Scientific paper

Two Oxidovanadium(V) Complexes with Hydrazone Ligands: Synthesis, Crystal Structures and Catalytic Oxidation Property

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Received: 11-23-2021

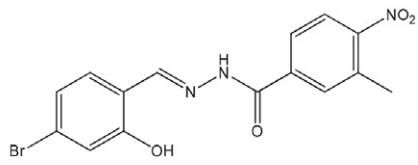
Abstract

Two new oxidovanadium(V) complexes, [VOL^1(aha)]DMF (**1**) and [VOL^2(mat)] (**2**), where L^1 and L^2 are the dianionic form of *N*'-(4-bromo-2-hydroxybenzylidene)-3-methyl-4-nitrobenzohydrazide and *N*'-(3,5-dibromo-2-hydroxybenzylidene) pivalohydrazide, respectively, and aha and mat are the monoanionic form of acetohydroxamic acid and maltol, respectively, have been synthesized and structurally characterized by physico-chemical methods and single crystal X-ray determination. X-ray analysis indicates that the V atoms in the complexes are in octahedral coordination. Crystal structures of the complexes are stabilized by hydrogen bonds. The catalytic property for epoxidation of styrene by the complexes was evaluated.

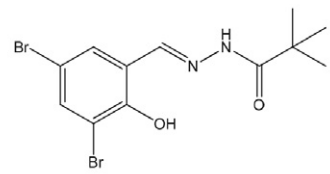
Keywords: Vanadium complex; hydrazone ligand; crystal structure; catalytic property

1. Introduction

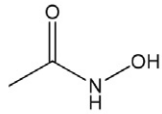
Hydrazones bearing typical –CH=N–NH–C(O)– group are a kind of Schiff base compounds, which represent one of the most attractive series of ligands in coordination chemistry.[1] The hydrazone ligands can adopt both ketone and enol forms during the coordination with various transition and rare earth metal atoms, to form complexes with versatile structures and properties like antibacterial, enzyme inhibition, magnetism, catalytic and photoluminescence.[2] In the last few years, a number of complexes with hydrazone ligands have been reported to have fascinating catalytic properties, such as oxidation of sulfides, polymerization and asymmetric epoxidation.[3] Among the hydrazone complexes, those with V centers are of particular interest for their catalytic applications.[4] Maltol and acetohydroxamic acid are bidentate ligands in vanadium complexes.[4b,5] In pursuit of new maltolate and acetohydroxamate coordinated vanadium complexes with hydrazone ligands, we report herein two new oxidovanadium(V)



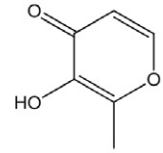
H_2L^1



H_2L^2



Haha



Hmat

Scheme 1. The ligands.

complexes, [VOL^1(aha)]DMF (**1**) and [VOL^2(mat)] (**2**), where L^1 and L^2 are the dianionic form of *N*'-(4-bromo-2-hydroxybenzylidene)-3-methyl-4-nitrobenzohydrazide (H_2L^1) and *N*'-(3,5-dibromo-2-hydroxybenzylidene) pivalohydrazide (H_2L^2), respectively, and aha and mat are the monoanionic form of acetohydroxamic acid (Haha) and maltol (Hmat), respectively (Scheme 1).

2. Experimental

2. 1. Materials

$VO(acac)_2$, 4-bromosalicylaldehyde, 3,5-dibromosalicylaldehyde, acetohydroxamic acid, and maltol were purchased from Aldrich. All other reagents with AR grade were used as received without further purification.

2. 2. Physical Measurements

Infrared spectra (4000–400 cm^{-1}) were recorded as KBr discs with a FTS-40 BioRad FT-IR spectrophotometer. The electronic spectra were recorded on a Lambda 35 spectrometer. Microanalyses (C,H,N) of the complex were carried out on a Carlo-Erba 1106 elemental analyzer. Solution electrical conductivity was measured at 298K using a DDS-11 conductivity meter. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph.

