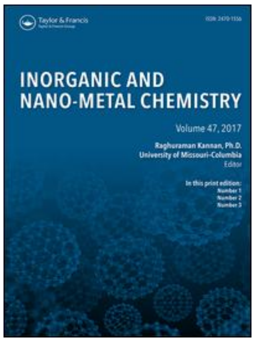

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Synthesis, crystal structures and catalytic activity of oxidovanadium(V) complexes with tridentate ONO aroylhydrazone ligands

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ABSTRACT

Two oxidovanadium(V) complexes, [VOL^1(OEt)] (**1**) and [V$_2$O$_2$(L^2)$_2$(OEt)$_2$] (**2**), where L^1 and L^2 are the anions of 2-amino-*N*′-(2-hydroxybenzylidene)benzohydrazide (H$_2$L^1) and *N*′-(2-hydroxybenzylidene)-4-hydroxybenzohydrazide (H$_2$L^2), respectively, have been synthesized and characterized by elemental analysis, infrared and electronic spectra, and ^{1}H NMR spectra. Structures of the complexes were further confirmed by single-crystal X-ray determination. The V atom in the mononuclear complex **1** is in square pyramidal coordination, and those in the dinuclear complex **2** are in octahedral coordination. Both aroylhydrazone ligands coordinate to the V atoms through the phenolate O, imino N, and enolate O atoms. The ethanol ligand in complex **1** is in terminal coordination mode, while that in complex **2** is in bridging coordination mode. The complexes function as effective olefin epoxidation catalysts with hydrogen peroxide as terminal oxidant and sodium hydrogen carbonate as a co-catalyst.

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KEYWORDS
Aroylhydrazone; vanadium complex; catalytic activity; crystal structure

Introduction

In recent years, much attention has been focused on the development of environmentally benign catalytic reactions with the increasing environmental and economical concerns. The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals since epoxides are key starting materials for a wide variety of products.[1–4] A variety of metal complexes with hydrazone ligands have been reported to have interesting catalytic oxidation properties.[5–9] The use of vanadium complexes in oxidation and oxotransfer catalysis has been noted.[10,11] Aroylhydrazones complexes are good candidates for catalytic oxidation studies because of their stability to resist oxidation. To continue exploring structural and catalytic property of vanadium complexes with aroylhdrazones applied in oxidation catalysis and as part of our research in the study of coordinating capabilities of aroylhydrazones and their coordination compounds,[12–15] we report herein the synthesis, characterization and catalytic property of two new oxidovanadium(V) complexes [VOL^1(OEt)] (**1**) and [V$_2$O$_2$(L^2)$_2$(OEt)$_2$] (**2**), where L^1 and L^2 are the anions of 2-amino-*N*′-(2-hydroxybenzylidene)benzohydrazide (H$_2$L^1; Scheme 1) and *N*′-(2-hydroxybenzylidene)-4-hydroxybenzohydrazide (H$_2$L^2; Scheme 1), respectively.

Experimental

Materials and methods

All chemicals and solvents used were of analytical reagent grade and used as received. Micro analyses for C, H, N were carried out using a Perkin Elmer 2400 CHNS/O elemental analyzer. FTIR spectra were recorded on a FTIR 8400-Shimadzu as KBr disks in the range of 400–4000 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. X-ray diffraction data were collected using a Bruker Smart 1000 CCD area diffractometer.

Synthesis of 2-amino-*N*′-(2-hydroxybenzylidene)benzohydrazide (H$_2$L^1)

An ethanolic solution (20 mL) containing 2-hydroxybenzaldehyde (1.0 mmol, 0.12 g) was added dropwise to an ethanolic solution of 2-aminobenzohydrazide (1.0 mmol, 0.15 g) with constant stirring. The mixture was refluxed for 30 min, then with the solvent removed by distillation. The white precipitate was re-crystallized from ethanol and obtained by filtration. Yield: 0.21 g, 82%. For C$_{14}$H$_{13}$N$_3$O$_2$: anal. calcd., %: C, 65.87; H, 5.13; N, 16.46. Found, %: C, 65.73; H, 5.26; N, 16.29. FT-IR (KBr), cm^{-1}: ν(OH) 3430, ν(NH) 3234, ν(CH) 2830–3100, ν(C=O) 1647, ν(C=N) 1611, ν(C–O) 1155. UV–Vis data in ethanol (λ, nm (ε, M^{-1} cm^{-1})]: 225 (22,120), 290 (17,350), 300 (18,515), 356 (14,272). ^{1}H NMR (500 MHz, DMSO-*d6*, ppm): $\delta = 11.71$ (s, 1H; O*H*), 10.87 (s, 1H; N*H*), 10.56 (s, 2H; N*H*$_2$), 8.63 (s, 1H; C*H*=N), 7.68 (d, 1H; Ar*H*), 7.62 (d, 1H; Ar*H*), 7.47 (t, 1H, Ar*H*), 7.10 (m, 2H; Ar*H*), 7.01 (m, 2H, Ar*H*), 6.85 (d, 1H, Ar*H*).

