130

Scientific paper

# Oxidovanadium(V) and Dioxidomolybdenum(VI) Complexes of N'-(3,5-Dichloro-2-hydroxybenzylidene)-4fluorobenzohydrazide: Synthesis, Characterization, Crystal Structures and Catalytic Property

Huan-Yu Liu,\* Yi-Shu Yin, Luo-Ju Yang, Xiao-Ling Zou and Ya-Fang Ye

<sup>1</sup> School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Zhongshan 528458, P.R. China

<sup>2</sup> Guangdong Cosmetics Engineering and Technology Research Center, Zhongshan 528458, P.R. China

\* Corresponding author: E-mail: liuhuanyu03@163.com

Received: 05-29-2019

#### **Abstract**

N'-(3,5-Dichloro-2-hydroxybenzylidene)-4-fluorobenzohydrazide (H<sub>2</sub>L) was used to prepare oxidovanadium(V) complex [VOL(OEt)(MeOH)] (1) and dioxidomolybdenum(VI) complex [MoO<sub>2</sub>L(OH<sub>2</sub>)]-[MoO<sub>2</sub>L(EtOH)] (2). The complexes were characterized by IR, UV-Vis, NMR spectroscopy, and single crystal X-ray diffraction. X-ray analysis indicates that the complexes are mononuclear species with the metal atoms in octahedral coordination. The complexes were studied for catalytic oxidation property on some olefins with *tert*-butyl hydroperoxide as oxidant.

Keywords: Hydrazone; Vanadium complex; Molybdenum complex; Crystal structure; Catalytic property

#### 1. Introduction

The oxidation of olefins is an important reaction and has received considerable attention in material chemistry. Vanadium and molybdenum complexes with high-valent metal atoms have attracted particular interest due to their important practical applications as efficient catalysts in the sulfoxidation and epoxidation of olefins, and the ammoxidation of propene *etc.*<sup>1</sup> Vanadium and molybdenum can form stable and versatile complexes with various organic ligands. Schiff base vanadium and molybdenum complexes have been reported to have efficient catalytic properties in both homogeneous and heterogeneous reactions.<sup>2</sup> Recently, we have reported some metal complexes with Schiff bases and their biological applications.<sup>3</sup> as well as catalytic properties.<sup>4</sup> In pursuit of

new catalytic materials based on vanadium and molybdenum complexes, in this work, a new oxidovanadium(V) complex [VOL(OEt)(MeOH)] (1) and a new dioxidomolybdenum(VI) complex [MoO<sub>2</sub>L(OH<sub>2</sub>)]·[MoO<sub>2</sub>L(EtOH)] (2), derived from the hydrazone compound N'-(3,5-dichloro-2-hydroxybenzylidene)-4-fluorobenzohydrazide (H<sub>2</sub>L) are presented.

# 2. Experimental

### 2. 1. Materials and Methods

 $VO(acac)_2$  and  $MoO_2(acac)_2$  and organic materials were purchased from Sigma-Aldrich and used as received. All other reagents were of analytical reagent grade. Elemental analyses of C, H and N were carried out in a Perkin-Elmer automated model 2400 Series II CHNS/O analyzer. FT-IR spectra were obtained on a Perkin-Elmer 377 FT-IR spectrometer with samples prepared as KBr pellets. UV-Vis spectra were obtained on a Lambda 900 spectrometer. X-ray diffraction was carried out on a Bruker APEX II CCD diffractometer.  $^{1}$ H and  $^{13}$ C NMR spectra were recorded on a Bruker FT-NMR 500 MHz spectrometer using  $d^6$ -DMSO as solvent. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph.