2. 3. X-ray Crystallography

Crystallographic data of the complexes were collected on a Bruker SMART CCD area diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298(2) K. Absorption corrections were applied by using the multi-scan program.[6] The structures of the complexes were solved by direct methods and successive Fourier difference syntheses, and anisotropic thermal parameters for all nonhydrogen atoms were refined by full-matrix least-squares procedure against F^2.[7] All non-hydrogen atoms were refined anisotropically. The amino H atom of complex **1** was located from a difference Fourier map and refined isotropically, with N–H distance restrained to 0.90(1) Å. The remaining hydrogen atoms were located at calculated positions, and refined isotropically with U_{iso}(H) values constrained to 1.2 U_{iso}(C) and 1.5 U_{iso}(O and methyl C). The C20 and O8 atoms in complex **1**, and the C10 atom in complex **2** are refined as isotropic behavior due to their disorder manner. The crystallographic data and experimental details for the structural analysis are summarized in Table 1.

2. 4. Synthesis of H_2L^1

A methanol solution (20 mL) of 3-methyl-4-nitrobenzohydrazide (1.9 g, 0.010 mol) was added to a methanol solution (20 mL) of 4-bromosalicylaldehyde (2.0 g, 0.010

Table 1. Crystallographic data for the single crystal of the complexes

	1	**2**
Empirical formula	$C_{20}H_{21}BrN_5O_8V$	$C_{18}H_{17}Br_2N_2O_6V$
Formula weight	590.27	568.09
Temperature (K)	298(2)	298(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pca2_1$
a (Å)	8.6210(10)	14.6120(11)
b (Å)	26.9525(13)	15.6777(12)
c (Å)	10.5418(12)	9.4641(11)
α (°)	90	90
β (°)	98.528(1)	90
γ (°)	90	90
V (Å^3)	2422.4(4)	2168.1(3)
Z	4	4
F(000)	1192	1120
μ, mm^{-1}	2.114	4.179
R_{int}	0.0640	0.0910
Collected data	14312	19236
Unique data	4514	3834
Observed data [$I > 2\sigma(I)$]	2931	2731
Restraints	13	19
Parameters	323	267
Goodness-of-fit on F^2	0.994	1.031
R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0507, 0.1162	0.0496, 0.0776
R_1, wR_2 indices (all data)	0.0893, 0.1357	0.0912, 0.0880
Large diff. peak and hole, *e* Å^{-3}	0.554, –0.425	0.655, –0.446

mol). The mixture was refluxed for 1 h, and three quarter of the solvent was evaporated to give yellow precipitate, which was filtered off and washed several times with methanol. The yield is 92%. Analysis calculated for $C_{15}H_{12}BrN_3O_4$: C, 47.64; H, 3.20; N, 11.11%; found: C, 47.47; H, 3.31; N, 11.25%. ^{1}H NMR (d_6-DMSO, 500 MHz): δ 2.62 (s, 3H, CH_3), 7.07 (d, 1H, ArH), 7.51 (s, 1H, ArH), 7.58 (d, 1H, ArH), 7.86 (d, 1H, ArH), 8.03 (s, 1H, ArH), 8.41 (d, 1H, ArH), 8.69 (s, 1H, CH=N), 10.76 (s, 1H, NH), 11.38 (s, 1H, OH). IR data (KBr, cm^{-1}): 3446 (br, w, ν_{OH}), 3222 (sh, w, ν_{NH}), 1657 (vs, $\nu_{\text{-C(O)-NH-}}$), 1602 (vs, $\nu_{C=N}$), 1520 (s, ν_{as} NO_2), 1338 (s, ν_s NO_2). UV-Vis data (λ_{max}, nm): 285, 345, 420.

