Synthesis, Crystal Structures, and Catalytic Oxidation Properties of Oxidovanadium(V) Complexes with Hydrazone and Hydroxamate Ligands

Kui-Hua Yang

School of Chemistry and Chemical Engineering, Mianyang Normal University, Mianyang 621000, P. R. China

* Corresponding author: E-mail: kuihua_yang@163.com

Abstract

Two new oxidovanadium(V) complexes with hydrazone ligands and hydroxamate ligands were synthesized and characterized by IR and ^{1}H NMR spectroscopy, elemental analysis and single crystal X-ray diffraction. The coordination sphere of each V atom is octahedral, constructed from three donor atoms of the hydrazone ligand, two donor atoms of the hydroxamate ligand, and one oxido oxygen. Both complexes show effective catalytic oxidation properties for the oxidation of cyclohexene, cyclopentene and benzyl alcohol using H_2O_2 as primary oxidant.

Keywords: Hydrazone; Oxidovanadium; Crystal structure; Catalytic property

1. Introduction

In recent years, the development of efficient new catalysts for various organic reactions has received considerable attention.[1] Among the transition metals, vanadium has proved to be particularly useful for catalytic applications. Oxidovanadium(V) complexes with various types of ligands have shown to possess effective catalytic ability.[2] Hydrazones are a kind of interesting compounds in coordination[3] and medicinal chemistry.[4] Several reports have indicated that oxidovanadium complexes with hydrazone ligands can catalyze the epoxidation of alkenes.[5] These epoxidation products are important industrial materials. During the search of literature, we found that most of the catalytically active oxidovanadium complexes with hydrazone ligands have solvent molecules such as methanol, ethanol, and so on, as the auxiliary ligands.[6] Hydroxamic acids are potential bidentate ligands in coordination chemistry.[7] The solvent molecules of the oxidovanadium complexes may be substituted by hydroxamate ligands. Hydrogen peroxide is particularly attractive as an oxidant, as it is cheap, reasonably stable, readily available, and gives only water as a by-product. Herein, we report the synthesis, characterization and catalytic oxidation properties of two hydroxamate coordinated oxidovanadium(V) complexes with hydrazone ligands.

2. Experimental

2. 1. Reagents and Measurements

All chemicals of AR grade were obtained from Sigma-Aldrich and used as received. ^{1}H NMR spectra were recorded on a 500 MHz Bruker NMR spectrometer using DMSO-d^6 solvent. IR spectra were obtained as KBr plates using a Bruker FT-IR spectrophotometer. Elemental analysis (C, H, N) were obtained with a Perkin-Elmer CHN analyzer 2400. GC analyses were carried out with a GC-17A Shimadzu instrument. The ligand 3-hydroxy-*N'*-(2-hydroxybenzylidene)-2-naphthohydrazide (H_2L^a) was prepared according to the literature method.[5d]

2. 2. Synthesis of N'-(2-Hydroxy-5-methyl-benzylidene)-4-hydroxybenzohydrazide (H_2L^b)

5-Methylsalicylaldehyde (10 mmol, 1.36 g) and 4-hydroxybenzohydrazide (10 mmol, 1.52 g) were dissolved in absolute ethanol (30 mL) and the mixture was stirred under reflux for 30 min. The resulting yellow solid was recrystallized from ethanol and the crystalline product was collected by suction filtration, washed successively with cold ethanol and diethyl ether and then air dried. Yield: 91%. Analysis: Found: C 55.7%, H 3.6%, N 13.8%. Calculated for $C_{14}H_{11}N_3O_5$: C 55.8%, H 3.7%, N 14.0%.

Selected IR data (ν/cm^{-1}, KBr): 3365 (ν$_{O-H}$), 3217 (ν$_{N-H}$); 1629 (ν$_{C=N}$). ^{1}H NMR (ppm): 12.27 (1H, s, N*H*), 11.30 (1H, s, O*H*), 11.06 (1H, s, O*H*), 8.81 (1H, s, C*H*=N); 7.82 (2H, d, *H*Ar), 7.53 (1H, s, *H*Ar), 7.08 (1H, d, *H*Ar), 6.85–6.97 (3H, m, *H*Ar), 2.40 (3H, s, C*H$_3$*).

