). Complex **1** was synthesized by the reaction of HL with $VOCl_3$ in chloroform. Dark brown crystals of **1** grew by thermal gradient method. ^1H NMR and ^{13}C NMR spectra of H_2L in DMSO-*d_6* (Figs. S1-S3) confirmed the proposed structure for the ligand (Scheme 1). In the ^1H NMR spectrum of the complex **1** (Figs. S4-S5)the absence of amidic N–H peak shows HL is coordinated to the metal ion as a mono-anionic ligand. The infrared spectrum of HL displays the characteristic bands at 3066, 1582 and 729 cm^{-1}, which are assigned respectively to υ(N-H), υ(C=N) and υ(C=O) functionality of the free Schiff base ligand. The N-H and C=O bands indicate that the HL exists in the keto form. The N-H and C=O bands of the free ligand are not detected in the FT-IR spectrum of the complex **1** which confirms the coordination of HL as a mono-negative ligand in the enol form (see Fig. S6). In the IR spectra of the complex **1**, the presence of the V=O moiety is indicated by the strong band at 960 cm^{-1} [30]. In addition, the infrared spectra of the complex **1** displays an FT-IR absorption band around 1597 cm^{-1} which can be assigned to the C=N stretching frequency of the coordinated ligand [31].

*3.2. Crystal structure of [VO(L)Cl$_2$] (**1**)*

In order to obtain structural details, single-crystal X-ray diffraction study was made on previously prepared crystals. Molecular structure of complex **1** is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The complex **1** is a mononuclear complex of V(V) with the hydrazone ligand coordinated to the V center. The amidic N−H hydrogen atom is eliminated during the complexation and as a result the Schiff base ligand is coordinated to the V1 ion as tridentate mono-negative ligand. The octahedral coordination environment of vanadium(V) is formed by one oxygen and two nitrogen atoms provided by Schiff base ligand, two chloride anions and the oxygen atom of the oxido group. Two chloride ligands oriented *trans* with respect to each other (Cl1—V1—Cl2 = 167.18(2)°). Chloride ligands together with nitrogen atom of the pyridine group (N4) and oxygen atom of hydrazone moiety (O1) form the equatorial plane of the octahedron. The axial positions are occupied by nitrogen atom of the azomethine group (N3) and the oxido atom, O1v. The V1−O1v bond length (1.6125(13) Å) is considerably shorter than the other bond lengths. The V1−N3 and V1-N4 bond lengths are 2.1589(15) and 2.11135(14) Å, respectively. The V1−N4 bond length is close to the other V−N$_{\text{pyridine}}$ bond lengths reported in the literature but the V1−N3 bond length which is located *trans* with respect to the V=O moiety is abnormally long compared to the usual V−N$_{\text{azomethine}}$ bond length because of the *trans* influence of the oxido group. The V−Cl bond lengths (V1−Cl1 = 2.3368(5) and V1−Cl2 = 2.4663(5)) are close to the previously reported V−Cl bond lengths [32].

Fig. 1.

Due to presence of V=O and V−Cl groups, hydrogen bonding is a predictable feature for this complex. Although complex **1** doesn't have strong hydrogen bonding donor groups like OH and NH, there are some other intermolecular C−H···O and C−H···Cl hydrogen bonding interactions (see Fig. 2 and Table 3).

Fig. 2.

Table 2.

Table 3.

3.3. Solvatomorphism

During our effort to select a single crystal suitable for X-ray diffraction, we found that for some specimens C centering was violated by a presence of forbidden reflections 30-50 I/σ(I), i.e. by weak but clearly observed reflections. When we applied anyway C centering for such data, disorder of the phenyl ring appeared, while when taking the forbidden reflections into the account using the symmetry *Pc*, we obtained two very similar molecules different by the phenyl position and elongation of ADPs of one molecule (Fig. S7). Moreover, refinement in *Pc* revealed two different types of channels, one of them filled with disordered weakly occupied water molecules (Fig. 3), while the structure with C centering had only one kind of channel without any lattice water. The sample with the symmetry *Cc* was taken from the same batch as the one with symmetry *Pc*, but four years later. We assume that the weakly bounded lattice water molecules simply left the channels of the structure over the time. The solvatomorph without C centering has no relevance for the structural description which is based on the C-centered structure. On the other hand, other physical measurements correspond to the structure containing the lattice water because these measurements were done using the fresh sample

Fig. 3.

3.3. Catalytic activity

The oxidation of cyclooctene as a representative substrate of olefins with 30% aqueous H_2O_2 was carried out in the presence of complex **1** as a homogeneous catalyst precursor. In order to find the optimum conditions for the oxidation reactions, oxidation of cyclooctene in various conditions was studied. As shown in Table 4, the conversion was increased with increasing the hydrogen peroxide:cyclooctene molar ratio from 0.5 to 2 (Table 4, entries 1-3) while further increasing of the amount of H_2O_2 could not improve the conversion. Thus, the hydrogen peroxide:cyclooctene molar ratio of 2:1 was selected as the optimal molar ratio for the oxidation reactions of olefins in the presence of complex **1**.