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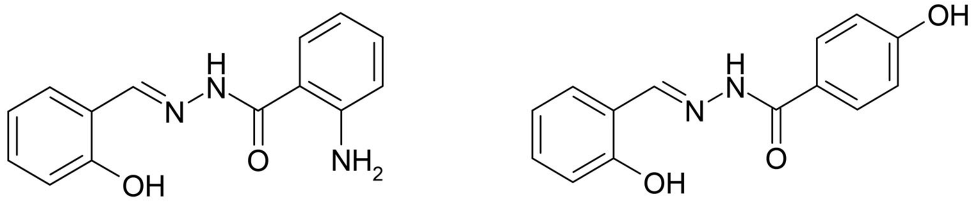
Supplemental data for this article can be accessed at publisher's website



H_2L^1 H_2L^2

Scheme 1. The aroylhydrazones.

Synthesis of N′-(2-hydroxybenzylidene)-4-hydroxybenzohydrazide (H_2L^2)

An ethanolic solution (20 mL) containing 2-hydroxybenzaldehyde (1.0 mmol, 0.12 g) was added dropwise to an ethanolic solution of 4-hydroxybenzohydrazide (1.0 mmol, 0.15 g) with constant stirring. The mixture was refluxed for 30 min, then with the solvent removed by distillation. The white precipitate was recrystallized from ethanol and obtained by filtration. Yield: 0.23 g, 90%. For $C_{14}H_{12}N_2O_3$: anal. calcd., %: C, 65.62; H, 4.72; N, 10.93. Found, %: C, 65.45; H, 4.63; N, 11.10. FTIR (KBr), cm^{-1}: ν(OH) 3542, 3434, ν(NH) 3216, ν(CH) 2830–3090, ν(C=O) 1650, ν(C=N) 1610, ν(C–O) 1160. UV–Vis data in ethanol (λ, nm (ε, $M^{-1}cm^{-1}$)]: 213 (18,720), 255 (13,230), 302 (18,153), 328 (22,305). ^{1}H NMR (500 MHz, DMSO-*d6*, ppm): $\delta = 12.20$ (s, 1H; O*H*), 11.76 (s, 1H; O*H*), 10.95 (s, 1H; N*H*), 8.65 (s, 1H; C*H*=N), 7.82 (d, 2H; Ar*H*), 7.63 (d, 1H; Ar*H*), 7.47 (t, 1H, Ar*H*), 7.12 (t, 1H; Ar*H*), 6.99 (d, 1H, Ar*H*), 6.83 (d, 2H, Ar*H*).

Synthesis of [VOL^1(OEt)] (1)

H_2L^1 (0.10 mmol, 26 mg) was dissolved in ethanol (15 mL). To the solution was added with stirring an ethanolic solution (10 mL) of $VO(acac)_2$ (0.1 mmol, 26.5 mg). The mixture was stirred at room temperature for 30 min to give deep brown solution. After keeping the solution in air for a few days, brown block-shaped single crystals, suitable for X-ray crystal structure determination were obtained. The crystals were isolated by filtration. Yield: 0.17 g, 47%. For $C_{16}H_{16}N_3O_4V$: anal. calcd., %: C, 52.61; H, 4.41; N, 11.50. Found, %: C, 52.75; H, 4.53; N, 11.38. FT-IR (KBr), cm^{-1}: ν(OH) 3372, ν(NH) 3226, ν(C=N) 1610, ν(C–O) 1155. UV–Vis data in ethanol (λ, nm (ε, $M^{-1}cm^{-1}$)]: 235 (19,610), 330 (5,630), 518 (2,325).