#### 2. 2. Synthesis of H<sub>2</sub>L

To the ethanolic solution (30 mL) of 4-fluorobenzohydrazide (0.010 mol, 1.54 g) was added an ethanolic solution (20 mL) of 3,5-dichlorosalicylaldehyde (0.010 mol, 1.91 g) with stirring. The mixture was stirred for 30 min at room temperature, and left to slowly evaporate to give colorless crystalline product, which were recrystallized from ethanol and dried in vacuum containing anhydrous CaCl<sub>2</sub>. Yield 91% (298 mg). Anal. Calc. for C<sub>14</sub>H<sub>9</sub>Cl<sub>2</sub>F-N<sub>2</sub>O<sub>2</sub>: C, 51.40; H, 2.77; N, 8.56%. Found: C, 51.27; H, 2.85; N, 8.72%. IR (KBr;  $v_{\text{max}}$ , cm<sup>-1</sup>): 3437 w v(OH), 3329 w  $\nu(NH)$ , 1653 s  $\nu(C=O)$ , 1605 w  $\nu(C=N)$ , 1518 m  $\nu$ (Ar–O), 1283 m  $\nu$ (C–O). UV-Vis data (EtOH;  $\lambda_{max}$ , nm): 220, 285, 337. <sup>1</sup>H NMR (500 MHz, d<sup>6</sup>-DMSO; δ, ppm): 12.50 (s, 1H, OH), 12.47 (s, 1H, NH), 8.57 (s, 1H, CH=N), 8.03 (t, 2H, ArH), 7.67 (s, 1H, ArH), 7.61 (s, 1H, ArH), 7.40 (t, 2H, ArH).  $^{13}$ C NMR (126 MHz,  $d^{6}$ -DMSO;  $\delta$ , ppm): 165.40, 163.41, 161.92, 146.97, 130.55, 130.48, 130.22, 128.65, 128.35, 122.89, 121.44, 115.69.

#### 2. 3. Synthesis of Complex 1

The hydrazone compound  $H_2L$  (0.10 mmol, 32.7 mg) and  $VO(acac)_2$  (0.10 mmol, 26.5 mg) were mixed in the mixture solvent of methanol and ethanol (20 mL; V:V = 1:1). The mixture was refluxed for 1 h and then cooled to room temperature. Single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation within a few days. The crystals were isolated by filtration. Yield 32% (150 mg). Anal. Calc. for  $C_{17}H_{16}Cl_2FN_2O_5V$ : C, 43.52; H, 3.44; N, 5.97%. Found: C, 43.37; H, 3.53; N, 5.89%. IR (KBr;  $\nu_{max}$ , cm<sup>-1</sup>): 3440 w  $\nu(OH)$ , 1605 s  $\nu(C=N)$ , 1423 m  $\nu(C=C)$ , 1335 m  $\nu(Ar-O)$ , 1108 m  $\nu(C-O)$ , 947 s  $\nu(V=O)$ . UV-Vis data (EtOH;  $\lambda_{max}$ , nm): 263, 326, 405.

#### 2. 4. Synthesis of Complex 2

The hydrazone compound  $H_2L$  (0.10 mmol, 32.7 mg) and  $MoO_2(acac)_2$  (0.10 mmol, 32.6 mg) were mixed in the mixture solvent of methanol and ethanol (20 mL; V:V = 1:1). The mixture was refluxed for 1 h and then cooled to room temperature. Single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation within a few days. The crystals were isolated by filtration. Yield 41% (199 mg). Anal. Calc. for  $C_{30}H_{22}Cl_4F_2Mo_2N_4O_{10}$ : C, 37.14; H, 2.29; N, 5.77%. Found: C, 36.33; H, 2.22; N, 5.85%. IR (KBr;  $v_{max}$ , cm<sup>-1</sup>): 3406 w v(OH), 1612 s v(C=N), 1431 m v(C=C), 1350 s v(Ar=O), 1156 m v(C=O), 944 s, 923 s, 906 s, 876 m v(Mo=O). UV-Vis data (EtOH;  $\lambda_{max}$ , nm): 238, 292, 303, 407.

### 2. 5. X-ray Crystallography

X-ray diffraction was carried out at a Bruker APEX II CCD area diffractometer equipped with  $MoK_{\alpha}$  radiation

 $(\lambda = 0.71073 \text{ Å})$ . The collected data were reduced with SAINT,<sup>5</sup> and multi-scan absorption correction was performed using SADABS.6 The structures of the complexes were solved by direct method, and refined against  $F^2$  by full-matrix least-squares method using SHELXTL.7 All of the non-hydrogen atoms were refined anisotropically. The methanol hydrogen atom in complex 1, and the ethanol hydrogen atom in complex 2 were located from electronic density maps and refined isotropically, with O-H distances restrained to 0.85(1) Å, and with  $U_{iso}(H)$  restrained to  $1.5U_{eq}(O)$ . The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The C16-C17 and C15-O4 bonds were restrained to 1.50(1) and 1.45(1) Å, respectively. The crystallographic data and refinement parameters for the compounds are listed in Table 1.