2. 3. Synthesis of [VOL^a(BZ)] · EtOH (1) (BZ = Benzohydroxamate)

H$_2$L^a (0.2 mmol, 61.2 mg), benzohydroxamic acid (0.2 mmol, 27.4 mg) and VO(acac)$_2$ (0.2 mmol, 53.0 mg) were mixed and added to methanol (20 mL), and the mixture was boiled under refluxed until the color of the solution turned to deep brown. Block-shaped single crystals of the complex were obtained by slow evaporation of the solution in air. The crystals were isolated by suction filtration, washed successively with cold ethanol and diethyl ether, and then air dried. Yield: 55%. Analysis: Found: C 58.8%, H 4.3%, N 7.5%. Calculated for C$_{27}$H$_{24}$N$_3$O$_7$V: C 58.6%, H 4.4%, N 7.6%. Selected IR data (ν/cm^{-1}, KBr): 3430 (ν$_{O-H}$); 3232 (ν$_{N-H}$); 1602 (ν$_{C=N}$); 975 (ν$_{V=O}$).

2. 4. Synthesis of [VOL^b(SZ)] · 3H$_2$O (2) (SZ = Salicylohydroxamate)

H$_2$L^b (0.2 mmol, 60.2 mg), salicylohydroxamic acid (0.2 mmol, 30.6 mg) and VO(acac)$_2$ (0.2 mmol, 53.0 mg) were added to ethanol (20 mL), and the mixture was boiled under reflux until the color of the solution turned to deep brown. Block-shaped single crystals of the complex were obtained after slow evaporation of the solution in air. The crystals were isolated by suction filtration, washed successively with cold ethanol and diethyl ether, and then air dried. Yield: 62%. Analysis: Found: C 48.7%, H 4.4%, N 7.9%. Calculated for C$_{22}$H$_{24}$N$_3$O$_{10}$V: C 48.8%, H 4.5%, N 7.8%. Selected IR data (ν/cm^{-1}, KBr): 3445 (ν$_{O-H}$); 3226 (ν$_{N-H}$); 1607 (ν$_{C=N}$); 978 (ν$_{V=O}$).

2. 5. X-ray Crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. The determination of unit cell parameters and data collection was performed with Mo-Kα radiation (λ = 0.71073 Å). The collected data were reduced with SAINT,[8] and multi-scan absorption corrections were made using SADABS.[9] Unit cell dimensions were obtained with least-squares refinements, and both structures were solved by direct methods. Both complexes were refined against F^2 by full-matrix least-squares methods using SHELXTL.[10] V atoms in the complexes were located from electron density maps. The non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squa-

res methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The amino H atoms in both complexes, and the water and hydroxyl H atoms in complex **2** were located from difference Fourier maps and refined isotropically, with N–H, O–H and H⋯H distances restrained to 0.90(1), 0.85(1) and 1.37(2) Å, respectively. The remaining hydrogen atoms were added theoretically as riding on the concerned atoms. Crystal structure refinement and parameters are listed in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-980584 for **1** and 980585 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336-033; E-mail: deposit@ccdc.com.ac.uk].