Synthesis of [$V_2O_2(L^2)_2(OEt)_2$] (2)

H_2L^1 (0.10 mmol, 26 mg) was dissolved in ethanol (15 mL). To the solution was added with stirring an ethanolic solution (10 mL) of $VO(acac)_2$ (0.1 mmol, 26.5 mg). The mixture was stirred at room temperature for 30 min to give deep brown solution. After keeping the solution in air for a few days, brown block-shaped single crystals, suitable for X-ray crystal structure determination were obtained. The crystals were isolated by filtration. Yield: 0.19 g, 53%. For $C_{32}H_{30}N_4O_{10}V_2$: anal. calcd., %: C, 52.47; H, 4.13; N, 7.65. Found, %: C, 52.28; H, 4.32; N, 7.53. FT-IR (KBr), cm^{-1}: ν(OH) 3389, ν(C=N) 1612, ν(C–O) 1162. UV–Vis data in ethanol (λ, nm (ε, $M^{-1}cm^{-1}$)]: 240 (20,320), 334 (7,180), 515 (3,120).

X-ray structure determination

The crystals of the complexes were measured on a Bruker SMART 1000 CCD area diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator at 25 °C. Unit cell and reflection data were obtained by the standard method and are summarized in Table 1.[16] The structures of both complexes were solved, refined, and prepared for publication using the SHEXTL package (structure solution refinements and molecular graphics).[17] The structures were solved using direct method and refined on F^2 using full-matrix least-squares techniques with anisotropic displacement factors for all nonhydrogen atoms. The amino and ethanol H atoms 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 1.43(2) Å, respectively. Positions of the remaining hydrogen atoms were calculated from the geometry of the molecular skeleton and their thermal displacement parameters were refined isotropically on a groupwise basis. Selected bond lengths and angles are reported in Table 2.

Catalytic epoxidation of olefins

To a solution of olefins (0.28 mmol), $NaHCO_3$ (0.11 mmol) and catalyst (9.4×10^{-4} mmol) in MeCN (0.5 mL) was added H_2O_2 (1.1 mmol, 30% H_2O solution) as oxidant. After the reaction was over, for the products analysis, the solution was subjected to multiple ether extraction, and the extract was also concentrated down to 0.5 mL by distillation in a rotary evaporator at room temperature and then a sample (2 μL) was taken from the solution and analyzed by GC. The retention times of the peaks were compared with those of commercial standards, and chlorobenzene was used as an internal standard for GC yield calculation.

Results and discussion

Synthesis and characterization

The reaction of $VO(acac)_2$ with the tridentate aroylhydrazone ligands in ethanol led to the formation of the

Table 1. Crystallographic data and refinement parameters for complexes **1** and **2**.

Parameters	1	2
Mr	365.26	742.48
Crystal color, habit	Brown, block	Brown, block
Crystal size (mm^3)	0.17 × 0.13 × 0.13	0.22 × 0.20 × 0.20
Crystal system	Monoclinic	Orthorhombic
Space group	*Pc*	*Pbca*
a, Å	6.0731(13)	11.5539(12)
b, Å	18.353(2)	14.6847(13)
c, Å	14.658(2)	19.113(2)
β, °	91.353(2)	90
V, Å^3	1633.3(5)	3242.8(6)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.485	1.500
μ, mm^{-1}	0.633	0.640
F(000)	752	1504
Number of unique data	4671	3008
Number of observed data ($I > 2\sigma(I)$)	2987	2165
Independent parameters	435	219
R_1, wR_2 ($I > 2\sigma(I)$)	0.0657, 0.1436	0.0383, 0.0983
R_1, wR_2 (all data)	0.1124, 0.1847	0.0599, 0.1148
Goodness of fit on F^2	1.024	1.029
Largest difference peak and hole, *e* Å^{-3}	0.406 and −0.367	0.307 and −0.395