The supplementary crystallographic data for 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1919016 and 1919017, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.ac.uk/conts/retrieving.html).

Table 1. Crystallographic and refinement data for the complexes

	1	2
Molecular formula	C <sub>17</sub> H <sub>16</sub> Cl <sub>2</sub> FN <sub>2</sub> O <sub>5</sub> V	C <sub>30</sub> H <sub>22</sub> Cl <sub>4</sub> F <sub>2</sub> Mo <sub>2</sub> N <sub>4</sub> O <sub>10</sub>
Formula weight	469.16	970.20
T, K	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	Cc	Pc
a, Å	19.683(2)	7.981(1)
b, Å	15.065(2)	13.610(1)
c, Å	7.633(2)	16.036(1)
$\beta$ , °	109.145(1)	90.887(2)
V, Å <sup>3</sup>	2138.2(7)	1741.6(3)
Z	4	2
$\rho_{calcd}$ , g cm <sup>-3</sup>	1.457	1.850
$\mu(\text{Mo}K_{\alpha}, \text{mm}^{-1})$	0.751	1.100
F(000)	952	960
Measured reflections	6136	9783
Unique reflections	3728	5992
Observed reflections $(I \ge 2\sigma(I))$	2522	5092
Parameters	257	473
Restraints	11	3
Goodness of fit on $F^2$	1.053	1.048
$R_1$ , $wR_2 (I \ge 2\sigma(I))^*$	0.0689, 0.1608	0.0486, 0.1211
$R_1$ , $wR_2$ (all data)*	0.1057, 0.1925	0.0630, 0.1412

<sup>\*</sup>  $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$ ,  $wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2]/\Sigma [w(F_0^2)^2]\}^{1/2}$ 

#### 2. 6. Catalytic Oxidation Experiment

Catalytic experiment was carried out in a 50 mL glass round-bottom flask fitted with a reflux condenser and placed in an oil bath at 353(2) K under continuous stirring. The catalytic oxidation experiment was carried out as follows: molybdenum(VI) complex (0.032 mmol)

was dissolved in 10 mL 1,2-dichloroethane. Then 10 mmol alkene was added to the reaction mixture and 30 mmol TBHP (*tert*-butyl hydroperoxide) was added. The reaction mixture was refluxed for 1 h. The reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

#### 3. Results and Discussion

#### 3. 1. Chemistry

The hydrazone compound  $H_2L$  was readily prepared by the condensation reaction of a 1:1 molar ratio of 4-fluorobenzohydrazide with 3,5-dichlorosalicylaldehyde in ethanol (Scheme 1). Complexes 1 and 2 were prepared by the reaction of the hydrazone compound with VO(a-cac)<sub>2</sub> and  $MoO_2(acac)_2$  in the mixture solvent of methanol and ethanol, respectively (Scheme 2). Elemental analyses of the compounds are in accordance with the molecular structures proposed by the X-ray analysis.

It is notable that very similar oxidovanadium complex as complex 1 was recently published. The only difference between the complexes is the presence of one MeOH

ligand in the present complex instead of EtOH ligand in the published one.

#### 3. 2. IR and UV Spectra

In the IR spectra of the hydrazone compound and the complexes, the weak and broad bands in the region 3400-3450 cm<sup>-1</sup> are assigned to the vibration of O-H bonds. The weak and sharp band located at 3329 cm<sup>-1</sup> of the hydrazone compound is assigned to the vibration of N-H bond. The position of the bands demonstrates that the N-H hydrazone protons are engaged in hydrogen bonding. The intense bands at 1653 cm<sup>-1</sup> of the hydrazone compound is generated by v(C=O) vibration, whereas the band at 1605 cm<sup>-1</sup> by the v(C=N) one. The non-observation of the v(C=O) bands, that present in the spectra of the hydrazone compound, indicates the enolization of the amide functionality upon coordination to the V- and Mo-centers. Instead strong bands at 1605 cm<sup>-1</sup> for 1 and 1612 cm<sup>-1</sup> for 2 are observed, which can be attributed to the stretching vibration of the C=N groups. The bands at 947 cm-1 for 1 is assigned to v(V=O), and the bands in the range of 876-944 cm<sup>-1</sup> for 2 are assigned to  $\nu(\text{Mo=O})$ .<sup>10</sup>