Table 1. Crystal data, data collection and structure refinement

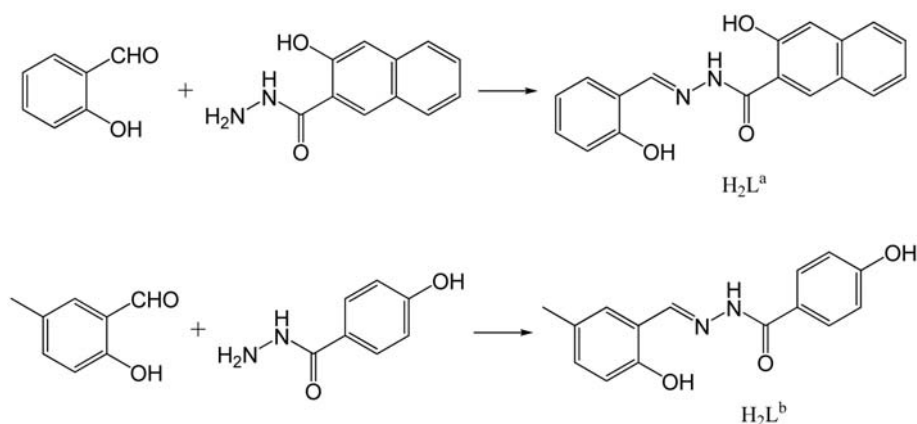| Complex	1	2
Molecular Formula	C$_{27}$H$_{24}$N$_3$O$_7$V	C$_{22}$H$_{24}$N$_3$O$_{10}$V
Formula weight	553.4	541.4
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P–1$
a (Å)	14.472(1)	10.204(1)
b (Å)	7.049(1)	10.659(1)
c (Å)	26.159(2)	12.036(1)
$α$ (°)		68.710(1)
$β$ (°)	102.395(2)	83.049(1)
$γ$ (°)		89.940(1)
V (Å^3)	2606.4(4)	1220.2(1)
Z	4	2
D_c (g cm^{-3})	1.410	1.474
F(000)	1144	5600
$μ$ (mm^{-1})	0.432	0.467
$θ$ range (°)	2.88–25.50	2.00–25.50
hkl range	−17 ≤ h ≤ 17	−12 ≤ h ≤ 12
	−8 ≤ k ≤ 8	−12 ≤ k ≤ 10
	−29 ≤ l ≤ 31	−14 ≤ l ≤ 14
Reflections		
Collected	24271	6358
Unique	4847	4481
Observed [$I > 2σ(I)$]	3702	4028
R_{int}	0.0372	0.0094
Parameters	349	351
Restraints	1	11
Final R index [$I > 2σ(I)$]	0.0674, 0.1622	0.0330, 0.0955
R index (all data)	0.0901, 0.1753	0.0373, 0.1001
Goodness-of-fit on F^2	1.097	1.024
Maximum/minimum Δ$ρ$ (e Å^{-3})	0.700, −0.471	0.296, −0.334

2. 6. Catalytic Oxidation Experiments

The liquid phase catalytic oxidations were carried out under ambient condition in a 25 mL round bottom flask equipped with a magnetic stirrer and immersed in a thermostated oil bath at 60 ± 1 °C. H$_2$O$_2$ (3 mmol) was ad-

ded to the flask containing the catalyst (1 mg) and a representative alkene, namely cyclohexene (1 mmol) in the required solvent (3 mL). The course of the reaction was monitored using a gas chromatograph equipped with a capillary column and a flame ionization detector. The oxidation products were identified by comparing their retention times with those of authentic samples or alternatively by ^{1}H NMR and GC-Mass analyses. Yields based on the added substrate were determined by a calibration curve. Control reactions were carried out in the absence of catalyst, under the same conditions as the catalytic runs. No products were detected.

3. Results and Discussion

3. 1. Synthesis

The condensation reactions of salicylaldehyde with 3-hydroxy-2-naphthohydrazide, and 5-methylsalicylaldehyde with 4-hydroxybenzohydrazide, resulted in the hydrazone ligands H_2L^a and H_2L^b respectively (Scheme 1). The complexes were readily prepared by the reaction of the hydrazone ligands, hydroxamic acids and VO(acac)$_2$ in ethanol (Scheme 2). All the compounds are soluble in polar solvents such as methanol, ethanol and acetonitrile.

Scheme 1. The synthesis of the hydrazone ligands.
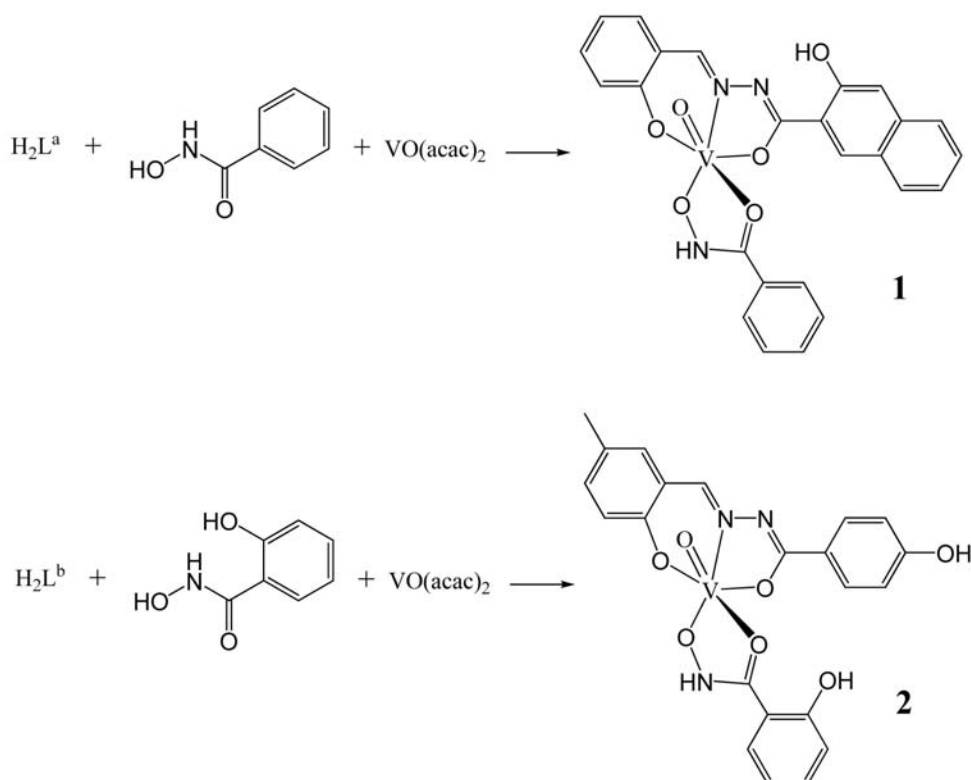
Scheme 2. The synthesis of the complexes.