2. 5. Synthesis of H_2L^2

A methanol solution (20 mL) of pivalohydrazide (1.1 g, 0.010 mol) was added to a methanol solution (20 mL) of 3,5-dibromosalicylaldehyde (2.8 g, 0.010 mol). The mixture was refluxed for 1 h, and three quarter of the solvent was evaporated to give colorless precipitate, which was filtered off and washed several times with methanol. The yield is 88%. Analysis calculated for $C_{12}H_{14}Br_2N_2O_2$: C, 38.12; H, 3.73; N, 7.41%; found: C, 38.31; H, 3.62; N, 7.32%. ^{1}H NMR (d_6-DMSO, 500MHz): δ 1.26 (s, 9H, $C(CH_3)_3$), 7.72 (s, 1H, ArH), 7.83 (s, 1H, ArH), 8.71 (s, 1H, CH=N), 11.22 (s, 1H, NH), 11.75 (s, 1H, OH). IR data (KBr, cm^{-1}): 3438 (br, w, ν_{OH}), 3121 (sh, w, ν_{NH}), 1653 (vs, $\nu_{\text{-C(O)-NH-}}$), 1605 (vs, $\nu_{C=N}$). UV-Vis data (λ_{max}, nm): 295, 305, 332, 400.

2. 6. Synthesis of [VOL^1(aha)]DMF (1)

H_2L^1 (1.0 mmol, 0.38 g) and [$VO(acac)_2$] (1.0 mmol, 0.26 g) were mixed and stirred in methanol (50 mL) for 30 min at 25 °C. Then, acetohydroxamic acid (1.0 mmol, 0.075 g) was added and the mixture was stirred for another 30 min. The brown solution was evaporated to remove three quarters of the solvents under reduced pressure, yielding deep brown solid of the complex. Yield: 65%. Well-shaped single crystals suitable for X-ray diffraction were obtained by re-crystallization of the solid from methanol. Analysis calculated for $C_{20}H_{21}BrN_5O_8V$: C, 40.70; H, 3.59; N, 11.86%; found: C, 40.54; H, 3.70; N, 11.95%. IR data (KBr, cm^{-1}): 3129 (sh, w, ν_{NH}), 1661 (vs, $\nu_{\text{-C(O)-NH-}}$), 1594 (vs, $\nu_{C=N}$), 1522 (s, ν_{as} NO_2), 1340 (s, ν_s NO_2), 973 (m, V=O). UV-Vis data (λ_{max}, nm): 260, 328, 410, 545.

2. 5. Synthesis of [VOL^2(mat)] (2)

H_2L^2 (1.0 mmol, 0.38 g) and [$VO(acac)_2$] (1.0 mmol, 0.26 g) were mixed and stirred in methanol (50 mL) for 30 min at 25 °C. Then, maltol (1.0 mmol, 0.13 g) was added and the mixture was stirred for another 30 min. The brown solution was evaporated to remove three quarters of the solvents under reduced pressure, yielding deep brown solid of the complex. Yield: 73%. Well-shaped single crystals suitable for X-ray diffraction were obtained by re-crystallization of the solid from methanol. Analysis calculated for $C_{18}H_{17}Br_2N_2O_6V$: C, 38.06; H, 3.02; N, 4.93%; found: C, 38.23; H, 2.95; N, 4.81%. IR data (KBr, cm^{-1}): 1611 (vs, $\nu_{C=N}$), 978 (m, V=O). UV-Vis data (λ_{max}, nm): 270, 340, 460.

2. 6. Styrene Epoxidation

The epoxidation reaction was carried out at room temperature in acetonitrile under N_2 atmosphere with constant stirring. The composition of the reaction mixture was 2.00 mmol of styrene, 2.00 mmol of chlorobenzene (internal standard), 0.10 mmol of the complexes (catalyst) and 2.00 mmol iodosylbenzene or sodium hypochlorite (oxidant) in 5.00 mL freshly distilled acetonitrile. When the oxidant was sodium hypochlorite, the solution was buffered to pH 11.2 with NaH_2PO_4 and NaOH. The composition of reaction medium was determined by GC with styrene and styrene epoxide quantified by the internal standard method (chlorobenzene). All other products detected by GC were mentioned as others. For each complex the reaction time for maximum epoxide yield was determined by withdrawing periodically 0.1 mL aliquots from the reaction mixture and this time was used to monitor the efficiency of the catalyst on performing at least two independent experiments. Blank experiments with each oxidant and using the same experimental conditions except catalyst were also performed.