Scheme 1. The synthetic procedure of H<sub>2</sub>L.

$$H_{2}L + VO(acac)_{2} \longrightarrow CI \longrightarrow NOO$$

$$CI \longrightarrow NOO$$

**Scheme 2.** The synthetic procedure of the complexes.

In the electronic spectra of the complexes, the lowest energy transition band is observed at 405 nm for 1 and 407 nm for 2, which is attributed to LMCT transition as charge transfer from p-orbital on the lone-pair of ligands' oxygen atoms to the empty d-orbital of the metal atoms. The other strong bands in the range of 260-330 nm and at about 220 nm in the spectra of both complexes are similar to the absorption band in the spectrum of the hydrazone compound, so they are attributed to the intra-ligand  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  absorption peak of the ligands.

# 3. 3. Structure Description of Complex 1

Molecular structure of complex 1 is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. The coordination geometry around the V atom can be described as distorted octahedral with the tridentate hydrazone ligand coordinated in a meridional fashion, forming five- and six-membered chelate rings with bite angles of 73.7(2)° and 83.8(3)°, typical for this type of ligand systems.<sup>11</sup> The ethanolato ligand lies trans to the hydrazone imino N atom. The methanol O atom trans to the oxido group completes the distorted octahedral coordination sphere at a rather elongated distance of 2.355(6) Å due to the trans influence of the oxido group. 12 As expected, the hydrazone ligand coordinates in its doubly deprotonated enolate form which is consistent with the observed O2-C8 and N2-C8 bond lengths of 1.304(9) and 1.328(9) Å, respectively. This agrees with reported vanadium complexes containing the enolate form of this ligand type. 13 The dihedral angle between the two benzene rings of the hydrazone ligand is 4.4(5)°.

In the crystal packing structure of the complex, the complex molecules are linked by methanol molecules through intermolecular hydrogen bonds of O–H···N (Table 3), leading to the formation of one-dimensional chains along the *c*-axis direction (Fig. 2).

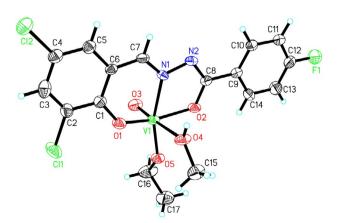
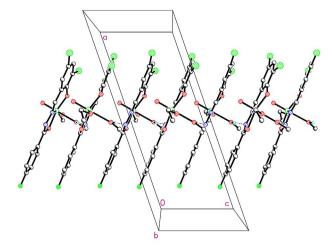


Fig. 1. Perspective view of complex 1 with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.



**Fig. 2.** Molecular packing structure of complex **1**, with hydrogen bonds shown as dotted lines.

# 3. 4. Structure Description of Complex 2

Molecular structure of complex 2 is shown in Fig. 3. Selected bond lengths and angles are listed in Table 2. The asymmetric unit of the complex contains two independent molecules, [MoO<sub>2</sub>L(OH<sub>2</sub>)] (A) and [MoO<sub>2</sub>L (EtOH)] (B). The coordination geometry around the Mo atoms in both molecules can be described as distorted octahedral with the tridentate hydrazone ligand coordinated in a meridional fashion, forming five- and six-membered chelate rings with bite angles of 71.3(3)° and 80.9(3)° for molecule A, and 70.9(3)° and 81.6(3)° for molecule B, typical for this type of ligand systems.<sup>14</sup> The oxido groups (O3 and O8) trans to the hydrazone imino N atoms form longer bonds with the Mo atoms than the other oxido groups (O4 and O9). The water and ethanol O atoms trans to the oxido groups (O4 and O9) completes the distorted octahedral coordination sphere at a rather elongated distances of 2.304(7) and 2.338(6) Å due to the *trans* influence of the oxido groups. As expected, the hydrazone ligands coordinate in their doubly deprotonated enolate form which is consistent with the observed O2-C8, N2-C8, and O7-C22, N4-C22 bond lengths of 1.307(10) and 1.319(11) Å, and 1.296(11) and 1.307(12) Å, respectively. This agrees with reported molybdenum complexes containing the enolate form of this ligand type. 15 The dihedral angles between the two benzene rings of the hydrazone ligand are 5.5(6)° for A and 1.2(6)° for B.