Another important factor influencing the yield of cyclooctene epoxide was the amount of the catalyst itself. With the use of 0.0005 g (1.18×10^{-3} mmol) and 0.001 g (2.36×10^{-3} mmol) of the catalyst precursor, respectively, the conversion reached 66% and 90%, while further increasing of the amount of the catalyst precursor was useless. In the blank reaction under similar conditions with cyclooctene, only 5% of cyclooctene was oxidized after 24 hours [33]. Thus, the presence of complex **1** as a catalyst precursor in running the oxidation reactions was essential.

Table 4.

Table 5.

Alternatively, the reaction was carried out at different temperatures. When temperature was increased (from room temperature to 80 °C), the conversion increased correspondingly (from

15% to 83%). In order to further optimize the process to achieve the maximum oxidation of cyclooctene, the effect of different solvents was studied (Table 5). The highest conversion was obtained for ethanol (90% after 5 hours) while the lowest one for *n*-hexane (7% after 5 hours).

To establish the scope for the activity of [$VOCl_2L$], this study was further extended to the catalytic oxidation of other linear and cyclic olefins, namely styrene, α-methyl styrene, 1-octene, 1-decene, cyclohexene and indene, using [$VOCl_2L$] (Table 6). Generally, good epoxide selectivity was observed for the tested aliphatic substrates and cyclooctene (Table 6, entries 5-6). Moreover, the present catalytic system was completely selective for the epoxidation of cyclooctene, indene, 1-octene and 1-decene, while for styrene byproducts benzaldehyde (19%) and benzoic acid (8%) were obtained, and for α-methyl styrene the byproduct acetophenone (38%) was obtained. The production of benzaldehyde in the oxidation of styrene is due to the over-oxidation of styrene epoxide in the presence of H_2O_2. The conversion of styrene and selectivity for styrene epoxide were also affected by the reaction time. The selectivity for styrene epoxide was increased from 73% to 91% upon decreasing the reaction time from 5 h to 2 h, which prevented the overoxidation at higher reaction times [34]. The lower catalytic activity of α-methyl styrene compared to styrene seems to be due to the steric hindrance of the methyl substituent [35].

Table 6.

In comparison with the previously reported catalysts, the [$VOCl_2L$] system exhibited superior activity for the oxidation of hydrocarbons. The previously reported [VOL^1Cl] (L^1 = $Me_2NCH_2CH_2N(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2{}^tBu_2)_2$), [$VOL^2Cl$] ($L^2$= $Me_2NCH_2CH(CH_3)N$(CH2-2-O-3,5-

$C_6H_2{}^tBu_2)_2$) and [(VOL^1)2(μ-O)] showed lower catalytic activity for the oxidation of cyclooctene in the presence of H_2O_2 as an oxidant [36].

The catalytic activity of complex **1** was also tested for the oxidation of methyl phenyl sulfide (thioanisole). In these reactions, H_2O_2 should be used carefully, due to the possibility of overoxidation reactions [37]. In control experiments without the catalyst precursor, the yield of sulfoxide was low (Table 7, entry 5). The effect of different amounts of H_2O_2 was investigated with a fixed amount of substrate (1 mmol) and the complex **1** (2.3×10^{-3} mmol) in 3 mL of EtOH. The reactions were carried out at room temperature. As shown in Table 7, the conversion and sulfoxide selectivity considerably increases with increasing molecular ratio of H_2O_2 to thioanisole from 0.5 to 1. Any attempt to further increase the ratio of H_2O_2 actually resulted in decreased yield, in consequence of sulfoxide to be further oxidized to the corresponding sulfone [38].

Table 7.

In the next step, the catalytic oxidation was studied in various solvents (Table 8). The catalytic activity decreases in the order acetonitrile (dielectric constant $\varepsilon/\varepsilon_0 = 37.5$) > methanol (32.7) > ethanol (24.3) > chloroform (5.5) at 25 ºC. Chloroform is not miscible with the aqueous H_2O_2 which could also be the reason for low catalytic efficiency in this case. In agreement with results previously reported in the literature, solvents of high hydrogen bonding capacity, such as methanol, favor the formation of sulfoxide [39]. However, the best performance was observed in acetonitrile.

Table 8.

The oxidation of *p*-Br-C_6H_4SMe was investigated under the optimal condition. Additional electron-withdrawing substituent (Br) in the *para*-position of the aromatic ring of sulfide reduces the conversion but increases sulfoxide selectivity (95%). Similar observation has been reported in literature [40,41].

Although the details of catalytic mechanism are not studied in the present work, on the basis of the electronic absorption spectroscopy studies (Fig. S8) and also by considering the previous studies on similar systems [33,42], it is predicted that the key step in this catalytic process is the oxidation of substrates by a peroxo-vanadium-hydrazone Schiff base species. Although such species are not identified in this study, electronic absorption spectroscopy indicates that the solution of [$VOCl_2L$] in methanol is sensitive towards addition of H_2O_2. By increasing H_2O_2 to the methanolic solution of complex **1**, the intensity of absorption band at about 400 nm increases. Moreover, the shoulder at about 275 nm overlaps with the new band with high extinction coefficients which observes below than 300 nm after H2O2 addition. These changes can be attributed to the formation of peroxido-VO(L) species by addition of H_2O_2 to the solution of complex **1** [33,41].

