Synthesis and X-ray Crystal Structures of N'-(2-Hydroxy-5-Methoxybenzylidene)-4-Dimethylaminobenzohydra Zide and Its Oxovanadium(V) Complex with Catalytic Property¹

Y. Z. Wang^a, Y. Gao^a, Y. Q. Su^{b, *}, P. Wang^b, and C. Li^b

^aDepartment of Chemical Science & Technology, Kunming College, Kunming, 650031 P.R. China ^bFaculty of Chemistry & Chemical Engineering, Yunnan Normal University, Kunming, 650500 P.R. China *e-mail: yongging su@163.com

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Abstract—A new benzohydrazone compound N'-(2-hydroxy-5-methoxybenzylidene)-4-dimethylaminobenzohydrazide (H₂L) and its oxovanadium(V) complex [VOL(BHA)] · H₂O, where HBHA is benzohydroxamic acid, were prepared and structurally characterized by physic-chemical methods and single crystal X-ray diffraction. The benzohydrazone compound crystallizes in the monoclinic space group C2/c with a =35.5873(12), b = 10.4628(4), c = 18.6059(6) Å, $\beta = 109.499(1)^\circ$, V = 6530.4(4) Å³, Z = 16, $R_1 = 0.0603$, and $wR_2 = 0.1575$. The oxovanadium(V) complex crystallizes in the triclinic space group P1 with a = 7.4775(4), b = 9.7837(5), c = 17.7076(8) Å, $\alpha = 99.457(2)^\circ$, $\beta = 98.699(2)^\circ$, $\gamma = 101.429(2)^\circ$, V = 1229.7(1) Å³, Z = 2, $R_1 = 0.0431$, and $wR_2 = 0.0937$. X-ray structural analysis indicates that the benzohydrazone ligand L²⁻ coordinates to the V atom through the phenolate O, imino N, and enolic O atoms. The V atom in complex I is coordinated by one benzohydrazone ligand and one BHA ligand, as well as one oxo O atom, forming an octahedral coordination. The crystal structures of H₂L and I are stabilized by hydrogen bonds. Complex I is an effective catalyst for sulfoxidation.

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INTRODUCTION

Schiff base complexes of transition metals have attracted much attention in metallo-organic and coordination chemistry because of their interesting structures and diverse range of applications [1-4], especially for their catalytic properties [5-7]. Sulfoxides are widely used as drug intermediates in pharmaceutical industries, and also sulfinyl groups have been used as auxiliaries in a variety of highly diastereoselective carbon-carbon bond forming reactions. including the synthesis of α -branched amines, α and β -amino acids, aziridines, and amino phosphonic acids [8, 9]. Sulfoxidation catalyzed by complexes of transition metals, such as titanium, manganese, iron, molybdenum, and vanadium, have produced interesting results in the synthesis of various sulfoxides [10-12]. As a continuation to explore effective catalysts used in sulfoxidation, in the present paper, a new benzohydrazone compound N'-(2-hydroxy-5-methoxybenzylidene)-4-dimethylaminobenzohydrazide (H_2L) and its oxovanadium(V) complex $[VOL(BHA)] \cdot H_2O$ (I), where HBHA is benzohydroxamic acid, were prepared and investigated for their peroxidic oxidation on sulfides.



EXPERIMENTAL

All chemicals were of reagent grade and used as purchased. Microanalyses of C, H, N were performed on a PerkinElmer-2400 Series II CHN analyser. FT-IR spectra (4000–200 cm⁻¹) of the ligand and the complex were recorded on a PerkinElmer Spectrum RX I FT-IR system with solid KBr pellets. ¹H NMR spectra were recorded on Bruker Avance 200 spectrometer.

Synthesis of H_2L . Equimolar quantities of 5-methoxysalicylaldehyde (0.152 g, 1 mmol) and 4-dimethylaminobenzohydrazide (0.179 g, 1 mmol) were mixed in 50 mL methanol. The mixture was stirred at reflux for 30 min and the solvent was evaporated to give

¹ The article is published in the original.

colorless crystalline product of H_2L , which was used without further purification.

For $C_{17}H_{19}N_3O_3$				
anal. calcd., %:	C, 65.16;	H, 6.11;	N, 13.41.	
Found, %:	C, 65.02;	H, 6.19;	N, 13.54.	

Synthesis of complex I. H_2L (31.3 mg, 0.1 mmol) and benzohydroxamic acid (13.7 mg, 0.1 mmol) were dissolved in 15 mL methanol. The solution was then added dropwise to a 10 mL gently warmed methanol solution of VO(Acac)₂ (26.5 mg, 0.1 mmol). The mixture was refluxed for 30 min and cooled to room temperature. The resulting deep brown solution was filtered and left undisturbed. After a few days, brown block shaped X-ray diffraction quality single crystals were formed and isolated by filtration. The yield was 28.2 mg (53%).