In the crystal packing structure of complex **2**, the complex molecules A and B are linked by intermolecular hydrogen bonds of O–H···O, O–H···N and C–H···O (Table 3), leading to the formation of 1D chains along the *a* axis. The chains are further linked *via* intermolecular hydrogen bonds of C–H···F (Table 3), to form 2D layers along the *ab* plane (Fig. 4).

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

1						
V1-O1	1.874(6)	V1-O2	1.923(5)			
V1-O3	1.576(6)	V1-O4	2.355(6)			
V1-O5	1.743(5)	V1-N1	2.135(5)			
O3-V1-O5	103.2(3)	O3-V1-O1	98.8(3)			
O5-V1-O1	101.7(3)	O3-V1-O2	98.8(3)			
O5-V1-O2	94.7(2)	O1-V1-O2	152.4(2)			
O3-V1-N1	94.8(3)	O5-V1-N1	160.0(3)			
O1-V1-N1	83.8(3)	O2-V1-N1	73.7(2)			
O3-V1-O4	174.9(2)	O5-V1-O4	81.8(2)			
O1-V1-O4	79.9(3)	O2-V1-O4	80.6(2)			
N1-V1-O4	80.2(2)					
2						
Mo1-O1	1.928(6)	Mo1-O2	2.022(6)			
Mo1-O3	1.704(6)	Mo1-O4	1.681(7)			
Mo1-O5	2.307(7)	Mo1-N1	2.256(7)			
Mo2-O6	1.930(6)	Mo2-O7	2.013(6)			
Mo2-O8	1.720(7)	Mo2-O9	1.673(7)			
Mo2-O10	2.343(6)	Mo2-N3	2.245(7)			
O4-Mo1-O3	105.2(3)	O4-Mo1-O1	99.9(3)			
O3-Mo1-O1	102.7(3)	O4-Mo1-O2	96.1(3)			
O3-Mo1-O2	98.0(3)	O1-Mo1-O2	149.5(3)			
O4-Mo1-N1	97.3(3)	O3-Mo1-N1	156.1(3)			
O1-Mo1-N1	80.9(3)	O2-Mo1-N1	71.3(3)			
O4-Mo1-O5	170.6(3)	O3-Mo1-O5	81.9(3)			
O1-Mo1-O5	84.3(3)	O2-Mo1-O5	76.5(3)			
N1-Mo1-O5	74.9(2)	O9-Mo2-O8	107.1(4)			
O9-Mo2-O6	95.0(4)	O8-Mo2-O6	106.4(3)			
O9-Mo2-O7	98.9(3)	O8-Mo2-O7	95.0(3)			
O6-Mo2-O7	149.7(3)	O9-Mo2-N3	94.4(3)			
O8-Mo2-N3	156.1(3)	O6-Mo2-N3	81.4(3)			
O7-Mo2-N3	70.9(3)	O9-Mo2-O10	170.6(3)			
O8-Mo2-O10	82.2(3)	O6-Mo2-O10	80.4(3)			
O7-Mo2-O10	81.6(2)	N3-Mo2-O10	76.8(3)			

## 3. 5. Catalytic Property of the Complexes

1-Butene, 1-pentene, 4-chloro-1-butene, phenylene 4-methylphenylene, 3-methylphenylene, 2-methylphenylene, nylene, 4-chlorophenylene, 3-chlorophenylene, and 2-chlorophenylene were used as the substrates. The catalytic oxidation results are given in Table 4. The conversions for both aliphatic and aromatic substrates are 100% for either the vanadium complex or the molybdenum complex.

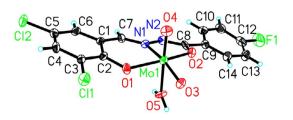
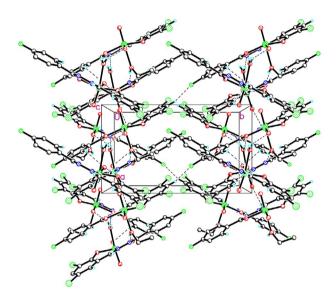


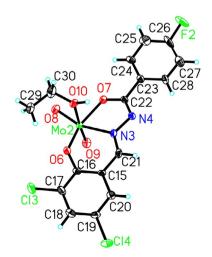
Table 3. Geometric parameters of hydrogen bonds for the complexes

