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Synthesis and Crystal Structures of Oxovanadium(V) and Dioxomolybdenum(VI) Complexes Derived From N'-(3-Bromo-2-hydroxybenzylidene)-2hydroxybenzohydrazide

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# Synthesis and Crystal Structures of Oxovanadium(V) and Dioxomolybdenum(VI) Complexes Derived From *N*'-(3-Bromo-2-hydroxybenzylidene)-2-hydroxybenzohydrazide

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*N'*-(3-Bromo-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H<sub>2</sub>BHH) reacts with [VO(acac)<sub>2</sub>] and [MoO<sub>2</sub>(acac)<sub>2</sub>], respectively, in methanol to give an oxovanadium(V) complex [VO(BHH)(OCH<sub>3</sub>)(CH<sub>3</sub>OH)] (1) and a dioxomolybdenum(VI) complex [MoO<sub>2</sub>(BHH)(CH<sub>3</sub>OH)] (2). Both complexes were characterized by elemental analysis, IR spectra, and single-crystal X-ray determination. The crystal of (1) crystallizes in the triclinic space group *P*I, with *a* = 10.248(1), *b* = 10.477(1), *c* = 18.133(1) Å,  $\alpha$  = 76.213(2)°,  $\beta$  = 74.068(2)°,  $\gamma$  = 78.076(2)°, *V* = 1797.2(2) Å<sup>3</sup>, *Z* = 4. The crystal of (2) crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*, with *a* = 7.411(1), *b* = 18.806(2), *c* = 12.632(1) Å,  $\beta$  = 104.451(3)°, *V* = 1704.9(3) Å<sup>3</sup>, *Z* = 4. The V atom in the oxovanadium(V) complex and the Mo atom in the dioxomolybdenum(VI) complex are all in octahedral coordination.

Keywords: Schiff base, oxovanadium(V) complex, dioxomolybdenum(VI) complex, crystal structure, coordination compound

## Introduction

Vanadium and molybdenum complexes have received considerable attention in coordination chemistry.<sup>[1–5]</sup> The interest of the study on the oxovanadium complexes stems from the discovery of two kinds of vanadium enzymes, vanadium-nitrogenases and vanadate-dependent haloperoxidases.<sup>[6,7]</sup> The insulin-like effect of vanadium complexes is another intriguing and promising feature that has further stimulated the vanadium coordination chemistry.<sup>[8-10]</sup> Molybdenum complexes have been intensively investigated as oxidation cata-lysts for variety of organic substrates,<sup>[11–13]</sup> particularly for sulfoxidation and epoxidation of olefins.<sup>[14–16]</sup> Schiff bases, especially those with hydrazone type, have attracted increasing interests in coordination chemistry. In the present paper, an oxovanadium(V) complex [VO(BHH)(OCH<sub>3</sub>)(CH<sub>3</sub>OH)] (1) and a dioxomolybdenum(VI) complex  $[MoO_2(BHH)]$  $(CH_3OH)$ ] (2), derived from the Schiff base ligand N'-(3-bromo-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H<sub>2</sub>BHH; Scheme 1), have been synthesized and characterized.



Sch 1. H<sub>2</sub>BHH.

## Experimental

#### Materials and Methods

3-Bromosalicylaldehyde and 2-hydroxybenzohydrazide were purchased from Alfa Aesar. [VO(acac)<sub>2</sub>] was prepared according to the literature method.<sup>[17]</sup> [MoO<sub>2</sub>(acac)<sub>2</sub>] was prepared according to the literature method.<sup>[18]</sup> All chemicals and solvents were of analytical grade and used as obtained. Microanalyses of the Schiff bases and the complexes were performed with a Vario EL III CHNOS elemental analyzer. Infrared spectra were recorded as KBr pellets with an FTS-40 spectrophotometer.

## Crystal Structure Determination

Data were collected on a Bruker SMART 1000 CCD area diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298(2) K. The data were corrected with the SADABS programs and refined on  $F^2$  with Siemens SHELXL software.<sup>[19,20]</sup> The structures were solved by

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direct methods and difference Fourier syntheses. All nonhydrogen atoms were refined anisotropically. Methanol hydrogen atoms were located from difference Fourier maps and refined isotropically, with O–H distances restrained to 0.85(1) Å. The remaining hydrogen atoms were placed in calculated positions and included in the last cycles of refinement. Crystal data and details of the data collection and refinement are listed in Table 1. Selected coordinate bond lengths and angles are listed in Table 2. Hydrogen bonding are given in Table 3.