For C₂₄H₂₅N₄O₇V

anal. caicd., %:	C, 54.14;	Н, 4.73;	N, 10.52.
Found, %:	C, 54.23;	H, 4.82;	N, 10.37.

X-ray crystallography. Diffraction quality single crystals of H₂L and complex I were mounted on a Broker AXS SMART diffractometer with a graphite monochromator and Mo K_{β} radiation ($\lambda = 0.71073$ Å). The crystallographic data collection was performed using multiscan technique at 298(2) K. Data collection and the unit cell refinement were performed using CrysAlisPRO software [13]. The structures of the compounds were solved by direct method procedures with SHELXS [14] and refined by full-matrix least squares based on F^2 with SHELXL [14]. The nonhydrogen atoms were refined with anisotropic factors. The amino H atoms in H₂L and the water H atoms in complex I were located in 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 positioned geometrically treated as riding on their parent atoms. The O(6)–C(24) methoxy group of H_2L is disordered over two sites, with occupancies of 0.475(3)and 0.525(3), respectively. The data collection and refinement parameters are listed in Table 1. Selected bond lengths and angles are given in Table 2. Geometric parameters of hydrogen bonds for compounds are in Table 3.

Supplementary material for structures H_2L and complex I has been deposited with the Cambridge Crystallographic Data Centre (nos. 901042 (H_2L), 901043 (I); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Catalytic oxidation. The oxovanadium complex (0.001 mol/L) and phenyl methyl sulfide (0.1 mol/L) were dissolved at room temperature in a mixture of CH₂Cl₂ and CH₃OH (6 : 4) together with 1,3,5-tri-

methoxybenzene (0.1 mol/L) as internal standard. The resulting solution was cooled to 283 K and H_2O_2 (35% w/w) added dropwise (0.125 M). An aliquot of the reaction solution (2.0 mL) was quenched with 5 mL of a stock 0.1 M solution of Na₂SO₃ at 60 min and 2 h and extracted with dichlormethane (three times 4 mL). From the collected organic phases, the solvent was removed under reduced pressure to complete dryness and the residue redissoived in deuterated chloroform (0.6 mL) and analyzed by ¹H NMR to determine the yields with reference to the internal standard 1,3,5-trimethoxybenzene.

RESULTS AND DISCUSSION

The condensation of 5-methoxysalicylaldehyde with 4-dimethylaminobenzohydrazide in methanol with 1 : 1 stoichiometric ratio gave H_2L . The benzohydrazone ligand reacts with VO(Acac)₂ in the presence of benzohydroxamic acid yielded the oxovanadium complex. Elemental analyses were found to be in good agreement with the formulae calculated from the X-ray determination.

The sharp absorption bands located at 3281 cm^{-1} in the infrared spectrum of H₂L and at 3332 cm^{-1} in the infrared spectrum of the complex are attributed to the N–H stretches. The broad and weak bands indicative of the v(O–H) vibrations of the hydroxyl groups of the ligand and water molecules are in the range 3350- 3480 cm^{-1} . The strong band observed at 1613 cm⁻¹ is attributed to the conjugated C=N–N=C moiety of the benzohydrazone ligand. The middle band at 970 cm^{-1} is assigned to the V=O stretch [15]. The bands due to v(V–O) and v(V–N) are occurred at 440, 533, and 598 cm⁻¹, respectively.

Figures 1 and 2 give perspective views of H_2L and the oxovanadium(V) complex. H_2L crystallizes in the monoclinic space group C2/c and complex I crystallizes in the triclinic space group $P\overline{1}$.

In the asymmetric unit of H_2L , there contains two independent molecules. In each of the molecules, there is an intramolecular O–H…N hydrogen bond, which contributes to the planarity of the benzene ring and the methylidene unit. The dihedral angle between the two benzene rings are $25.1(3)^{\circ}$ for one molecule and $64.7(3)^{\circ}$ for the other. Complex I, derived from H₂L and benzohydroxamic acid, is a mononuclear compound. The benzohydrazone ligand L²⁻ forms one five- and one six-membered chelate rings with bite angles of 74.77(8)° and 84.10(8)°. The benzohydroxamic acid ligand BHA- forms one five-membered chelate ring with bite angle of 74.86(7)°. The V atom is in a distorted octahedral O₅N coordination sphere. The phenolate O(l) atom, imine N(l) atom, and enolic O(2) atom of the benzohydrazone ligand L^{2-} , and the O(5) atom of the benzohydroxamic acid ligand BHA⁻ constitute the equatorial plane of the octahedral coordination. The axial positions of the octahedral coordi-