Conclusion

In summary, a new oxidovanadium(V) complex containing the $VOCl_2^+$ core was synthesized and characterized by various analyses and its structure was determined by single crystal X-ray diffraction analysis. The complex was used as a catalyst precursor in the oxidation of olefins and sulfides in the presence of hydrogen peroxide as a green oxidant. The results showed that this system corresponds to an active and selective catalyst for the oxidation of olefins and methyl phenyl sulfides in the presence of H_2O_2. Using this catalytic system in the oxidation of sulfides, sulfoxides were obtained as the main products, together with variable amounts of sulfones, depending on the nature of the substrate. The catalytic potential of complex **1** in the oxidation of olefins was also studied, choosing the oxidation of cyclooctene, styrene, α-methyl styrene, indene, cyclohexene, 1-octene and 1-decne as the model reactions.

Acknowledgments

The authors are grateful to the University of Zanjan for financial support of this study. The crystallographic part was supported by the project 14-03276S of the Czech Science Foundation using instruments of the ASTRA lab established within the Operation program Prague Competitiveness - project CZ.2.16/3.1.00/24510.

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Scheme, Figures and Tables Caption

Scheme 1. a) General structure of hydrazone ligands and their tautomeric forms, b) coordination environment of oxidovanadium complexes with hydrazone ligands, c) structure of complex **1**

Fig. 1. Molecular structure of complex **1**.

Fig. 2. Hydrogen bonding interactions in the crystal structure of complex **1,** hydrogen atoms not involved in hydrogen bonding were omitted for the sake of clarity.

Fig. 3. The channels in direction of *c* axis in a) structure **1a** b) structure **1b**

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

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

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

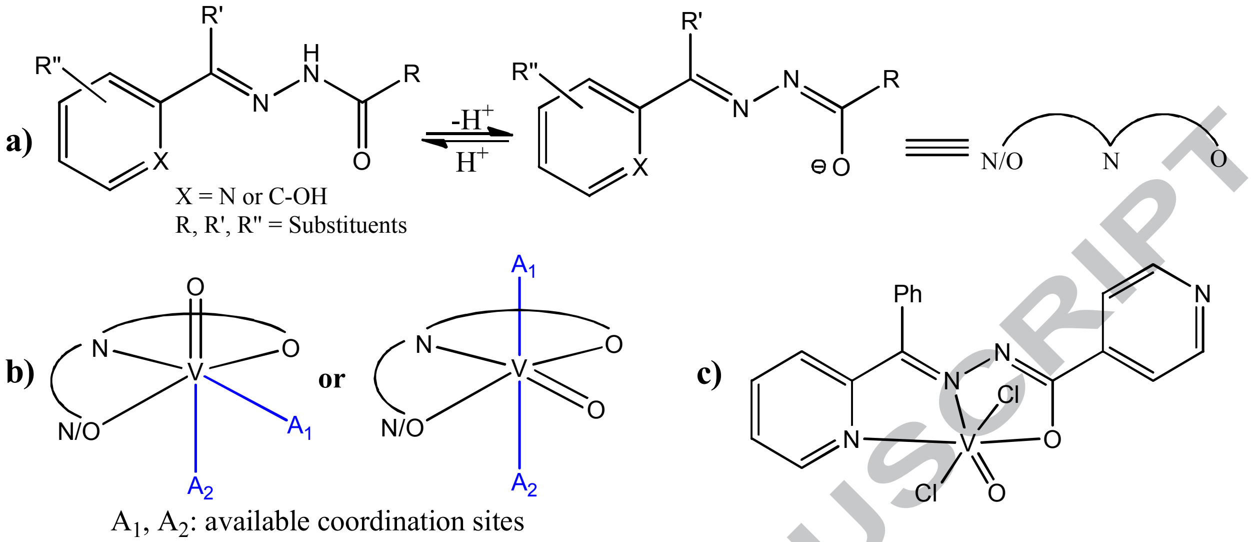
Table 4. Catalytic activity of [$VOCl_2L$] on cyclooctene oxidation [a]

Table 5. Effect of various solvents on cyclooctene oxidation by [$VOCl_2L$][a]

Table 6. Oxidation of alkenes with H_2O_2 catalyzed by the [$VOCl_2L$] [a]

Table 7. Oxidation of thioanisole by the [$VOCl_2L$]/H_2O_2 [a]

Table 8. Solvent effect on the oxidation of methyl phenyl sulfide with [$VOCl_2L$]/H_2O_2 [a]



Scheme 1. a) General structure of hydrazone ligands and their tautomeric forms, b) coordination environment of oxidovanadium complexes with hydrazone ligands, c) structure of complex **1**