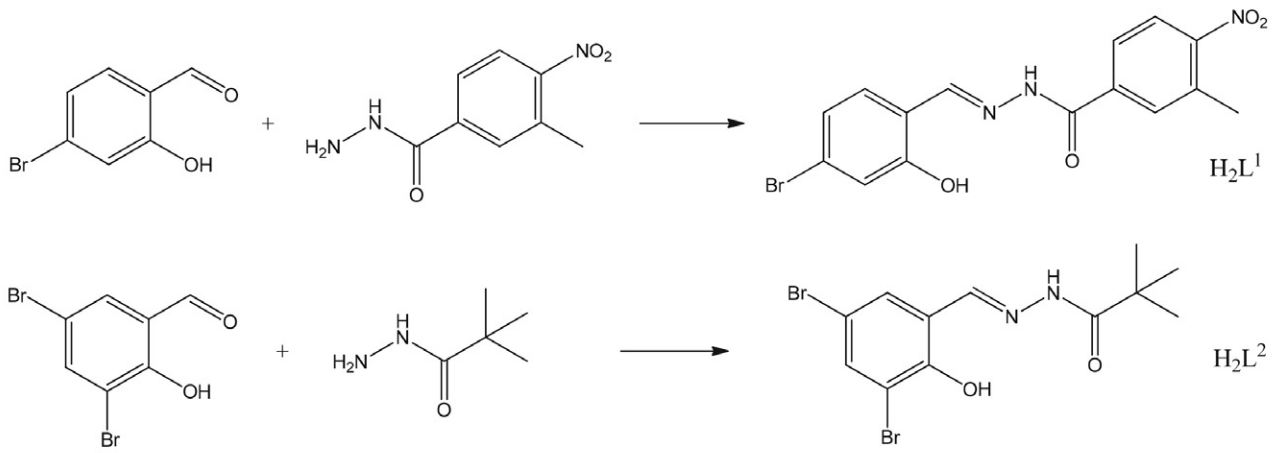
3. Results and Discussion

3. 1. Chemistry

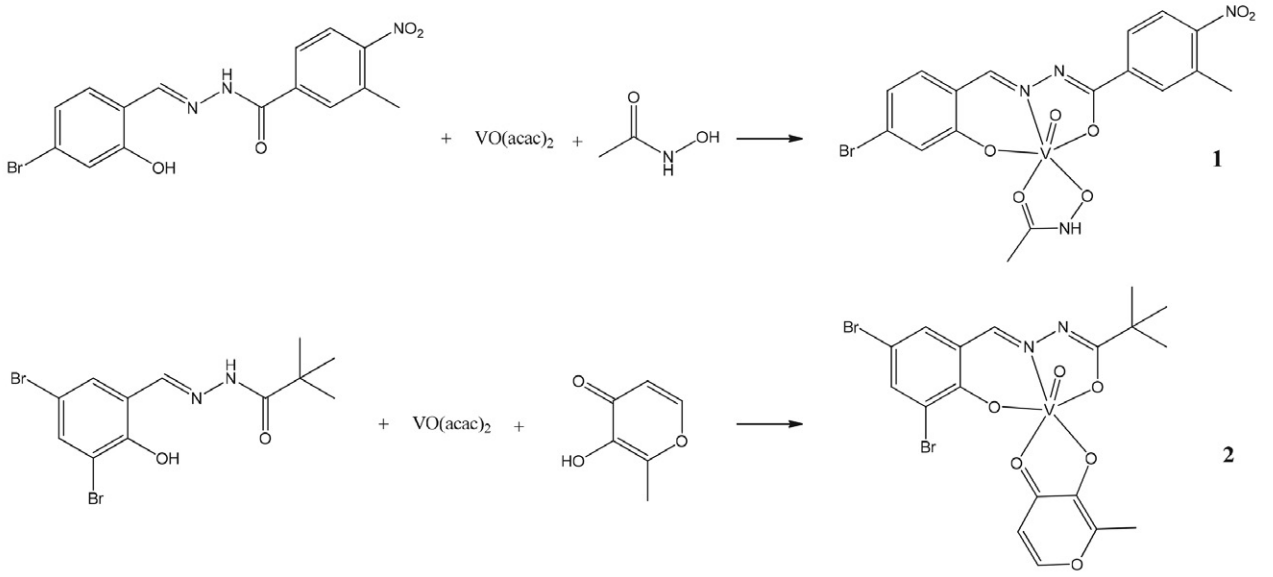
The hydrazones H_2L^1 and H_2L^2 were synthesized by reaction of 3-methyl-4-nitrobenzohydrazide with 4-bromosalicylaldehyde, and pivalohydrazide with 3,5-dibromosalicylaldehyde, respectively in methanol (Scheme 2). The complexes **1** and **2** were prepared by the reaction of the hydrazone ligands with $VO(acac)_2$ in the presence of acetohydroxamic acid and maltol (Scheme 3). The reaction progresses are accompanied by an immediate color change of the solution from colorless to deep brown. The hydrazones were deprotonated during the coordination. The oxidation of V(IV) in $VO(acac)_2$ to V(V) in both complexes during the reaction in air is not uncommon.[4c,8] The molar conductivities (Λ_M = 35 Ω^{-1} cm^2 mol^{-1} for **1** and 30 Ω^{-1} cm^2 mol^{-1} for **2**) are consistent with the values expected for non-electrolyte.[9]

3. 2. Crystal Structure Description of the Complexes

Selected bond lengths and angles for the complexes are listed in Table 2. Single crystal X-ray analysis indicates that the complexes are mononuclear oxidovanadium(V)



Scheme 2. The synthesis of the hydrazones.



Scheme 3. The synthesis of the complexes.

compounds. The ORTEP plots of the complexes **1** and **2** are shown in Figs. 1 and 2, respectively. The V atoms in the complexes are in octahedral geometry. In complex **1**, the V atom is coordinated by the O_2N donor atoms of the hydrazone ligand L^1 and the hydroxyl O atom of the acetylhydroxamate ligand in the equatorial plane, and by the carbonyl O atom of the acetylhydroxamate ligand