Table 1.	Crystal data	and structure	refinement	for H	I_2L and	complex I
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Demonster	Value			
Parameter	H ₂ L	Ι		
Formula weight	313.4	532.4		
Crystal system	Monoclinic	Triclinic		
Space group	C2/c	$P\overline{1}$		
Crystal color/shape	Colorless/block	Brown/block		
Unit cell dimensions:				
a, Å	35.5873(12)	7.4775(4)		
b, Å	10.4628(4)	9.7837(5)		
<i>c</i> , Å	18.6059(6)	17.7076(8)		
α , deg	90	99.457(2)		
β, deg	109.4990(10)	98.699(2)		
γ, deg	90	101.429(2)		
Volume, Å ³	6530.4(4)	1229.66(11)		
Ζ	16	2		
ρ_{calcd},gcm^{-3}	1.275	1.438		
Absorption coefficient, mm ⁻¹	0.089	0.455		
<i>F</i> (000)	2656	552		
θ Range for data collection, deg	2.23-25.00	2.17-25.50		
Reflections collected	32616	13531		
Independent reflections	5587	4562		
Observed reflections, $I > 2\sigma(I)$	3226	3048		
Restraints	31	4		
Parameters	447	337		
Max and min transmission	0.9850 and 0.9894	0.9105 and 0.9226		
Goodness-of-fit on F^2	1.031	1.032		
Final <i>R</i> indices, $I > 2\sigma(I)$	0.0603	0.0431		
<i>R</i> indices, all data	0.1575	0.0937		
Largest diff. peak and hole, $e \text{ Å}^{-3}$	0.421 and -0.351	0.217 and -0.312		

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Bond	d, Å	Bond	$d, \mathrm{\AA}$		
H ₂ L					
C(8)–N(1)	1.275(4)	N(1)–N(2)	1.371(4)		
N(2)-C(9)	1.362(4)	C(9)–O(2)	1.239(4)		
C(25)-N(40)	1.280(4)	N(4)–N(5)	1.381(4)		
N(5)-C(26)	1.364(4)	C(26)-O(5)	1.232(3)		
]		Į		
V(1)–O(1)	1.8520(19)	V(1)–O(2)	1.9315(19)		
V(1)–N(1)	2.079(2)	V(1)–O(4)	2.2440(19)		
V(1)–O(5)	1.8604(17)	V(1)–O(6)	1.5875(19)		
C(8)–N(1)	1.292(3)	N(1)–N(2)	1.390(3)		
N(2)-C(9)	1.299(3)	C(9)–O(2)	1.316(3)		
Angle	ω, deg	Angle	ω, deg		
	H	$_{2}L$			
C(8)N(1)N(2)	118.9(3)	N(1)N(2)C(9)	118.1(3)		
N(2)C(9)O(2)	120.7(3)	C(25)N(4)N(5)	118.6(3)		
N(4)N(5)C(26)	117.4(2)	N(5)C(26)O(5)	119.2(3)		
]		1		
O(6)V(1)O(1)	99.61(10)	O(6)V(1)O(5)	96.07(9)		
O(1)V(1)O(5)	107.15(8)	O(6)V(1)O(2)	101.65(10)		
O(1)V(1)O(2)	151.81(9)	O(5)V(1)O(2)	88.81(8)		
O(6)V(1)N(1)	98.15(9)	O(1)V(1)N(1)	84.10(8)		
O(5)V(1)N(1)	160.11(8)	O(2)V(1)N(1)	74.77(8)		
O(6)V(1)O(4)	170.67(9)	O(1)V(1)O(4)	81.34(8)		
O(5)V(1)O(4)	74.86(7)	O(2)V(1)O(4)	80.67(7)		
N(1)V(1)O(4)	91.17(7)	C(8)N(1)N(2)	115.9(2)		
N(1)N(2)C(9)	108.9(2)	N(2)C(9)O(2)	121.2(2)		

Table 2. Selected bond lengths and bond angles for H_2L and complex I

Table 3. Geometric parameters of hydrogen bonds for H_2L and complex I

D. HA	Ι	Angle				
D-IIA	D–H	Н…А	D···A	DHA, deg		
H ₂ L						
$N(2)-H(2)\cdots O(5)^{i}$	0.90(1)	1.98(2)	2.825(3)	155(3)		
N(5)-H(5)…O(2)	0.90(1)	2.09(2)	2.954(3)	162(3)		
$O(4) - H(4) \cdots N(4)$	0.82	1.86	2.579(4)	145		
O(1)-H(1)…N(1)	0.82	1.88	2.598(4)	145		
I						
O(7)-H(72)····O(4)	0.85(1)	2.05(2)	2.866(3)	163(3)		
O(7)-H(71)····O(3) ⁱⁱ	0.85(1)	2.07(2)	2.884(3)	161(3)		
N(4)-H(4)···O(7)	0.90(1)	1.89(2)	2.775(3)	167(3)		

* Symmetry codes: ${}^{i}x$, 1 - v, -1/2 + z; ${}^{ii} - 1 + x$, 1 + v, z.