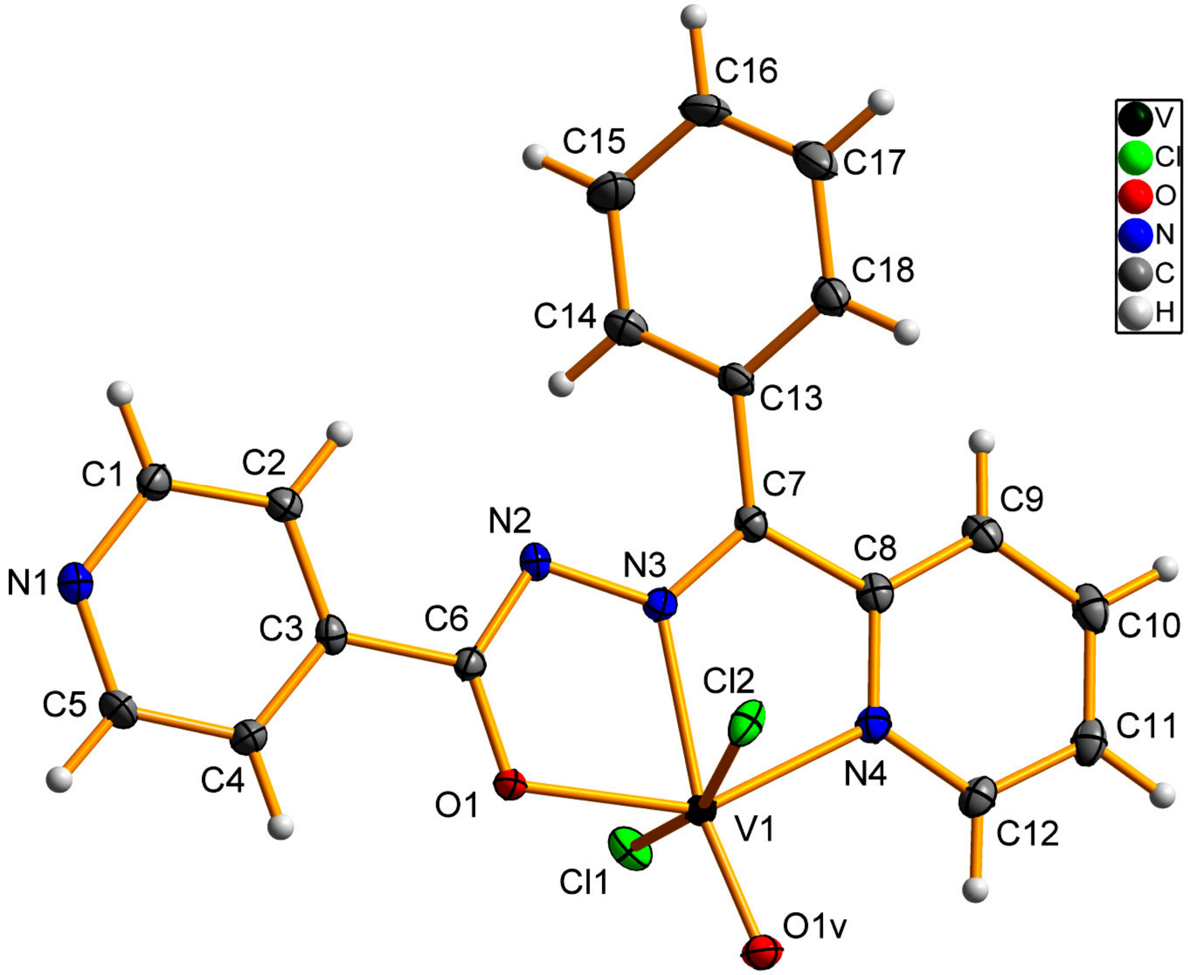


Fig. 1. Molecular structure of complex **1**.