and the oxido O atom at the two axial positions. In complex **2**, the V atom is coordinated by the O_2N donor atoms of the hydrazone ligand L^2 and the hydroxyl O atom of the maltolate ligand in the equatorial plane, and by the carbonyl O atom of the maltolate ligand and the oxido O atom at the two axial positions. The V atoms displaced toward the axial oxido O atoms (O3) by 0.269(1) Å for **1**, and 0.322(1) Å for **2**, from the equatorial planes of both complexes. The distortion of the octahedral coordination of the complexes can be observed from the bond angles related to the V atoms. The *cis*- and *trans*- angles related to the V atoms at the equatorial planes are in the ranges of 75.22(15)–100.1(2)° and 154.24(16)–172.90(17)° for **1** and 74.6(2)–101.3(2)° and 153.6(2)–177.3(2)° for **2**. The deviations from the ideal octahedral geometry are mainly origin from the strain created by the five-membered chelate rings V1-N1-N2-C8-O2 and V1-O4-C17-N4-O5 for **1** or V1-O4-C13-C14-O5 for **2**. The bond lengths of V–O and V–N of both complexes are similar to each other, and comparable to those in other V complexes in literature.[4,10] The terminal V1–O3 [1.57–1.58 Å] bond distances of both complexes agree well with the corresponding values reported for related systems.[9] Because of the *trans* influence of the oxido groups, the distances to the O4 atoms (2.20–2.31 Å) are considerably elongated, making the O4 atoms weakly coordinated to the V atoms. Such elongation has previously been observed in other complexes with similar structures. The hydrazone ligands coordinate to the V atoms through dianionic form, which can be observed from the bond