D-H···A	D-H (Å)	HA (Å)	DA (Å) I	D-HA (°)
		1		
$O4-H4\cdots N2^{i}$	0.85(1)	2.01(2)	2.856(8)	172(6)
		2		
O10-H10···N2 <sup>ii</sup>	0.93	1.92	2.839(9)	169(6)
O5-H5BO8 <sup>iii</sup>	0.85	2.06	2.803(10)	145(5)
O5-H5AN4iv	0.85	1.97	2.806(10)	167(5)
C6-H6···O3 <sup>v</sup>	0.93	2.55	3.317(8)	140(6)
C7-H7···O3 <sup>v</sup>	0.93	2.50	3.314(8)	146(6)
C18-H18···F2 <sup>vi</sup>	0.93	2.39	3.273(8)	159(6)
C21-H21···O4 <sup>vi</sup>	i 0.93	2.46	3.144(8)	131(6)
C24-H24···O3 <sup>v</sup>	0.93	2.52	3.112(8)	122(6)

Symmetry codes:  ${}^{i}-x$ , 1-y, -z;  ${}^{ii}-x$ , 1-y, -1-z;  ${}^{iii}x$ , -1+y, z;  ${}^{iv}-x$ , 1-y, -z;  ${}^{v}x$ , -y,  ${}^{1/2}+z$ ;  ${}^{vi}-1+x$ , 1+y, z;  ${}^{vii}-1+x$ , y, z.



**Fig. 4.** Molecular packing structure of complex **2**, with hydrogen bonds shown as dotted lines.



 $\textbf{Fig. 3.} \ \ \text{Perspective view of complex 2} \ \ \text{with the atom labeling scheme.} \ \ \text{Thermal ellipsoids are drawn at the 30\% probability level}.$ 

High epoxide yields (83–89%) are obtained for aliphatic substrates for the molybdenum complex, while somewhat lower yields (76-85%) for the vanadium complex. As for the aromatic substrates, the epoxide yields (93–100%) are

**Table 4.** Details of the catalytic oxidation of olefins catalyzed by the complexes  $^{\star}$ 

Substrate	Product	Yields, %**		
		1	2	
	$\bigcirc$	78.7	85.1	
	<u></u>	76.1	83.3	
CI	cı	84.7	88.7	
	√o	94.9	96.5	
		93.1	93.6	
		95.5	94.9	
		93.7	95.8	
CI	CI	100	100	
CI	CI	100	100	
CI	CI	100	100	

<sup>\*</sup>The molar ratio of catalyst:substrate: TBHP is 1:300:1000. The reaction was performed in mixture of  $CH_3OH-CH_2Cl_2$  (v:v = 3:1). \*\*The yields (%) were measured relative to the starting substrate after 1 h.

higher than the aliphatic substrates for both complexes. The catalytic oxidation property of the molybdenum complex is comparable to those of the dioxidomolybdenum(-VI) complexes with phloroglucinol and resorcinol derived ligands <sup>16</sup> and with hydrazone ligands. <sup>17</sup> The catalytic oxidation property of the vanadium complex is also similar to those of the oxidovanadium(V) complexes with hydrazone ligands. <sup>18</sup>

#### 4. Conclusion

In summary, a new oxidovanadium(V) complex and a new dioxidomolybdenum(VI) complex were obtained from the hydrazone ligand  $N^2$ -(3,5-dichloro-2-hydroxybenzylidene)-4-fluorobenzohydrazide. The V and Mo atoms in the complexes are in octahedral coordination. The complexes have effective catalytic properties on oxidation of various olefins with tert-butyl hydroperoxide as the oxidant.

#### Acknowledgments

We acknowledge the special funds of key disciplines construction from Guangdong and Zhongshan cooperating. Guangdong Pharmaceutical University Cosmetics Talent Practice Teaching Base.