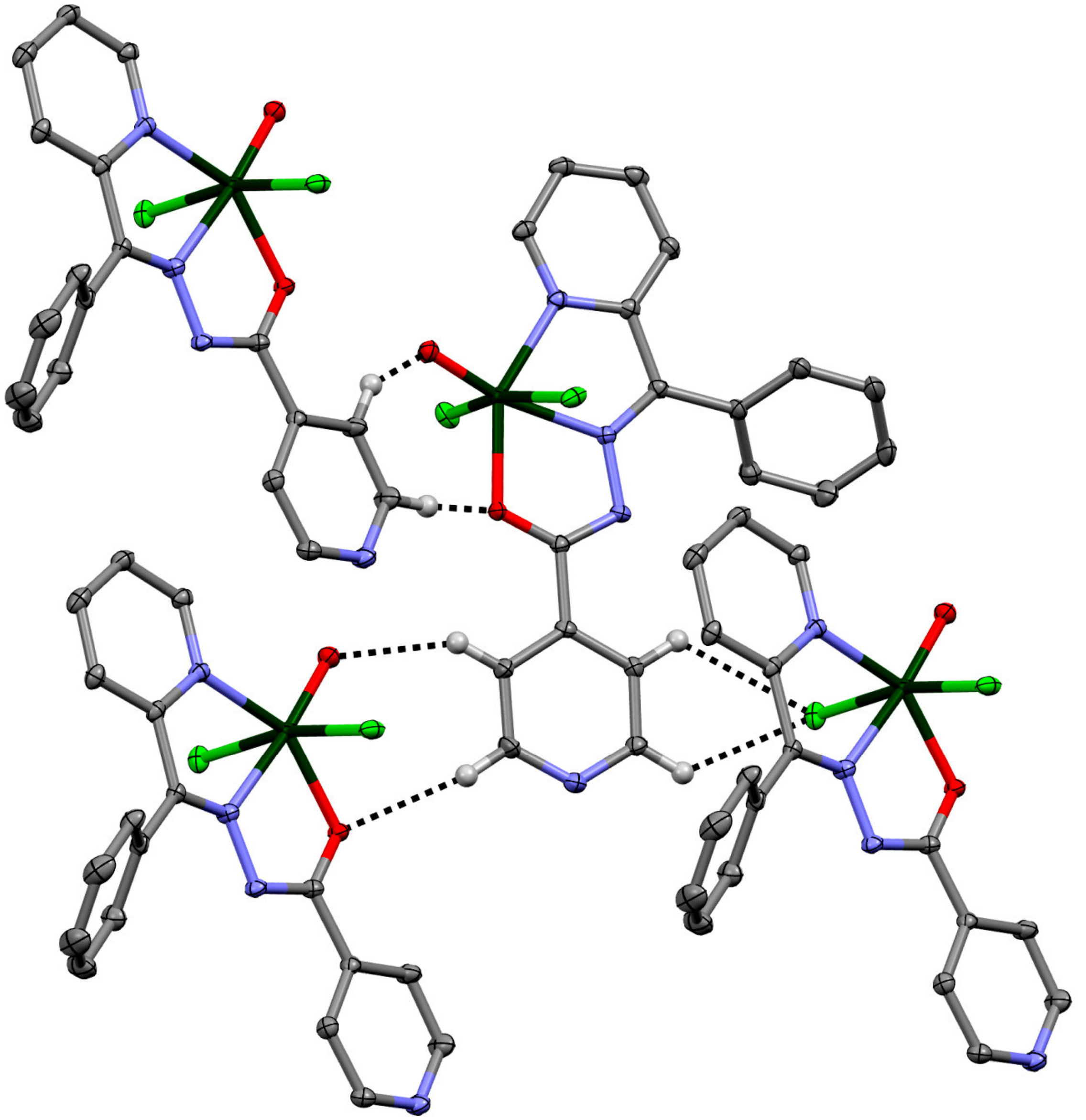


Fig. 2. Hydrogen bonding interactions in the crystal structure of complex **1,** hydrogen atoms not involved in hydrogen bonding were omitted for the sake of clarity.