## Preparation

H<sub>2</sub>BHH. A mixture of 3-bromosalicylaldehyde (2.01 g, 10 mmol) and 2-hydroxybenzohydrazide (1.52 g, 10 mmol) in 50 mL methanol was refluxed for 2 h. After reducing the solvent to 15 mL and cooling to room temperature, the precipitated colorless solid was filtered off, washed with methanol and dried. Recrystallization from methanol yielded pure product of H<sub>2</sub>BHH. Yield 2.77 g (83%). Anal. Calcd. for C<sub>14</sub>H<sub>11</sub>BrN<sub>2</sub>O<sub>3</sub> (%): C, 50.2; H, 3.3; N, 8.4. Found: C, 50.0; H, 3.4; N, 8.2. IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3378 (OH), 3235 (NH), 1659 (C=O), 1645 (C=N).

## $[VO(BHH)(OCH_3)(CH_3OH)](1)$

A stirred solution of  $H_2BHH$  (0.335 g, 1 mmol) in absolute methanol (20 mL) was mixed with [VO(acac)<sub>2</sub>] (0.265 g,

Table 1. Crystallographic data for complexes (1) and (2)

	(1)	(2)	
Formula	C <sub>16</sub> H <sub>16</sub> BrN <sub>2</sub> O <sub>6</sub> V	C <sub>15</sub> H <sub>13</sub> BrMoN <sub>2</sub> O <sub>6</sub>	
Formula weight	463.2	493.1	
Crystal system	triclinic	monoclinic	
Space group	$P\overline{1}$	$P2_1/c$	
<i>a</i> [Å]	10.248(1)	7.411(1)	
<i>b</i> [Å]	10.477(1)	18.806(2)	
c [Å]	18.133(1)	12.632(1)	
α [°]	76.213(2)	90	
$\beta$ [°]	74.068(2)	104.451(3)	
γ [°]	78.076(2)	90	
$V[Å^3]$	1797.2(2)	1704.9(3)	
Ζ	4	4	
$T[\mathbf{K}]$	298(2)	298(2)	
λ [Å]	0.71073	0.71073	
$\rho_{\rm calcd.} [\rm g \ cm^{-3}]$	1.712	1.921	
$\mu [\mathrm{mm}^{-1}]$	2.811	3.147	
Measured reflections	16866	16064	
Independent reflections	6789	3252	
Observed reflections	5229	2822	
$(I > 2\sigma(I))$			
R <sub>int</sub>	0.0309	0.0343	
$R_1^a$	0.0425	0.0303	
$wR_2^{b}$	0.1069	0.0748	
GOF on $F^2$	1.060	1.071	

 $\overline{{}^{a}R_{1} = \sum(||F_{o}| - |F_{c}||)/\sum|F_{o}|}, {}^{b}wR_{2} = \{\sum[w(F_{o}^{2} - F_{c}^{2})^{2}]/\sum[w(F_{o}^{2})^{2}]\}^{1/2}, w_{(1)} = 1/[\sigma^{2}(F_{o}^{2}) + (0.0515P)^{2} + 1.9422P], w_{(2)} = 1/[\sigma^{2}(F_{o}^{2}) + (0.0352P)^{2} + 2.1108P], where P = (F_{o}^{2} + 2F_{c}^{2})/3.$ 

**Table 2.** Selected bond lengths (Å) and angles ( $^{\circ}$ ) for the complexes (1) and (2)

(1)			
V1-O1	1.863(2)	V1-O2	1.953(3)
V1-O4	1.764(3)	V1-O5	2.404(3)
V1-O6	1.583(3)	V1-N1	2.098(3)
V2-O7	1.868(3)	V2-O8	1.958(3)
V2-O11	1.761(3)	V2-O12	1.569(3)
V2-O10	2.329(3)	V2-N3	2.130(3)
O6-V1-O4	102.1(1)	O6-V1-O1	98.8(1)
O4-V1-O1	104.5(1)	O6-V1-O2	103.1(1)
O4-V1-O2	90.5(1)	O1-V1-O2	150.3(1)
O6-V1-N1	93.5(1)	O4-V1-N1	160.8(1)
O1-V1-N1	84.0(1)	O2-V1-N1	74.8(1)
O6-V1-O5	170.0(1)	O4-V1-O5	87.6(1)
O1-V1-O5	75.7(1)	O2-V1-O5	79.5(1)
N1-V1-O5	77.7(1)	O12-V2-O11	104.2(1)
O12-V2-O7	99.2(1)	O11-V2-O7	100.8(1)
O12-V2-O8	98.3(1)	O11-V2-O8	94.8(1)
O7-V2-O8	152.9(1)	O12-V2-N3	97.4(1)
O11-V2-N3	157.2(1)	O7-V2-N3	82.5(1)
O8-V2-N3	74.8(1)	O12-V2-O10	174.8(1)
O11-V2-O10	81.0(1)	O7-V2-O10	80.3(1)
O8-V2-O10	80.4(1)	N3-V2-O10	77.3(1)
(2)			
Mo1-O1	1.912(2)	Mo1-O2	2.009(2)
Mo1-O4	1.696(3)	Mo1-O5	1.699(2)
Mo1-O6	2.361(3)	Mo1-N1	2.239(2)
O4-Mo1-O5	105.7(1)	O4-Mo1-O1	100.2(1)
O5-Mo1-O1	102.4(1)	O4-Mo1-O2	95.2(1)
O5-Mo1-O2	97.6(1)	O1-Mo1-O2	150.2(1)
O4-Mo1-N1	96.2(1)	O5-Mo1-N1	156.7(1)
O1-Mo1-N1	81.0(1)	O2-Mo1-N1	72.1(1)
O4-Mo1-O6	170.6(1)	O5-Mo1-O6	82.8(1)
O1-Mo1-O6	81.5(1)	O2-Mo1-O6	79.4(1)
N1-Mo1-O6	74.9(1)		