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

1			
V(1)-O(1)	1.846(7)	V(1)-O(2)	1.941(6)
V(1)-O(3)	1.580(7)	V(1)-O(4)	1.763(7)
V(1)-N(1)	2.113(8)	V(2)-O(5)	1.834(8)
V(2)-O(6)	1.929(6)	V(2)-O(7)	1.593(8)
V(2)-O(8)	1.762(7)	V(2)-N(3)	2.110(8)
O(3)-V(1)-O(4)	102.5(4)	O(3)-V(1)-O(1)	100.1(4)
O(4)-V(1)-O(1)	101.1(3)	O(3)-V(1)-O(2)	101.3(3)
O(4)-V(1)-O(2)	94.2(3)	O(1)-V(1)-O(2)	150.2(3)
O(3)-V(1)-N(1)	96.6(4)	O(4)-V(1)-N(1)	159.7(3)
O(1)-V(1)-N(1)	82.2(3)	O(2)-V(1)-N(1)	75.0(3)
O(7)-V(2)-O(8)	103.0(4)	O(7)-V(2)-O(5)	101.4(4)
O(8)-V(2)-O(5)	101.9(4)	O(7)-V(2)-O(6)	98.8(3)
O(8)-V(2)-O(6)	94.8(3)	O(5)-V(2)-O(6)	150.1(3)
O(7)-V(2)-N(3)	94.7(4)	O(8)-V(2)-N(3)	160.7(3)
O(5)-V(2)-N(3)	81.7(3)	O(6)-V(2)-N(3)	74.7(3)
2			
V(1)-O(1)	1.8299(19)	V(1)-O(2)	1.9330(19)
V(1)-O(3)	1.578(2)	V(1)-O(4)	1.8176(17)
V(1)-O(4A)	2.3634(18)	V(1)-N(1)	2.105(2)
O(3)-V(1)-O(4)	103.07(10)	O(3)-V(1)-O(1)	100.72(10)
O(4)-V(1)-O(1)	105.99(8)	O(3)-V(1)-O(2)	98.65(9)
O(4)-V(1)-O(2)	89.21(8)	O(1)-V(1)-O(2)	151.81(8)
O(3)-V(1)-N(1)	96.17(10)	O(4)-V(1)-N(1)	156.30(8)
O(1)-V(1)-N(1)	83.52(8)	O(2)-V(1)-N(1)	74.18(8)
O(3)-V(1)-O(4A)	176.71(9)	O(4)-V(1)-O(4A)	74.46(7)
O(1)-V(1)-O(4A)	82.15(7)	O(2)-V(1)-O(4A)	79.25(7)
N(1)-V(1)-O(4A)	85.73(7)		

Symmetry code for A: 2 − *x*, − *y*, 1 − *z*.

vanadium complexes. The aroylhydrazone ligands contribute to their enolic form in the complexes. The complexes are stable at room temperature and soluble in DMSO, DMF, ethanol, acetonitrile and less soluble in other common solvents like dichloromethane, chloroform, and insoluble in benzene, *n*-hexane, and CCl_4.

Structure description of complex 1

The molecular structure of the mononuclear vanadium complex **1** is shown in Figure 1. The asymmetric unit of the complex contains two mononuclear vanadium compounds. The V atom in the complex is in square pyramidal coordination, with the phenolate O, imino N, and enalate O atoms of the hydrazone ligand, and the ethanolate O atom defining the basal plane, and with the oxo O atom locating at the apical position. The V atoms deviate from the least-squares plane defined by the corresponding equatorial atoms by 0.340(1) Å for V(1) and 0.324(1) Å for V(2). The coordinate bond lengths in the complex are similar to those observed in vanadium complexes with hydrazone ligands.[18,19] The distortion of the square pyramidal coordination can be observed from the coordinate bond angles, ranging from 74.7(3)° to 103.5(4)° for the perpendicular angles, and from 150.1(3)° to 160.7(3)° for the diagonal angles. The dihedral angles between the two benzene rings of the hydrazone ligands are 9.7(5)° for V(1) molecule and 2.1(5)° for V(2) molecule. In the crystal structure of the complex, molecules are linked through C(4)–H(4)···O(7) hydrogen bonds [C(4)–H(4) = 0.93 Å, H(4)···O(7)^i = 2.36 Å, C(4)···O(7)^i = 3.1963(7) Å, C(4)–H(4)···O(7)^i = 150(5)°, symmetry code for i: *x*, 1 – *y*, −1/2 + *z*], to form dimers (Figure 2).