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H ₂ L					
C(8)N(1)N(2)	118.9(3)	N(1)N(2)C(9)	118.1(3)		
N(2)C(9)O(2)	120.7(3)	C(25)N(4)N(5)	118.6(3)		
N(4)N(5)C(26)	117.4(2)	N(5)C(26)O(5)	119.2(3)		
]	[,		
O(6)V(1)O(1)	99.61(10)	O(6)V(1)O(5)	96.07(9)		
O(1)V(1)O(5)	107.15(8)	O(6)V(1)O(2)	101.65(10)		
O(1)V(1)O(2)	151.81(9)	O(5)V(1)O(2)	88.81(8)		
O(6)V(1)N(1)	98.15(9)	O(1)V(1)N(1)	84.10(8)		
O(5)V(1)N(1)	160.11(8)	O(2)V(1)N(1)	74.77(8)		
O(6)V(1)O(4)	170.67(9)	O(1)V(1)O(4)	81.34(8)		
O(5)V(1)O(4)	74.86(7)	O(2)V(1)O(4)	80.67(7)		
N(1)V(1)O(4)	91.17(7)	C(8)N(1)N(2)	115.9(2)		
N(1)N(2)C(9)	108.9(2)	N(2)C(9)O(2)	121.2(2)		

nation are occupied by the O(4) atom of the benzohydroxamic acid ligand and one oxo O(6) atom. The displacement of the V atom from the equatorial plane towards the axial oxo group is 0.289(1) Å. The cis bond angles are in the range $74.8(1)^{\circ}$ -107.2(1)°, and the trans bond angles are in the range $151.8(1)^{\circ}$ - $170.7(1)^{\circ}$, indicating the octahedral coordination is much distorted. The V-O and V-N bond lengths in the complex are similar to those observed in other similar oxovanadium(V) complexes with octahedral coordination [16–18]. In the benzohydrazone ligand of complex I, the dihedral angle between the two benzene rings is $7.3(3)^{\circ}$.

The coordination of H_2L to the V atom can be reflected by the changes of the corresponding bond lengths and angles (Table 2). The bond lengths of C(8)=N(1) and N(1)-N(2) in complex I are much longer than those observed in H₂L. However, the distance between atoms C(9) and N(2) in complex I is much shorter than those in H₂L, and the distance between atoms C(9) and O(2) in the complex is much longer than those in H_2L , indicating the enolisation of the N(2)-C(9)-O(2) group.

In the crystal structure of H₂L, benzohydrazone molecules are linked through intermolecular N-H-O hydrogen bonds, forming chains running along the z axis (Fig. 3). In the crystal structure of the oxovanadium complex, the complex molecules are linked by water molecules through intermolecular O-H-O hydrogen bonds, forming chains running along the *y* axis (Fig. 4).

The catalytic oxidation test of complex I on the oxidation of sulfide under homogeneous conditions in solution using methyl phenyl sulfide as a substrate is the following:





Fig. 1. Molecular structure with atomic numbering for H_2L . Hydrogen atoms which not related to hydrogen bonding (dashed lines) are omitted for clarity.



Fig. 2. Molecular structure with atomic numbering for complex I.

As oxidant hydrogen peroxide was used in a slight excess of 1.25 equivalents based on the sulfide substrate. Reactions were run with 1 mol % of catalyst based on the substrate at a temperature of 10°C. NMR techniques have been used to monitor the formation of the sulfoxides with 1,3,5-trimethoxybenzene as internal standard to determine the yields. The reaction was started by the addition of hydrogen peroxide. A control reaction under the same condition without any complex present leads to less than 1% sulfide conversion within 4 h. In the presence of the complex conversion of 85% of sulfide to sulfoxide within 60 min reaction time were observed. After about 2 h the con-

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version of a total amount of sulfide was complete. Under the given conditions no over oxidation to the sulfone could be detected. It can be seen that the complex has effective catalytic property for the sulfoxidation.

Thus, in the present work, a new benzohydrazone compound N'-(2-hydroxy-5-methoxybenzylidene)-4-dimethylaminobenzohydrazide and a new oxovanadium(V) complex derived from the benzohydrazone compound and benzohydroxamic acid have been successively prepared and structurally characterized. The benzohydrazone ligand coordinates to the V atom through the phenolate O, imino N, and enolic O atoms. The complex is an effective catalyst for the sulfoxidation reaction of sulfide to sulfoxide.

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Fig. 3. Molecular packing diagram of H₂L, viewed along the y axis. Hydrogen bonds are shown as dashed lines.

the x axis. Hydrogen bonds are shown as dashed lines.