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3. 2. IR Spectra

The IR spectra of the free hydrazones contain bands at around 1628 cm^{-1} which is due to the presence of C=N groups. In the IR spectra of the vanadium complexes, these bands were observed at lower wave numbers, 1602 cm^{-1} for **1** and 1607 cm^{-1} for **2**. This suggests coordination through the nitrogen atom of the C=N groups. Furthermore, broad and medium bands observed at 3300–3500 cm^{-1} are indicative of the presence of O–H containing solvent molecules. Weak and sharp bands located at around 3230 cm^{-1} is indicative of the presence of amino groups. The typical bands at 975 cm^{-1} for **1** and 978 cm^{-1} for **2** are assigned to the V=O coordinate bonds.

3. 3. Crystal Structure Descriptions of the Complexes

The molecular structures of complexes **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond lengths are given in Table 2. Both compounds contain an octahedral coordinated vanadium complex molecule. In addition, complex **1** has an ethanol molecule, and complex **2** has three water molecules of crystallization. The hydrazone ligands coordinate to the V atoms through the phenolate oxygen, imino nitrogen and enolate oxygen, and the hydroxamate ligands coordinate to the V atoms through the hydroxy oxygen and carbonyl oxygen. The bond lengths of C8–N2 [1.293(5) Å] and C8–O2 [1.321(4) Å] in **1**, as well as C9–N2 [1.310(2) Å] and C9–O2 [1.305(2) Å] in **2** approve them as enolate form, rather than ketone form. Both ligands supply five donor atoms, with the sixth position occupied by one oxido oxygen. The three donor atoms of the hydrazone ligand and the hydroxy oxygen of the hydroxamate ligand constitute the equatorial plane of

the octahedral coordination, with the V atom deviating from the plane by 0.277(1) Å for **1** and 0.209(1) Å for **2**. The axial bonds V1–O4 are much longer than the other bonds in both complexes, distorting the octahedron. This distortion can also be observed from the bond angles,

Table 2. Coordinate bond lengths (Å) and bond angles (°)

1			
Bond lengths			
V1–O1	1.840(3)	V1–O2	1.922(3)
V1–O5	1.860(3)	V1–O6	1.583(3)
V1–N1	2.095(3)	V1–O4	2.266(2)
Bond angles			
O6–V1–O1	101.54(16)	O6–V1–O5	95.64(14)
O1–V1–O5	100.71(13)	O6–V1–O2	98.67(15)
O1–V1–O2	152.55(13)	O5–V1–O2	95.55(12)
O6–V1–N1	97.72(14)	O1–V1–N1	83.46(13)
O5–V1–N1	164.91(11)	O2–V1–N1	75.55(12)
O6–V1–O4	170.02(14)	O1–V1–O4	82.62(12)
O5–V1–O4	74.59(10)	O2–V1–O4	80.57(10)
N1–V1–O4	91.74(10)		
2			
Bond lengths			
V1–O1	1.8512(14)	V1–O2	1.9565(13)
V1–O4	2.1643(14)	V1–O5	1.8758(13)
V1–N1	2.0939(15)	V1–O7	1.5917(14)
Bond angles			
O7–V1–O1	99.83(7)	O7–V1–O5	89.55(6)
O1–V1–O5	108.20(6)	O7–V1–O2	102.62(7)
O1–V1–O2	149.39(6)	O5–V1–O2	92.59(5)
O7–V1–N1	94.77(7)	O1–V1–N1	83.61(6)
O5–V1–N1	166.57(6)	O2–V1–N1	74.07(5)
O7–V1–O4	164.48(6)	O1–V1–O4	81.41(6)
O5–V1–O4	75.48(5)	O2–V1–O4	82.46(6)
N1–V1–O4	100.73(5)		