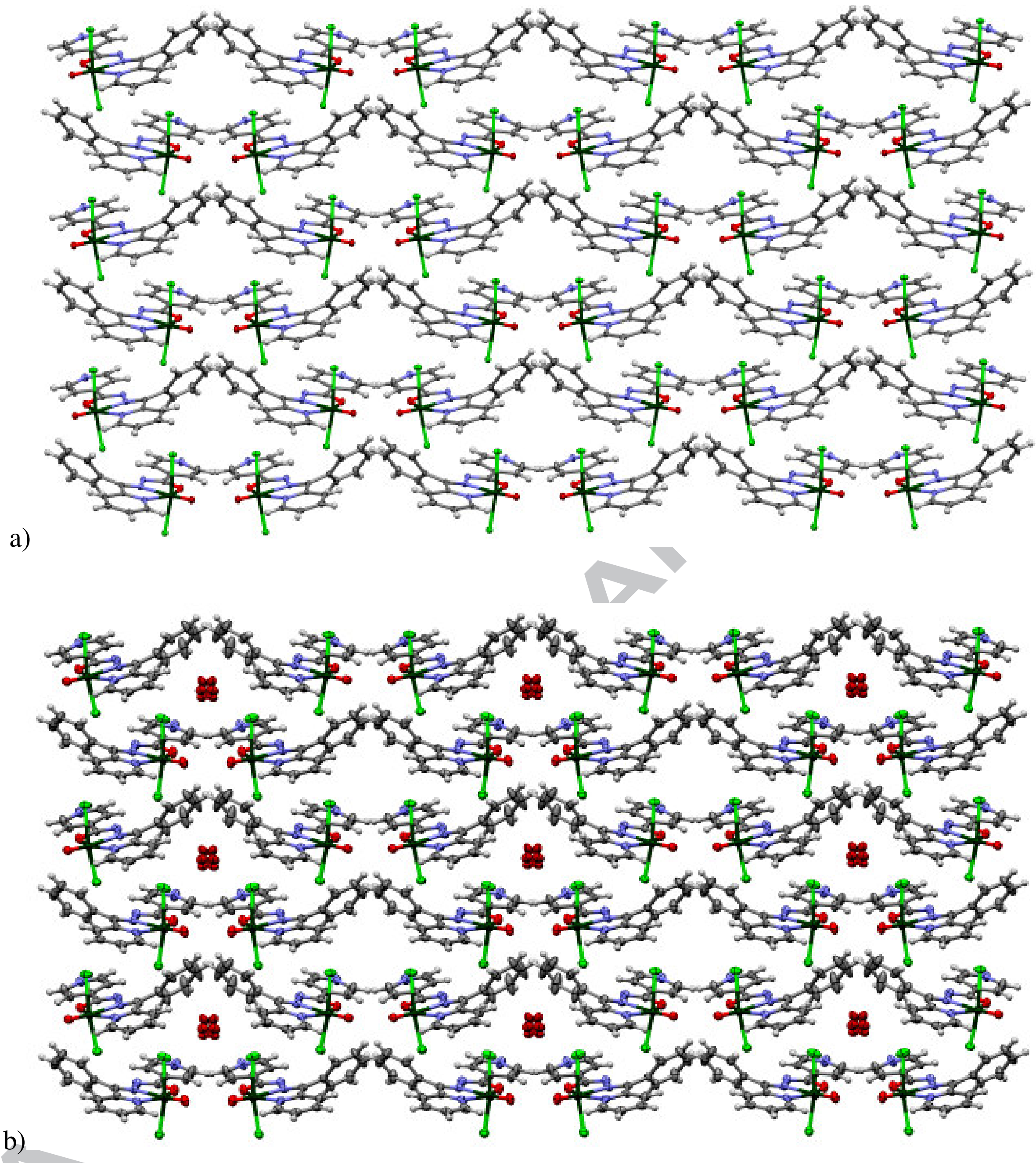


Fig. 3. The channels in direction of *c* axis in a) structure **1a** b) structure **1b**

Table 1. Crystal data and structure refinement parameters for **1**. The structures **1a** and **1b** are solvatomorphs, **1a** corresponding to the aged product.

Identification code	**1a**	**1b**
Net formula	$C_{18}H_{13}Cl_2N_4O_2V$	$C_{18}H_{13}Cl_2N_4O_2V$ 0.369(H_2O)
Formula weight, g mol^{-1}	439.2	445.82
Radiation	MoKα	CuKα
Diffractometer	SuperNova	Gemini ultra
T, K	95	121
Crystal size, mm	0.22 × 0.11 × 0.05	0.50 × 0.38 × 0.17
Crystal shape, color	Prism, brown	Prism, brown
Crystal system	Monoclinic	Monoclinic
Space group	*C c*	*P c*
a, Å	10.1605 (2)	10.2498 (2)
b, Å	19.2565 (4)	19.3887 (4)
c, Å	9.8426 (2)	9.8457 (2)
β, deg	97.0030 (17)	97.6495 (17)
Volume, Å^3	1911.39 (7)	1939.23 (7)
Z	4	4
Density (calc.), g cm^{-3}	1.526	1.525
Absorption coefficient, mm^{-1}	0.82	7.02
F(000)	888	900
Θ range, deg	4.2 – 29.3	4.3 – 67.0
Independent reflections	4696	6791
Measured reflections	15906	50266
Reflections with $I > 3\sigma(I)$	4491	6378
Index ranges *hkl*	h = –13 → 13	h = –12 → 12
	k = –26 → 25	k = –22 → 22
	l = –12 → 12	l = –11 → 11
R_{int}	0.024	0.047
restraints/parameters	0/245	0/518
Goodness of fit on F^2	1.18	2.37
$R[F^2 > 3\sigma(F^2)]$	0.024	0.049
$wR(F^2)$	0.065	0.133
Max electron density/e·Å^{-3}	0.26	0.32
Min electron density/e·Å^{-3}	–0.22	–0.60
CCDC number	1470224	1470225

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

Bond	Length	Bond	Angle
V1—Cl1	2.3368 (5)	Cl1—V1—Cl2	167.18 (2)
V1—Cl2	2.4663 (5)	Cl1—V1—O1v	100.39 (5)
V1—O1v	1.6125 (12)	Cl1—V1—N4	88.94 (4)
V1—N4	2.1135 (14)	Cl1—V1—O1	88.18 (4)
V1—O1	2.0190 (12)	Cl1—V1—N3	87.33 (4)
V1—N3	2.1589 (15)	Cl2—V1—O1v	92.12 (4)
N4—C8	1.360 (2)	Cl2—V1—N4	92.19 (4)
N4—C12	1.345 (2)	Cl2—V1—O1	83.95 (4)
O1—C6	1.295 (2)	Cl2—V1—N3	80.84 (4)
		O1v—V1—N4	97.64 (6)
		O1v—V1—O1	115.05 (6)
		O1v—V1—N3	167.58 (6)
		N4—V1—O1	147.17 (5)
		N4—V1—N3	72.59 (5)
		O1—V1—N3	74.60 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1c1···Cl1^{i}	0.96	2.78	3.4491 (18)	127
C2—H1c2···Cl1^{i}	0.96	2.86	3.4824 (18)	123
C4—H1c4···O1v^{ii}	0.96	2.28	3.105 (2)	144
C5—H1c5···O1^{ii}	0.96	2.46	3.387 (2)	163
C10—H1c10···Cl2^{iii}	0.96	2.92	3.549 (2)	124
C17—H1c17···O1v^{iv}	0.96	2.44	3.375 (2)	165

Symmetry codes: (i) *x*-1/2, −*y*+1/2, *z*+1/2; (ii) *x*, −*y*+1, *z*+1/2; (iii) *x*+1/2, −*y*+1/2, *z*–1/2; (iv) *x*–1/2, *y*–1/2, *z*.