1 mmol), and the resulting reaction mixture was refluxed on a water bath for 1 h, and then cooled to room temperature, yielding a deep brown solution. The solution was stand still at ambient temperature to slow evaporation of the solvent, yielding brown crystals of (1). Yield 0.213 g (46%). Anal. Calcd. for C<sub>16</sub>H<sub>16</sub>BrN<sub>2</sub>O<sub>6</sub>V (%): C, 41.5; H, 3.5; N, 6.0. Found: C, 41.3; H, 3.4; N, 6.2. IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3359 (OH), 1616 (C=N), 1346 (C–O, enolic), 1241 (C–O, phenolate), 1061 (N–N), 980 (V=O), 626, 594, 473 (V–O, V–N).

## $[MoO_2(BHH)(CH_3OH)] (2)$

A stirred solution of H<sub>2</sub>BHH (0.335 g, 1 mmol) in absolute methanol (20 mL) was mixed with [MoO<sub>2</sub>(acac)<sub>2</sub>] (0.326 g, 1 mmol), and the resulting reaction mixture was refluxed on a water bath for 1 h, and then cooled to room temperature, yielding a yellow solution. The solution was stand still at ambient temperature to slow evaporation of the solvent, yielding orange crystals of (2). Yield 0.270 g (55%). Anal. Calcd. for C<sub>15</sub>H<sub>13</sub>BrMoN<sub>2</sub>O<sub>6</sub> (%): C, 36.5; H, 2.7; N, 5.7. Found: C, 36.6; H, 2.8; N, 5.6. IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3373 (OH), 1620 (C=N), 1350 (C-O, enolic), 1250 (C-O, phenolate), 1060 (N-N), 923 (Mo=O), 599, 466 (Mo-O, Mo-N).

D–H···A	<i>d</i> ( <i>D</i> –H) (Å)	$d(\mathbf{H}\cdots A)(\mathbf{\mathring{A}})$	$d(D\cdots A)$ (Å)	Angle( $D$ -H···A) (°)
(1)				
O5–H5····O9 <sup>i</sup>	0.85(1)	2.04(2)	2.860(4)	163(5)
O10–H10…O3 <sup>ii</sup>	0.85(1)	1.92(1)	2.758(4)	171(6)
O9–H9…N4	0.82	1.85	2.570(4)	146
O3–H3…N2	0.82	1.86	2.588(4)	147
(2)				
06–H6…O3 <sup>iii</sup>	0.85(1)	1.95(1)	2.786(3)	171(5)
O3–H3…N2	0.82	1.87	2.597(3)	146

Table 3. Hydrogen bonding for complexes (1) and (2)

Symmetry codes: (i) x, -1 + y, z; (ii) 1 + x, y, z; (iii) -x, 1 - y, 2 - z.

## **Results and Discussion**

An overview of the two complexes is shown in Scheme 2. Reaction between equimolar quantities of H<sub>2</sub>BHH with [VO (acac)<sub>2</sub>] and [MoO<sub>2</sub>(acac)<sub>2</sub>], respectively, in absolute methanol, afforded complexes (1) and (2). The ligand BHH adopts enolic tautomeric form on complexation. On aerial oxidation in methanol, the V<sup>IV</sup> atom in VO(acac)<sub>2</sub> is changed to V<sup>V</sup> in complex (1).



Sch 2.  $[VO(BHH)(OCH_3)(CH_3OH)]$  and  $[MoO_2(BHH)(CH_3OH)]$ .