Table 3. Hydrogen bonding information

D–H⋯A	d (D–H)	d (H⋯A)	d (D⋯A)	<(D–H⋯A)
1				
O3–H3A⋯N2	0.82	1.91	2.634(4)	146.7
O7–H7⋯O4^i	0.82	1.96	2.779(4)	174.3
2				
O6–H6⋯N2^{ii}	0.82	1.93	2.728(2)	164.6
O9–H9B⋯O9^{iii}	0.90(1)	2.25(3)	2.764(8)	117(3)
O9–H9A⋯O1^{iv}	0.85(1)	2.34(2)	3.045(4)	139(3)
O9–H9A⋯O4^{iv}	0.85(1)	2.56(2)	3.207(4)	133(3)
O10–H10B⋯O8^v	0.85(1)	2.12(2)	2.858(4)	146(3)
O10–H10A⋯O9	0.85(1)	1.877(12)	2.731(5)	173(3)
N3–H3B⋯O6	0.90(1)	2.06(3)	2.612(2)	119(2)
N3–H3B⋯O2	0.90(1)	2.16(2)	2.910(2)	141(3)
O3–H3⋯O8^i	0.85(1)	1.916(13)	2.733(3)	167(3)
O8–H8A⋯O7	0.85(1)	2.174(18)	2.978(3)	153(3)

Symmetry codes: i) *x*, 1 + *y*, −1 + *z*; ii) 1 + *x*, *y*, *z*; iii) − *x*, 1 − *y*, 1 − *z*; iv) 1 − *x*, 1 − *y*, 1 − *z*; v) 1 − *x*, − *y*, 1 − *z*; vi) 2 − *x*, 1 − *y*, − *z*.