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

	1	**2**
V1–O1	1.856(3)	1.841(7)
V1–O2	1.944(3)	1.901(7)
V1–O3	1.579(3)	1.575(6)
V1–O4	2.207(3)	2.309(7)
V1–O5	1.848(3)	1.856(6)
V1–N1	2.089(4)	2.098(7)
O3–V1–O5	96.46(16)	101.2(3)
O3–V1–O1	100.10(18)	98.1(3)
O5–V1–O1	98.23(14)	100.7(3)
O3–V1–O2	97.63(17)	99.5(3)
O5–V1–O2	98.18(14)	94.9(3)
O1–V1–O2	154.24(15)	153.7(3)
O3–V1–N1	98.39(16)	99.6(3)
O5–V1–N1	164.42(15)	158.0(3)
O1–V1–N1	83.78(14)	83.1(3)
O2–V1–N1	75.23(13)	74.8(3)
O3–V1–O4	172.88(16)	177.2(3)
O5–V1–O4	76.53(14)	76.9(3)
O1–V1–O4	82.37(14)	84.2(3)
O2–V1–O4	82.31(13)	78.7(3)
N1–V1–O4	88.50(13)	82.0(3)

lengths of C8–O2 and C8–N2. The bonds C8–O2 are obviously longer than typical double bonds, while the bonds C8–N2 are obviously shorter than typical single bonds.

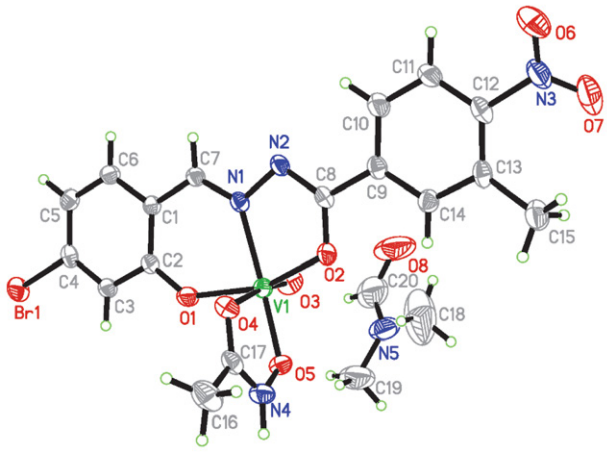


Fig. 1. ORTEP diagram of complex **1** with 30% thermal ellipsoid.

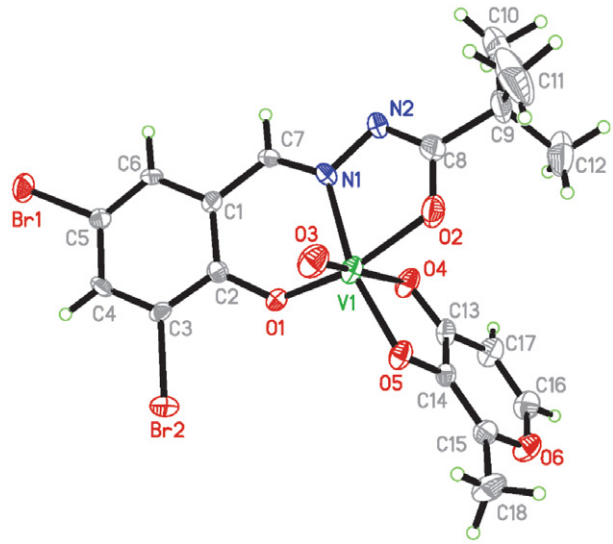


Fig. 2. ORTEP diagram of complex **2** with 30% thermal ellipsoid.