Structure description of complex 2

The molecular structure of the dinuclear vanadium complex **2** is shown in Figure 3. The molecule of the complex possesses crystallographic inversion center symmetry. The two V atoms are bridged by deprotonated ethanol ligands, with distance of 3.345(2) Å. The V atom in the complex is in octahedral coordination, with the phenolate O, imino N and enalate O atoms of the hydrazone ligands, and the

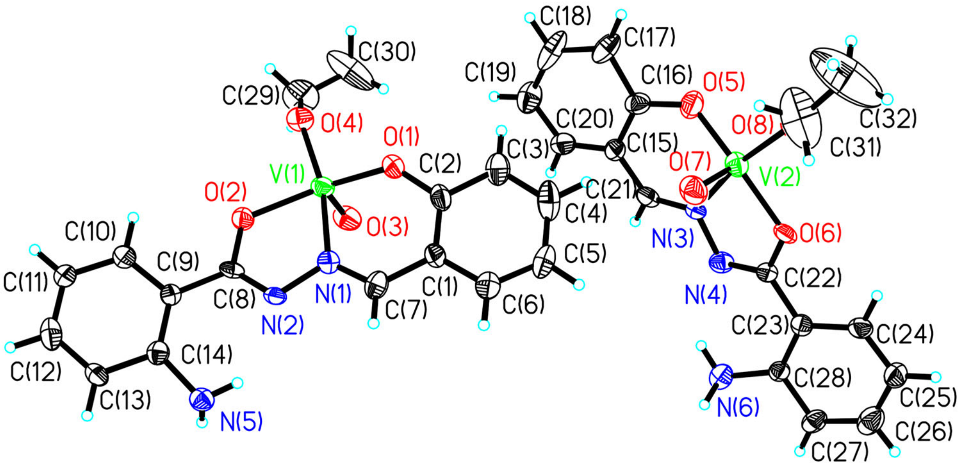


Figure 1. Molecular structure of complex **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

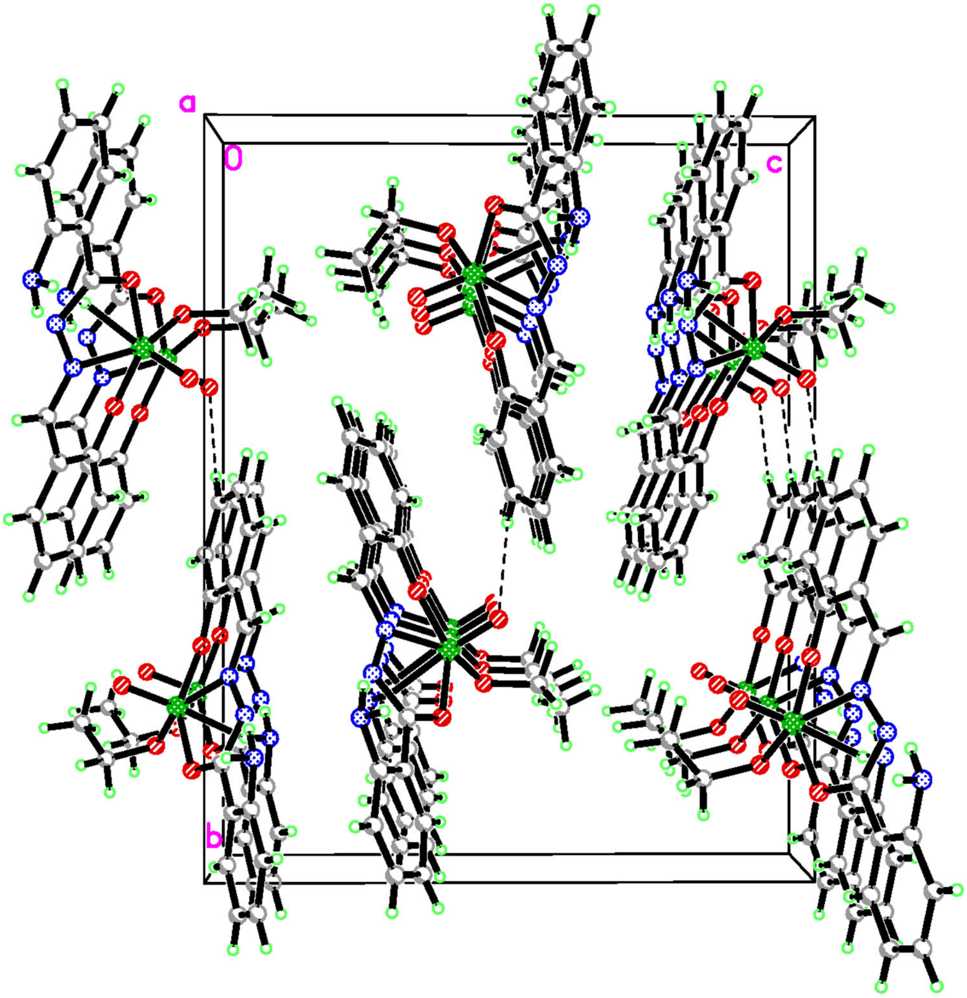


Figure 2. Crystal packing of complex **1**. Hydrogen bonds are shown as dashed lines.