which range from 74.1(1) to 108.2(1)° for the *cis* angles and from 149.4(1) to 170.0(1)° for the *trans* angles. The dihedral angles between the two aromatic rings of the hydrazone ligands are 8.8(3)° for **1** and 9.8(2)° for **2**. The hydrazone and hydroxamate ligands, due to the steric hindrance and coordination orientation, are nearly perpendicular to each other. The hydroxyl group of the hydrazone ligand in **1** and the amino group of the hydroxamate ligand in **2** are involved in intramolecular hydrogen bonds. The bond length pattern within the bridging C–C=N–C moiety reflects the delocalization of the electron density throughout this fragments: the formally single bonds are shorter
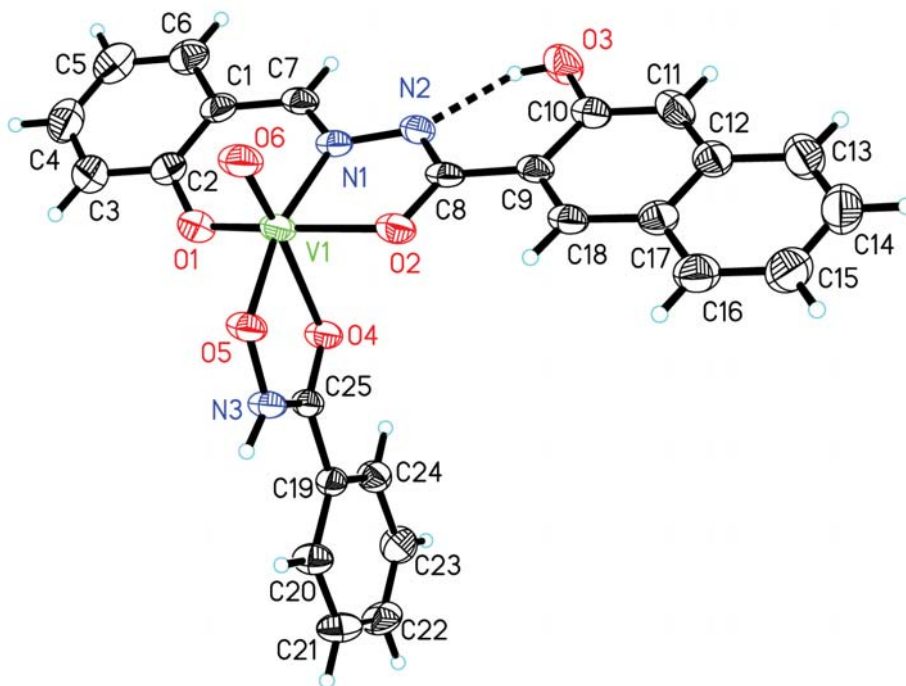
Figure 1. Perspective view of complex molecule of **1** with atom labeling scheme. Displacement ellipsoids are drawn at 30% probability level; hydrogen atoms are depicted as spheres of arbitrary radii. Intramolecular hydrogen bond is shown as a dashed line.
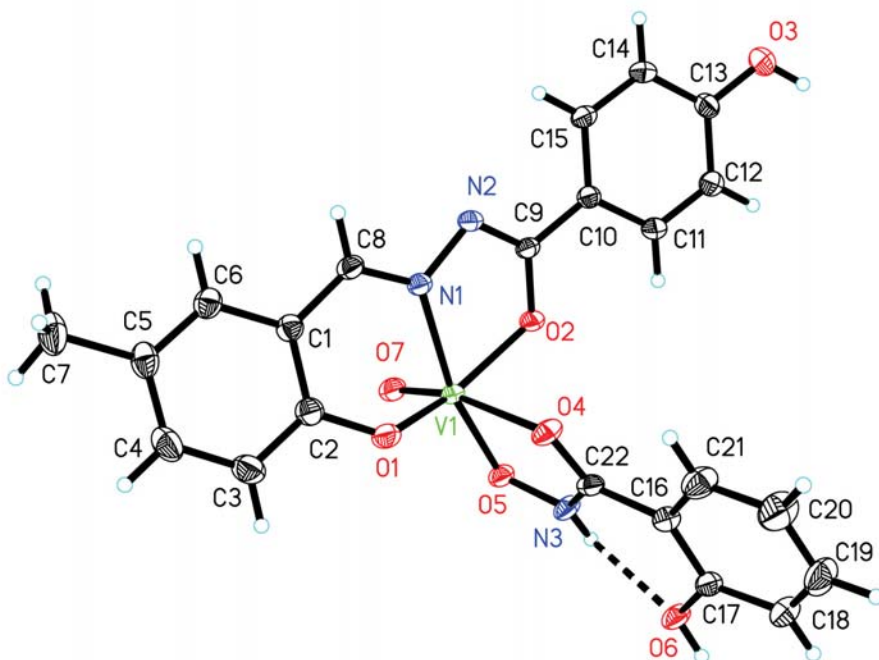

Figure 2. Perspective view of complex molecule of **2** with atom labeling scheme. Displacement ellipsoids are drawn at 30% probability level; hydrogen atoms are depicted as spheres of arbitrary radii. Intramolecular hydrogen bond is shown as a dashed line.

and formally double bonds are longer than the typical values.[11] The V=O bond lengths of 1.583(3) Å in **1** and 1.592(1) Å in **2** are comparable to those observed in similar oxidovanadium(V) complexes.[6]

In the crystal structure of complex **1**, the vanadium complex molecules are linked by ethanol molecules through intermolecular O–H···O and N–H···O hydrogen bonds (Table 3), to form 1D chains running along the *b*-axis direction
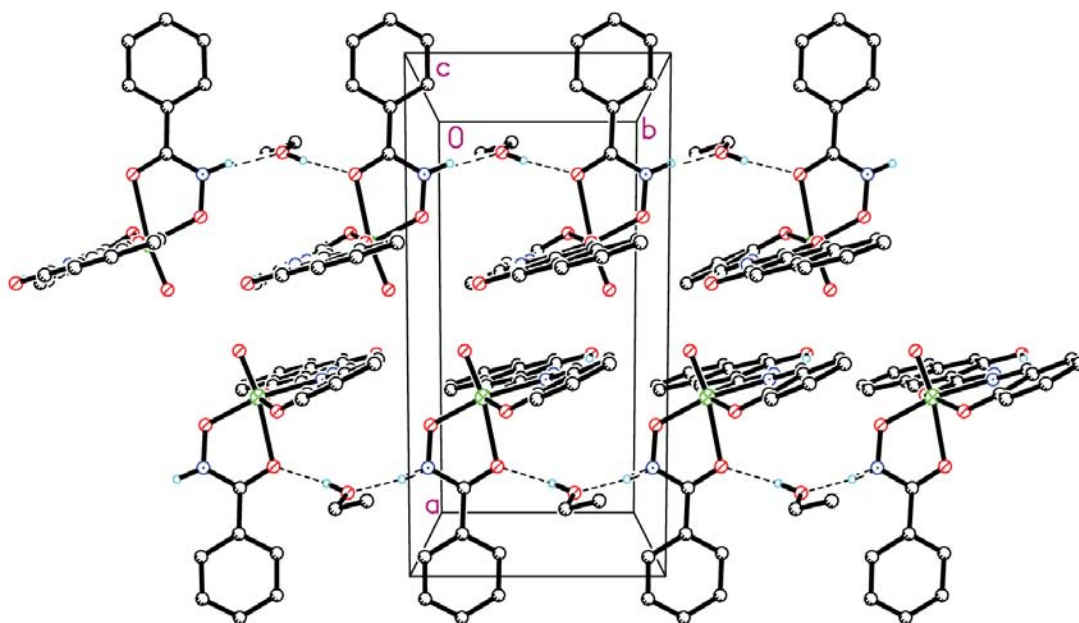