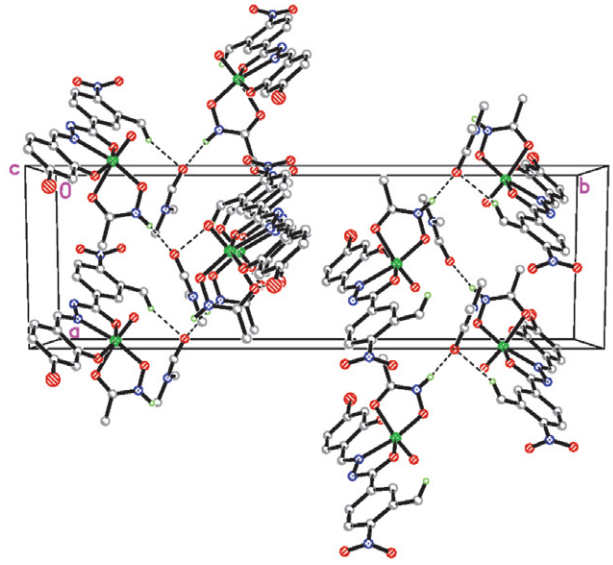


Fig. 3. Molecular packing structure of complex **1** linked by hydrogen bonds (dashed lines).

This phenomenon is not uncommon for hydrazone complexes.[4,5a,10]

The crystal structure of complex **1** is stabilized by N–H···N and C–H···O hydrogen bonds (Table 3), to gener-

Table 3. Hydrogen bond distances (Å) and bond angles (°) for the complexes

D*–H···*A	***d*(*D*–H)**	***d*(H···*A*)**	***d*(*D*···*A*)**	**Angle (*D*–H···*A*)**
1				
N4–H4···O8$^{\#1}$	0.90	1.83	2.698(4)	164(5)
C15–H15B···O8$^{\#2}$	0.96	2.44	3.334(4)	156(5)
2				
C6–H6···O4$^{\#3}$	0.93	2.54	3.404(5)	154(6)
C16–H16···O3$^{\#4}$	0.93	2.59	3.347(5)	139(6)

Symmetry codes: #1: 1½ + *x*, ½ – *y*, ½ + *z*; #2: 1 + *x*, *y*, *z*; #3: 1½ – *x*, *y*, ½ + *z*; #4: *x*, *y*, –1 + *z*.

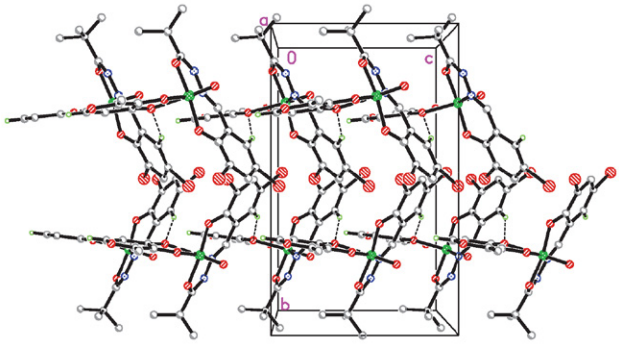


Fig. 4. Molecular packing structure of complex **2** linked by hydrogen bonds (dashed lines).

ate chains along the *a* axis (Fig. 3). The crystal structure of complex **2** is stabilized by C–H···O hydrogen bonds (Table 3), to generate chains along the *c* axis (Fig. 4).