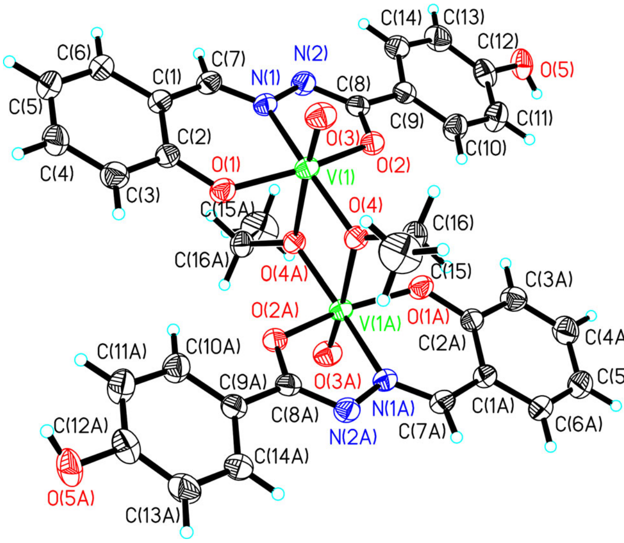


Figure 3. Molecular structure of complex **2**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The symmetry code for A is 2 − *x*, − *y*, 1 − *z*.

ethanolate O atom defining the equatorial plane, and with the oxo O atom and the other ethanolate O atom locating at the axial positions. The V atoms deviate from the least-squares plane defined by the corresponding equatorial atoms by 0.331(1) Å. The coordinate bond lengths in the complex are similar to those observed in complex **1** and other vanadium complexes with hydrazone ligands.[20,21] The distortion of the octahedral coordination can be observed from the coordinate bond angles, ranging from 74.18(8)° to 105.99(8)° for the perpendicular angles, and from 151.81(8)° to 176.71(9)° for the diagonal angles. The dihedral angle between the two benzene rings of the hydrazone ligand is 4.3(6)°. In the crystal structure of the complex, molecules are stack along the *c* axis *via* $\pi\cdots\pi$ interactions (Figure 4).

IR and UV–vis spectra of the complexes

The ν(C=N) absorptions are observed at 1610 cm^{-1} for **1** and 1612 cm^{-1} for **2**.[22] The intense bands indicative of the C=O vibrations and the sharp bands indicative of the N–H vibrations are absent in the complexes, indicating the enolization of the hydrazone ligands. The weak peaks in the low wave numbers in the region 450–700 cm^{-1} may be attributed to V–O and V–N bonds in the complexes. Complexes **1** and **2** exhibit typical bands at 957 and 955 cm^{-1}, respectively, which are assigned to the V=O vibrations.[23]