Figure 3. The crystal packing of complex **1** as seen along *c*-axis. The dashed lines denote hydrogen bonds.
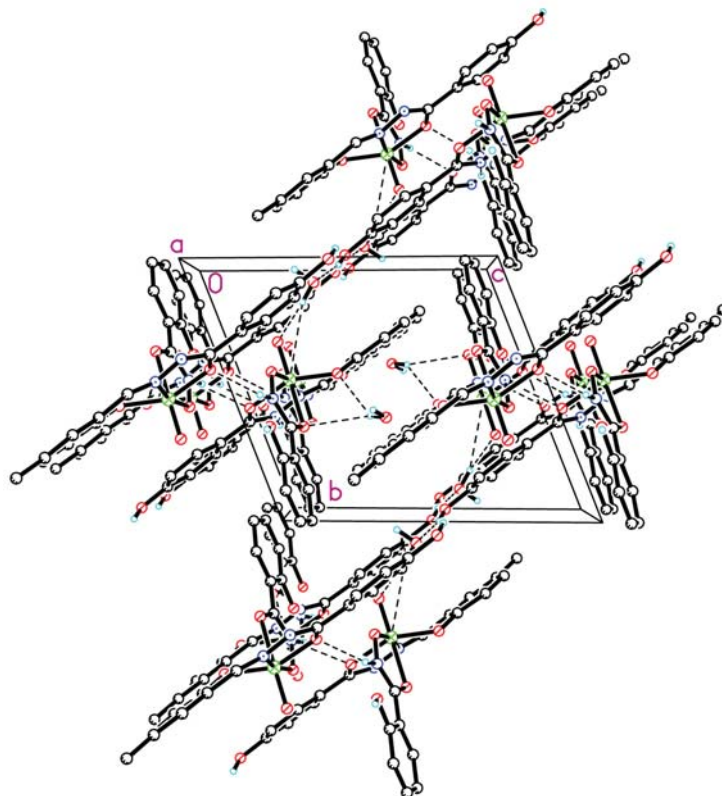
Figure 4. The crystal packing of complex **2** as seen along *c*-axis. The dashed lines denote hydrogen bonds.

(Figure 3). In the crystal structure of complex **2**, the vanadium complex molecules and the water molecules are linked through intermolecular O–H···O, N–H···O and O–H···N hydrogen bonds (Table 3), to form 2D layers (Figure 4).

3. 4. Catalytic Studies

Both complexes were investigated as catalysts for the oxidation of various hydrocarbons with the results shown in Table 4. The molar ratio of the catalyst employed in the oxidation reactions and the substrate is 1:500. In the first set of experiments, oxidation of cyclohexene was studied with H_2O_2 in the presence of the complexes. All reactions were carried out with 1 mmol of cyclohexene in acetonitrile at 60 °C. Cyclohexene oxide was the sole product. The results of control experiments revealed that the presence of both catalyst and oxidant were essential for the oxidation; thus, oxidation of cyclohexene in the absence of H_2O_2 was not observed, and in the absence of catalyst the oxidation proceeded only up to 5% after 48 h. While the reaction at 25 °C was negligible, increasing the reaction temperature to 60 °C resulted in a considerable increase in cyclohexene conversion, up to 72% for **1** and 67% for **2** after 1 h.