## 5. References

- (a) I. Gryca, K. Czerwinska, B. Machura, A. Chrobok, L. S. Shulpina, M. L. Kuznetsov, D. S. Nesterov, Y. N. Kozlov, A. J. L. Pombeiro, I. A. Varyan, G. B. Shulpin, *Inorg. Chem.* 2018, 57, 1824–1839; DOI:10.1021/acs.inorgchem.7b02684
   (b) I. S. Fomenko, A. L. Gushchin, L. S. Shulpina, N. S. Ikonnikov, P. A. Abramov, N. F. Romashev, A. S. Poryvaev, A. M.
  - nikov, P. A. Abramov, N. F. Romashev, A. S. Poryvaev, A. M. Sheveleva, A. S. Bogomyakov, N. Y. Shmelev, *New J. Chem.* **2018**, *42*, 16200–16210; **DOI:**10.1039/C8NJ03358G
  - (c) D.-L. Peng, *Transit. Met. Chem.* **2016**, *41*, 843–848; **DOI:**10.1007/s11243-016-0086-8
  - (d) M. Sutradhar, L. M. D. R. S. Martins, S. A. C. Carabineiro, M. F. C. G. da Silva, J. G. Buijnsters, J. L. Figueiredo, A. J. L. Pombeiro, *ChemCatChem* **2016**, *8*, 2254–2266;

DOI:10.1002/cctc.201600316

- (e) X. W. Zhu, *Russ. J. Coord. Chem.* **2018**, *44*, 421–424; **DOI**:10.1134/S1070328418070084
- (f) M. R. Maurya, C. Haldar, A. Kumar, M. L. Kuznetsov, F. Avecilla, J. C. Pessoa, *Dalton Trans.* **2013**, *42*, 11941–11962. **DOI:**10.1039/c3dt50469g
- (a) D. L. Peng, Russ. J. Coord. Chem. 2017, 43, 404–410;
   DOI:10.1134/S1070328417060045
  - (b) S. Gazi, W. K. H. Ng, R. Ganguly, A. M. P. Moeljadi, H. Hirao, *Chem. Sci.* **2015**, *6*, 7130–7142; **DOI**:10.1039/C5SC02923F

- (c) I. Sheikhsoaie, A. Rezaeffard, N. Monadi, S. Kaafi, *Polyhedron* 2009, 28, 733–738; DOI:10.1016/j.poly.2008.12.044
  (d) S. Rayati, N. Rafiee, A. Wojtczak, *Inorg. Chim. Acta* 2012, 386, 27–35. DOI:10.1016/j.ica.2012.02.005
- (a) H.-Y. Liu, Russ. J. Coord. Chem. 2013, 39, 583–587;
   DOI:10.1134/S1070328413070063
   (b) H. Y. Liu, G. W. Li, Z. L. Li, J. Y. Wu, Y. C. Cai, Russ. J. Coord. Chem. 2011, 37, 668–673;
   (c) H.-Y. Liu, J. Struct. Chem. 2014, 55, 134–138.
   DOI:10.1016/j.mineng.2013.10.001
- (a) H. Y. Liu, L. Q. Zhang, J. L. Lv, Russ. J. Coord. Chem. 2015, 41, 451–455; DOI:10.1134/S1070328415070052
   (b) H. Y. Liu, H. H. Yang, Y. X. Diao, Y. F. Ye, X. L. Zou, Russ. J. Coord. Chem. 2018, 44, 572–578.
   DOI:10.1134/S1070328418090063
- SMART (version 5.625) and SAINT (version 6.01). Madison (WI, USA): Bruker AXS Inc., 2007.
- G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector, Göttingen (Germany): University of Göttingen, 1996.
- G. M. Sheldrick, SHELXTL (version 5.1), Software Reference Manual, Madison (WI, USA): Bruker AXS, Inc., 1997.
- 8. L.-Y. He, X.-Y. Qiu, J.-Y. Cheng, S.-J. Liu, S.-M. Wu, *Polyhedron* **2018**, *156*, 105–110. **DOI:**10.1016/j.poly.2018.09.017
- L. Li, K. W. Lv, Y. T. Li, G.-F. Jiang, Y. Xin, L. Ye, Y. Zhang, H. Liu, C.-N. Shang, Z.-L. You, *Chinese J. Inorg. Chem.* 2017, 33, 905–912.
- 10. A. Sarkar, S. Pal, *Polyhedron* **2007**, *26*, 1205–1210. **DOI:**10.1016/j.poly.2006.10.012
- (a) M. Liang, N. Sun, D.-H. Zou, *Acta Chim. Slov.* 2018, 65, 964–969; DOI:10.17344/acsi.2018.4625
  (b) H. H. Monfared, S. Alavi, R. Bikas, M. Vahedpour, P. Mayer, *Polyhedron* 2010, 29, 3355–3362.
  DOI:10.1016/j.poly.2010.09.029
- (a) S. Guo, N. Sun, Y. Ding, A. Li, Y. Jiang, W. Zhai, Z. Li, D. Qu, Z. You, Z. Anorg. Allg. Chem. 2018, 644, 1172–1176;
   DOI:10.1002/zaac.201800060