Table 4. Catalytic activity of [$VOCl_2L$] on cyclooctene oxidation [a]

Entry	[H_2O_2]/[C_8H_{12}] Molar ratio	Conversion (%)[b]	Epoxide selectivity (%)	TON[c]	TOF(h^{-1})[d]
1	0.5	13	>99	56.52	11.30
2	1	30	>99	130.4	26
3	2	54	>99	234.7	46.94
4	3	56	>99	237	47.4

[a] *Reaction conditions*: catalyst ([$VOCl_2L$]) (2.36×10^{-3} mmol); reaction temperature, 60 °C; cyclooctene, 1 mmol; CH_3CN (solvent), 3 mL; reaction time, 5 h.;

[b] Conversions are based on the starting substrate for homogeneous conditions;

[c] TON = (mmol of epoxide)/(mmol of catalyst);

[d] TOF = TON/time(h)

Table 5. Effect of various solvents on cyclooctene oxidation by $[VOCl_2L]$[a]

Entry	Solvent	Conversion (%)[b]	Epoxide selectivity (%)	TON[c]	TOF (h^{-1})[d]
1	MeOH	83	>99	360.8	72.16
2	EtOH	90	>99	391.3	78.26
3	CH_3CN	83	>99	360.8	72.16
4	CH_2Cl_2	19	>99	82.6	16.52
5	$CHCl_3$	12	>99	52.17	10.43
6	n-hexane	7	>99	30.4	6.08

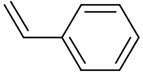
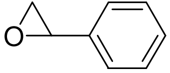
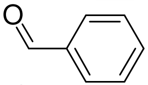
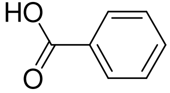
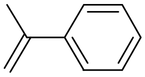
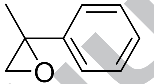
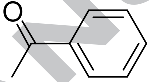
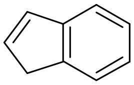
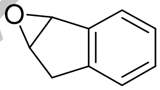
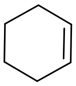
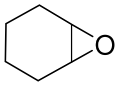
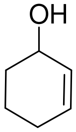
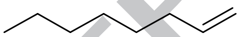
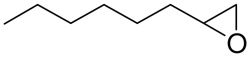
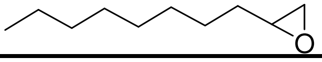
[a] *Reaction conditions*: catalyst ($[VOCl_2L]$) (2.3×10^{-3} mmol); reaction temperature, 80˚C; cyclooctene, 1 mmol; solvent, 3 mL; reaction time, 5 h; H_2O_2, 2 mmol.

[b] Conversions are based on the starting substrate;

[c] TON = (mmol of epoxide)/(mmol of catalyst);

[d] TOF = TON/time(h)

Table 6. Oxidation of alkenes with H_2O_2 catalyzed by the $[VOCl_2L]$ [a]

Entry	Substrate	Conversion (%)[b]	Product(s)	Selectivity (%)	TON	TOF (h^{-1})
1		100		73	435	87
				19		
				8		
2		93		62	404	80.8
				38		
3		60		100	261	52.2
4		85		88	369	73.8
				12		
5		56		100	243	48.6
6		12.5		100	54.3	10.8

[a] Reaction conditions: catalyst (0.001 g, 2.3 × 10^{-3} mmol), substrate (1.0 mmol), EtOH (3 mL), H_2O_2 (2 mmol) and temperature 80 ºC

[b] Conversions are based on the starting substrates

Table 7. Oxidation of thioanisole by the [$VOCl_2L$]/H_2O_2 [a]

Entry	Conversion (%)	H_2O_2:Substrate molar ratio	Sulfoxide selectivity (%)[b]	TON	TOF (h^{-1})
1	38	0.5[a]	79[c]	165	165
2	90	1[a]	89[c]	391	391
3	95	1.5[a]	78[c]	413	413
4	100	2[a]	68[c]	435	435
5	12	1[d]	58[c]	52	52

[a] *Reaction conditions*: catalyst (0.001 g, 2.3 × 10^{-3} mmol), MeSPh 1 mmol, EtOH 2 mL, temperature 25 ± 1 ºC and time 60 min

[b] Conversions are based on the starting substrate;

[c] Sulfoxide selectivity: %sulfoxide / (sulfoxide+sulfone);

[d] Without catalyst; reaction temperature, 25 ˚C; MeSPh 1.0 mmol, EtOH 2 mL; reaction time, 60 min; H_2O_2, 2 mmol