3. 4. IR and UV-vis Spectra of the Compounds

The weak and broad absorptions in the region 3400–3500 cm^{-1} of the free hydrazones are attributed to the O–H bonds of the phenol groups. The weak absorptions at 3120–3230 cm^{-1} for the free hydrazones and complex **1** are assigned to the stretching vibrations of the N–H groups. The intense bands at 1657 cm^{-1} for H_2L^1, 1653 cm^{-1} for H_2L^2, and 1661 cm^{-1} for complex **1** are assigned to the vibrations of the C=O groups.[11] The typical bands for the azomethine groups, ν(C=N), are observed at 1590–1611 cm^{-1} for the compounds.[12] The characteristic of the spectra of both complexes is the exhibition of sharp bands at about 973 cm^{-1} for **1** and 978 cm^{-1} for **2**, corresponding to the V=O stretching vibration.[13] The appearance of a single band in this region indicates the existence of monomeric six-coordinated V=O units instead of the polymeric units.[14] This is approved by the single crystal structure determination. The weak bands in the range of 400–650 cm^{-1} are assigned to the vibrations of the V–O and V–N bonds.

In the UV-Vis spectra of the compounds, the bands at 320–350 nm are attributed to the azomethine chromophore π-π* transitions. The bands at higher energy (260–300 nm) are associated with the benzene π-π* transitions.[15] The weak bands at 545 nm for **1** and 460 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 V atoms.[16]

3. 5. Catalytic Properties of the Complexes

The percentage of conversion of styrene, selectivity for styrene oxide, yield of styrene oxide and reaction time to obtain maximum yield using both the oxidants are given in Table 4. The data reveals that the complexes as catalysts convert styrene most efficiently in the presence of both oxidants. Nevertheless, the catalysts are selective towards the formation of styrene epoxides despite of the formation of by-products which have been identified by GC-MS as benzaldehyde, phenylacetaldehyde, styrene epoxides derivative, alcohols *etc.* From the data it is also clear that the complexes exhibit excellent efficiency for styrene epoxide yield. When the reactions are carried out with PhIO and NaOCl, styrene conversions of complexes **1** and **2** were about 85% and 81%, and 78% and 75%, respectively. It is evident that between PhIO and NaOCl, the former acts as a better oxidant with respect to both styrene conversion and styrene epoxide selectivity. The epoxide yields for the complexes **1** and **2** using PhIO and NaOCl as oxidants are 76% and 86%, and 74% and 81%, respectively.

Table 4. Catalytic epoxidation results of complexes **1** and **2***

	1	**1**	**2**	**2**
Oxidant	PhIO	NaOCl	PhIO	NaOCl
Conversion (%)	85	78	81	75
Epoxide yield (%)	76	74	86	81
Selectivity (%)	93	90	95	87

* The time is 2 h for PhIO, and 3 h for NaOCl.

4. Conclusion

Two new mononuclear oxidovanadium(V) complexes derived from hydrazone ligands have been synthesized and characterized. Single crystal X-ray analysis indicates that the V atoms in both complexes are in distorted octahedral coordination. The complexes have effective catalytic property for the epoxidation of styrene, with conversions over 75% and selectivities over 87%.

Supplementary Material

CCDC 2123401 for **1** and 2123402 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

This work was financially supported by the Scientific Research Foundation of Chengdu Technological University (Grant No. 2021RC004).

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Povzetek

Sintetizirali smo dva nova oksidovanadijeva(V) kompleksa, [VOL^1(aha)]DMF (**1**) in [VOL^2(mat)] (**2**), kjer sta L^1 in L^2 dianionski obliki *N*'-(4-bromo-2-hidroksibenziliden)-3-metil-4-nitrobenzohidrazida in *N*'-(3,5-dibromo-2-hidroksibenziliden)pivalohidrazida ter aha in mat monoanionski obliki acetohidroksaminske kisline in maltola ter ju okarakterizirali s fizikalno-kemijskimi metodami in monokristalno rentgensko difrakcijo. Rentgenska analiza razkriva, da imajo V atomi v kompleksih oktaedrično koordinacijo. Kristalni strukturi kompleksov sta stabilizirani z vodikovimi vezmi. Proučili smo katalitske lastnosti kompleksov za epoksidacijo stirena.