## Structure Description

## $[VO(BHH)(OCH_3)(CH_3OH)](1)$

The crystal structure of (1) with atom numbering scheme is shown in Figure 1. The asymmetric unit of the compound contains two independent molecules. Ligands BHH form five-membered and six-membered chelate rings with bite angles of  $74.8(1)^{\circ}$  and  $84.0(1)^{\circ}$  for V1 molecule, and  $74.8(1)^{\circ}$ and 82.5(1)° for V2 molecule, with the V atoms. The V atoms are in distorted octahedral O<sub>5</sub>N coordination spheres. The phenolate O, imine N, and enolic O atoms of BHH, and one methoxy O atom constitute the equatorial plane, with mean deviations of 0.065 Å for V1 molecule and 0.028 Å for V2 molecule. The two axial positions are occupied by one oxo O atom and one methanol O atom. The displacement of the V atoms from the equatorial planes toward the axial oxo groups are 0.316(2) Å for V1 molecule and 0.334(2) Å for V2 molecule. The *cis* bond angles are in the range  $74.8(1)-104.5(1)^{\circ}$ , and the *trans* bond angles are within  $150.3(1)-174.8(1)^{\circ}$ . The V-O and V-N bond lengths in the complex are comparable with the bond lengths reported for oxovanadium(V) complexes with similar ligands.<sup>[21,22]</sup> As commonly observed in analogous species, the elongated V–O<sub>methanol</sub> bonds *trans* to the oxo groups in the complex indicate weak coordination of the methanol ligands at the axial positions. In the crystal structure of the complex (Figure 2), molecules are stacked together by O–H···O hydrogen bonds, to form chains.

## $[MoO_2(BHH)(CH_3OH)](2)$

Molecular structure of (2) with atom numbering scheme is shown in Figure 3. The ligand BHH forms one five-membered and one six-membered chelate rings with bite angles of  $72.1(1)^{\circ}$  and  $81.0(1)^{\circ}$  with the Mo atom. The Mo atom is in distorted octahedral O<sub>5</sub>N coordination sphere. The phenolate O, imine N, and enolic O atoms of BHH, and one oxo O atom constitute the equatorial plane, with mean deviation of 0.042 Å. The two axial positions are occupied by one oxo O atom and one methoxy O atom. The displacement of the Mo atom from the equatorial plane towards the axial oxo group is 0.329(2) Å. The *cis* bond angles are in the range 72.1(1)- $105.7(1)^{\circ}$ , and the *trans* bond angles are within 150.2(1)-170.6(1)°. The Mo-O and Mo-N bond lengths in the complex are comparable with the bond lengths reported for dioxomolybdenum(VI) complexes with similar ligands.<sup>[23,24]</sup> As commonly observed in analogous species, the elongated Mo-Omethanol bond trans to the oxo group in the complex indicates weak coordination of the methanol ligand at the axial



Fig. 1. ORTEP plots (30% probability level) and numbering scheme for (1). Hydrogen bonds are indicated by dashed lines.



**Fig. 2.** Molecular packing diagram for (1), viewed along the *c* axis. Hydrogen bonds are indicated by dashed lines.

position. In the crystal structure of the complex (Figure 4), molecules are stacked together by  $O-H\cdots O$  hydrogen bonds, to form dimers.

#### **IR Spectra**

The weak and broad bands in the region 3320–3400 cm<sup>-1</sup> of the Schiff base and the complexes are assigned to the  $\nu$ (O–H) vibrations. The  $\nu$ (C=O) vibration at 1659 cm<sup>-1</sup> and the sharp  $\nu$ (NH) vibration of 3235 cm<sup>-1</sup> for H<sub>2</sub>BHH are



**Fig. 3.** ORTEP plots (30% probability level) and numbering scheme for (2). Hydrogen bond is indicated by a dashed line.



Fig. 4. Molecular packing diagram for (2), viewed along the *b* axis. Hydrogen bonds are indicated by dashed lines.

absent in the complexes, indicating the enolization of the amide functionality and subsequent proton replacement by metal atoms, which is accord with the results analyzed by the X-ray determination. The v(C-O)(enolic) of complexes (1) and (2) are appeared at 1346 and 1350 cm<sup>-1</sup>, respectively. The strong bands at 1616 cm<sup>-1</sup> in (1) and 1620 cm<sup>-1</sup> in (2) are assigned to the azomethine groups. The bands observed at 980 cm<sup>-1</sup> for (1) and 923 cm<sup>-1</sup> for (2) are assigned to the V=O and Mo=O stretches, respectively.

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## **Supplementary Material**

CCDC 919062 and 919063 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.

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