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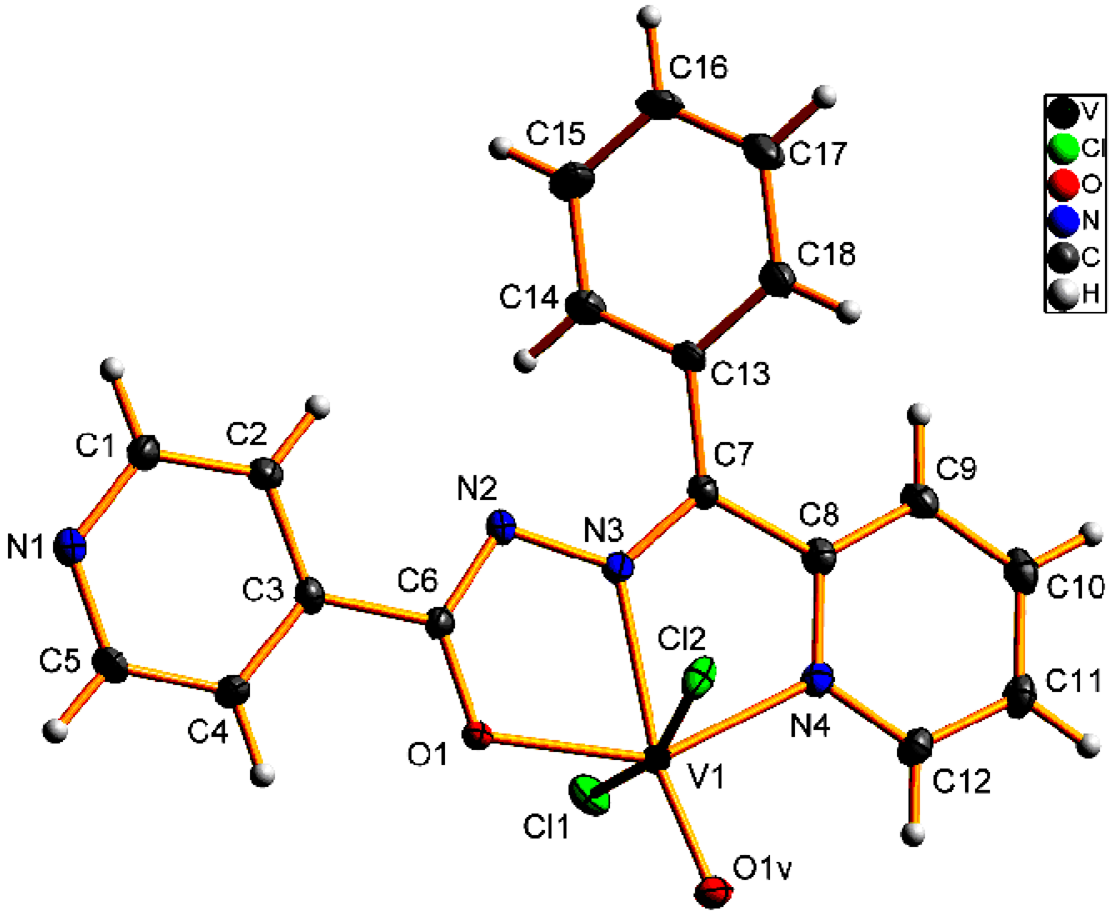
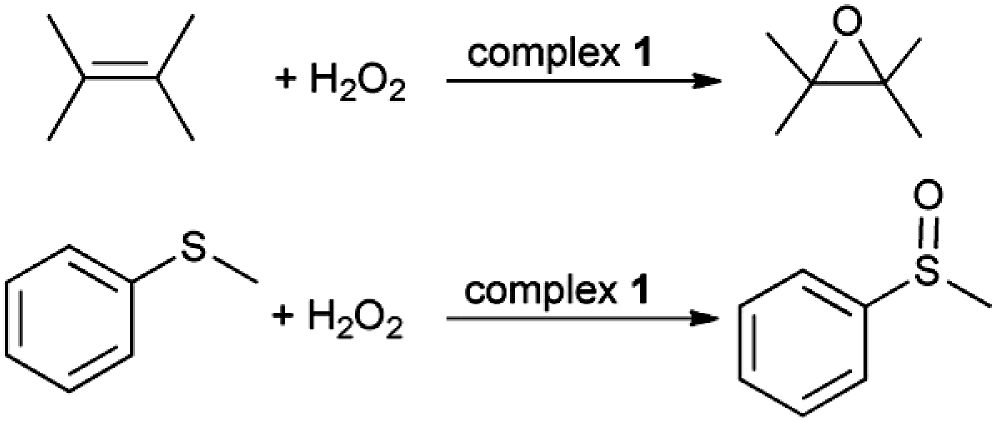
Table 8. Solvent effect on the oxidation of methyl phenyl sulfide with $[VOCl_2L]/H_2O_2$ [a]

Entry	Solvent	Conversion(%)[b]	Sulfoxide selectivity(%)[c]	TON	TOF(h^{-1})
1	EtOH	90	89	391	391
2	$CHCl_3$	30	72	130	130
3	CH_3CN	100	79	435	435
4	MeOH	95	93	413	413

[a] *Reaction conditions*: catalyst 0.001 g (0.0023 mmol), MeSPh 1.0 mmol, solvent 1 mL, H_2O_2 1 mmol, time 60 min, temperature 25 ± 1 ºC;
[b] Conversions are based on the starting substrate;
[c] sulfoxide selectivity: %sulfoxide/(sulfoxide+sulfone).

Graphical abstract





Graphical Abstract (Synopsis)

Synthesis and crystal structure of a new oxidovanadium(V) complex with hydrazone ligand is reported. The oxidovanadium(V) complex is used as catalyst for epoxidation of olefins and oxidation of sulfides by H_2O_2 as green oxidant.

Highlights:

- ✓ Synthesis and crystal structure of a new oxidovanadium(V) complex with hydrazone ligand is reported.
- ✓ Vanadium(V) complex is used as catalyst for epoxidation of olefins and oxidation of sulfides by hydrogen peroxide as green oxidant.