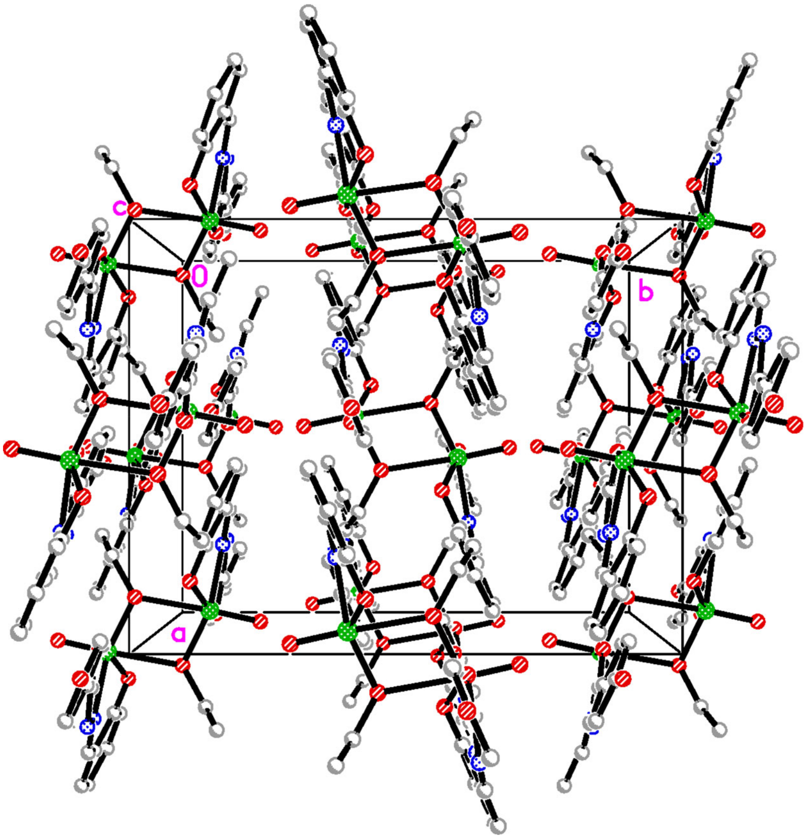
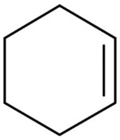
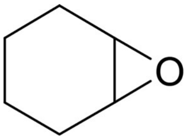
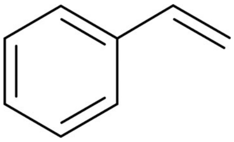
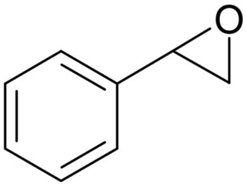
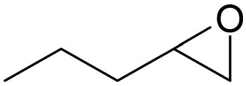
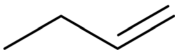
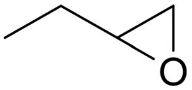


Figure 4. Crystal packing of complex **2**.

Table 3. The catalytic oxidation results.[a]

Substrate	Product	Complex	Conversion (%)[b] (TON)[c]
		1 2	100 (338) 100 (327)
		1 2	100 (315) 100 (343)
		1 2	98 (316) 95 (325)
		1 2	95 (302) 93 (287)

[a] The molar ratios for catalyst:substrate:$NaHCO_3$:H_2O_2 are 1:298:117:1170. The reactions were performed in (70:30) mixture of CH_3OH/CH_2Cl_2 (1.2 mL) under air at room temperature. The pH of the medium is 8.4.

[b] The GC conversion (%) are measured relative to the starting olefin after 75 min.

[c] TON = (mmol of product)/mmol of catalyst.

The UV–vis spectra of the complexes were recorded in 10^{-5} mol L^{-1} in ethanol, in the range 200–500 nm. The weak bands centered at 330 nm for **1** and 334 nm for **2** are attributed to intramolecular charge transfer transitions from the p_π orbital on the nitrogen and oxygen to the empty *d* orbitals of the metal.[23] The intense bands observed at 230–240 nm for the complexes are assigned to intraligand π–π^* transition. The bands centered at 518 nm for **1** and 515 nm for **2** are attributed to the ligand-to-metal charge transfer transitions (LMCT).[24]

Catalytic property

The complexes show good catalytic property in the oxidation of various olefins to their corresponding epoxides. The details of catalytic properties with respect to epoxidation of olefins with the complexes as catalysts are given in Table 3. Good epoxide yields and selectivity were observed for all aliphatic and aromatic substrates. The results of catalytic studies using the catalysts reveal that the efficiency of catalyst toward all the substrates is similar with maximum conversion, TON, and selectivity. When H_2O_2 was used as a sole oxidant the catalytic efficiency is not high, but when $NaHCO_3$ was added as a co-catalyst the efficiency of the system increases many times. The key aspect of such a reaction is that H_2O_2 and hydrogen carbonate react in an equilibrium process to produce peroxymonocarbonate, HCO_4^-, which is a more reactive nucleophile than H_2O_2 and speeds up the epoxidation reaction.

Conclusion

A mononuclear and a dinuclear oxidovanadium(V) complexes with similar aroylhydrazone ligands 2-amino-*N*′-(2-hydroxybenzylidene)benzohydrazide and *N*′-(2-hydroxybenzylidene)-4-hydroxybenzohydrazide have been prepared and structurally characterized using X-ray structure analysis. The V atoms in the mononuclear and dinuclear complexes have square pyramidal and octahedral geometry, respectively. The slight difference of the aroylhydrazones leads to the formation of different complexes. Both complexes showed effective catalytic property on the oxidation of various olefins to their corresponding epoxides.

Supplementary material

CCDC reference numbers 1851433 (**1**) and 1851434 (**2**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk, or from Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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