The effect of solvent was also studied. Methanol, acetonitrile and dichloromethane were used as solvents for the epoxidation of cyclohexene (Figure 5). The highest conversion was observed in acetonitrile, while the lowest conversion was observed in dichloromethane. Hence, acetonitrile is a suitable solvent for this reaction.

The catalytic activities of the complexes were further examined for the oxidation of various hydrocarbons at 60 °C for 5 h in acetonitrile solvent (Table 5). Cyclohexene and cyclopentene were both converted to the corresponding epoxides with high yields and quantitative selec-
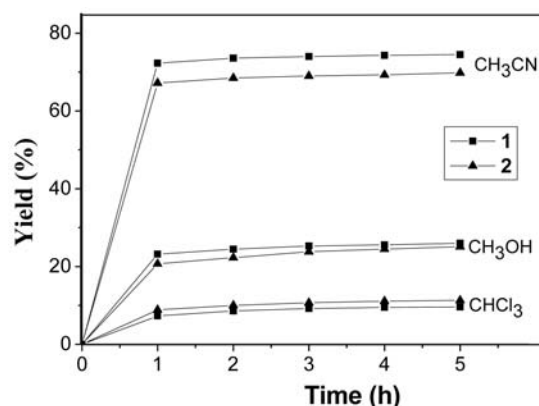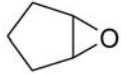
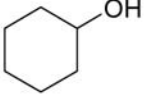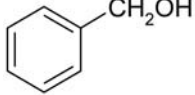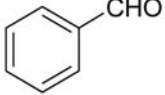**Figure 5.** Solvent effects on the epoxidation of cyclohexene. The complexes as catalyst (2.0 µmol V), cyclohexene (1 mmol), solvent (3 mL), NaHCO₃ (1 mmol), H_2O_2 (3 mmol); 60 °C.

Table 4. Catalytic results for cyclohexene [a]

Catalyst	Oxidant	Temperature (°C)	Time (h)	Conversion (%)[b]
1	H_2O_2	25	3	0
1	H_2O_2	60	1	72
2	H_2O_2	25	3	0
2	H_2O_2	60	1	67

[a] The complex (2.0 µmol V), cyclohexene (1 mmol), CH₃CN (3 mL), NaHCO₃ (1 mmol), H_2O_2 (3 mmol). [b] based on cyclohexene.

Table 5. Catalytic oxidation results of various substrates[c]

Substrate	Products	Complex	Yield (%)[d]	Conversion (%)
cyclohexene	cyclohexene oxide	**1**	76	93
		2	71	90
cyclopentene	cyclopentene oxide	**1**	83	91
		2	75	96
cyclohexane	cyclohexanol (OH)	**1**	45	69
		2	53	62
benzyl alcohol (CH₂OH)	benzaldehyde (CHO)	**1**	87	95
		2	85	97

[c] The complex (2.0 µmol V), substrate (1 mmol), CH₃CN (3 mL), NaHCO₃ (1 mmol), H_2O_2 (3 mmol). Temperature: 60 °C. [d] based on the starting substrates

tivity. Cyclohexane was converted to cyclohexanol with yields of 45% for **1** and 53% for **2**, and with cyclohexanone as the by-product (1%). Oxidation of benzyl alcohol by the complexes produced benzaldehyde with high yields and quantitative selectivity.

4. Conclusion

In summary, two new hydrazone ligands and their oxidovanadium(V) complexes with hydroxamate co-ligands have been synthesized and characterized. The complexes are effective catalysts for the oxidation of cyclohexene, cyclopentene and benzyl alcohol by H_2O_2 as oxidant.

5. Acknowledgments

6. References

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Povzetek

Dva nova oksidovanadijeva(V) kompleksa s hidrazonskim in hidroksamatnim ligandom sta bila sintetizirana in okarakterizirana z IR in ^{1}H NMR spektroskopijo, elementno analizo ter rentgensko strukturno analizo. Koordinacijska sfera vsakega od vanadijevih atomov je oktaedrična, zgrajena iz treh donorskih atomov hidrazonskega liganda, dveh donorskih atomov hidroksamatnega liganda in kisika iz oksido skupine. Oba kompleksa sta učinkovita katalizatorja za oksidacijo cikloheksena, ciklopentena in benzil alkohola ob uporabi H_2O_2 kot primarnega oksidanta.