- (b) J. Wang, D. Qu, J.-X. Lei, Z. You, J. Coord. Chem. **2016**, 70, 544–555. **DOI**:10.1080/00958972.2016.1262538
- (a) R. Bikas, M. Ghorbanloo, S. Jafari, V. Eigner, M. Dusek, Inorg. Chim. Acta 2016, 453, 78–85;

DOI:10.1016/j.ica.2016.07.058

(b) D. Sadhukhan, M. Maiti, E. Zangrando, S. Pathan, S. Mitra, A. Patel, *Polyhedron* **2014**, *69*, 1–9;

DOI:10.1016/j.poly.2013.11.007

- (c) M. R. Maurya, S. Agarwal, C. Bader, M. Ebel, D. Rehder, *Dalton Trans.* **2005**, 537–544. **DOI:**10.1039/b416292g
- (a) L. Xu, Y. Li, M. Duan, Y. Li, M. Han, J. Wu, Y. Wang, K. Dong, Z. You, *Polyhedron* 2019, 165, 138–142;

**DOI:**10.1016/j.poly.2019.03.016

(b) Y. Li, L. Xu, M. Duan, J. Wu, Y. Wang, K. Dong, M. Han, Z. You, *Inorg. Chem. Commun.* **2019**, *105*, 212–216;

DOI:10.1016/j.inoche.2019.05.011

(c) C. Wang, N. Xing, W. Feng, S. Guo, M. Liu, Y. Xu, Z. You, *Inorg. Chim. Acta* **2019**, 486, 625–635.

DOI:10.1016/j.ica.2018.11.020

- 15. (a) M. Ghorbanloo, R. Bikas, G. Malecki, *Inorg. Chim. Acta* **2016**, *445*, 8–16; **DOI:**10.1016/j.ica.2016.02.018
  - (b) V. Vrdoljak, B. Prugovecki, D. Matkovic-Calogovic, T. Hrenar, R. Dreos, P. Siega, *Cryst. Growth Des.* **2013**, *13*, 3773–3784; **DOI:**10.1021/cg400782c
  - (c) X.-W. Zhu, *Acta Chim. Slov.* **2018**, *65*, 939–945. **DOI:**10.17344/acsi.2018.4607
- R. Bikas, V. Lippolis, N. Noshiranzadeh, H. Farzaneh-Bonab,
   A. J. Blake, M. Siczek, H. Hosseini-Monfared, T. Lis, Eur. J. Inorg. Chem. 2017, 999–1006. DOI:10.1002/ejic.201601359
- 17. (a) Y.-M. Cui, L. Qiao, Y. Li, Q. Wang, W. Chen, W.-X. Yan, *Transition Met. Chem.* **2017**, *42*, 51–56;

**DOI:**10.1007/s11243-016-0105-9

- (b) H. H. Monfared, R. Bikas, P. Mayer, *Inorg. Chim. Acta* **2010**, *363*, 2574–2583. **DOI**:10.1016/j.ica.2010.04.046
- H. H. Monfared, S. Alavi, A. Farrokhi, M. Vahedpour, P. Mayer, *Polyhedron* 2011, *30*, 1842–1848.
   DOI:10.1016/j.poly.2011.04.043

#### Povzetek

Z ligandom N'-(3,5-dikloro-2-hidroksibenziliden)-4-fluorobenzohidrazidom ( $H_2L$ ) smo sintetizirali oksidovanadije-v(V) kompleks [VOL(OEt)(MeOH)] (1) in dioksidomolibdenov(VI) kompleks [MoO<sub>2</sub>L(OH<sub>2</sub>)]-[MoO<sub>2</sub>L(EtOH)] (2). Spojini smo okarakterizirali z IR, UV-Vis in NMR spektroskopijo ter rentgensko monokristalno analizo. Kompleksi so enojedrne zvrsti s kovinskim ionom v oktaedrični koordinacijo. Spojine smo testirali kot katalizatorje pri oksidacijah olefinov s t-butil hidroperoksidom kot oksidantom.



Except when otherwise noted, articles in this journal are published under the terms and conditions of the Creative Commons Attribution 4.0 International License