

2-羟基萘甲醛苯甲酰肼作配体的钼和钒 两个化合物的合成和晶体结构

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摘要: 2-羟基萘甲醛苯甲酰肼 (H_2L) 由 2-羟基萘甲醛和苯甲酰肼在乙醇溶液中制得。利用 H_2L 分别合成了钼和钒的配合物, $[MoO_2(EtOH)L](1)$ 和 $[VO(OMe)L(MeOH)](2)$, 并测定了它们的晶体结构。配合物 **1** 和 **2** 是类似的结构单元, 钼和钒都采取扭曲的八面体配位构型。

关键词: 2-羟基萘甲醛苯甲酰肼; 钼和钒; 合成和结构

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Synthesis and Structures of Molybdenum and Vanadium Two Complexes with 2-Hydroxy Naphthaldehyde Benzoylhydrazone Ligand (H_2L)

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Abstract: The new aroyl-hydrazone ligand, 2-Hydroxy naphthaldehyde benzoylhydrazone (H_2L), was prepared by the reaction of 2-Hydroxy naphthaldehyde and benzoylhydrazine in an ethanol solution. Two complexes, $[MoO_2(EtOH)L](1)$ and $[VO(OMe)L(MeOH)](2)$, based on the H_2L ligand have been synthesized and characterized by single crystal X-ray diffraction analysis. Complexes **1** and **2** exhibit analogous structural units, the metal atom in which has a distorted octahedral coordination geometry. CCDC: 298811 (**1**), 298810 (**2**).

Key words: 2-hydroxy naphthaldehyde benzoylhydrazone; molybdenum and vanadium; synthesis and structure

The coordination chemistry of molybdenum (VI) and vanadium has attracted much attention due to its recently discovered biochemical significance^[1-5], as well as for the involvement of Mo(VI) compound as catalysts in several industrial processes such as amoxidation of propene^[6], epoxidation of olefins^[7], olefin metathesis^[8] and isomerization of allylic alcohols^[9]. And the aroyl-hydrazone complexes have ever been

extensively studied. As a part of our expanded investigations on the molybdenum and vanadium complexes, we synthesized a new aroyl-hydrazone ligand (H_2L) with oxygen and nitrogen donor atoms. We report herein the synthesis and characterization of Mo and V complexes incorporating H_2L ligands, $[MoO_2(EtOH)L](1)$ and $[VO(OMe)L(MeOH)](2)$.

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1 Experimental

1.1 General procedures

MoO₂(acac)₂ and VO(acac)₂ were prepared according to the references^[10,11], respectively. The other materials were obtained from commercial suppliers and used without further purification.

1.2 Synthesis of naphthaldehyde benzoylhydrazone(H₂L)

The H₂L was prepared by the reaction of benzoylhydrazide (8.6 g, 0.05 mol) and naphthaldehyde (6.2 g, 0.05 mol) in absolute ethanol with the process of refluxing for 2 h. The resulting yellow compound was filtered, washed twice with ethanol, and dried in the air. M.p.: 220~222 °C. Yield: 9.50 g(64 %). Anal. calcd for C₁₈H₁₄N₂O₂(%): C, 74.40; H, 4.82; N, 9.64. Found(%): C, 74.57; H, 4.52; N, 9.60. IR(KBr pellet, cm⁻¹): 3415(s), 3176(m), 3053(m), 1644(s), 1624(m), 1604(s), 1577(s), 1493(m), 1469(s), 1413(m), 1332(s), 1291(s), 1242(m), 960(s), 817(s), 691(s), 531(m), 420(m).

1.3 Synthesis of complex [MoO₂(EtOH)L] (1)

To a solution of H₂L(0.293 g, 1 mmol) in 20 ml ethanol was dropped triethylamine (0.2 mL). The solution was then added to a mixture of MoO₂(acac)₂ (0.33 g, 1 mmol) in EtOH (10 mL), resulting in the red-orange precipitate immediately. The reaction mixture was further refluxed for 1.5 h. After being cooled slowly down to room temperature, the red-orange product was collected and filtrated, and then washed with ether and dried in air. Yield: 0.41 g (98 %, according to Mo). The crystal suitable for X-ray diffraction was obtained by dissolve the compound in ethanol and evaporated in the air at the room temperature. Anal. Calcd. for C₂₀H₁₈MoN₂O₅(%): C, 51.96; H,

3.92; N, 6.06. Found(%): C, 52.05; H, 3.60; N, 6.02. IR(KBr, cm⁻¹): (O=Mo=O) 912(m).

1.4 Synthesis of the complex [VO(OMe)L (MeOH)] (2)

To a cold solution of H₂L (0.145 g, 0.5 mmol) in methanol and CH₂Cl₂ (10 mL, 1:1) in ice bath was added ethylenediamine (0.030 mL). A solution of VO(acac)₂ (0.131 g, 0.5 mmol) in dichloromethane (15 mL) cooled by ice bath was added dropwise to the solution above. The color of the reaction mixture changed soon from yellow to dark green. The mixture was stirred for 2~3 h, and then was allowed to stand in refrigerator at 0 °C for two days. After being filtered, the filtrate was kept at room temperature for 3 days, resulting black crystals. Yield: 0.20 g (95 %, based on V). Anal. Calcd for C₂₀H₁₉N₂O₅V (%): C, 57.43; H, 4.58; N, 6.70. Found (%): C, 57.77; H, 4.15; N, 6.82. IR (KBr, cm⁻¹): (V=O) 975(s).

1.5 Structure determination

The determination of the unit cell and the data collection for the crystals of **1** and **2** were performed on a Siemens SMART CCD, and all of the data were collected using graphite-monochromatized MoKα radiation(λ = 0.071 073 nm) at 293(2) K. The data sets were corrected by the SADABS program^[12]. The structures were solved by patterson methods, and refined by full-matrix least-squares methods. The structural solution and refinement were carried out using the SHELX-97 software package^[13]. In any case, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were determined with theoretical calculation and refined isotropically. Crystal data and structure refinement parameters are listed in Table 1, and selected bond lengths and angles are given in Table 2-3.

CCDC: 298811 (**1**); 298810 (**2**).

Table 1 Crystal data and structure refinement for complexes **1** and **2**

Complex	1	2
Formula	C ₂₀ H ₁₈ MoN ₂ O ₅	C ₂₀ H ₁₉ N ₂ O ₅ V
Formula weight	462.30	418.31
Crystal size / mm	0.48×0.30×0.10	0.72×0.34×0.08
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / nm	0.787 04(2)	1.286 92(7)

Continued Table 1

b / nm	0.981 93(3)	0.794 54(4)
c / nm	1.262 360(10)	1.936 53(10)
$\alpha / (^{\circ})$	92.550(2)	90
$\beta / (^{\circ})$	93.263(2)	103.870(2)
$\gamma / (^{\circ})$	103.614(2)	90
V / nm^3	0.944 9(4)	1.922 4(17)
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.625	1.445
Z	2	4
μ / mm^{-1}	0.729	0.550
$F(000)$	468	864
T / K	293(2)	293(2)
$\lambda(\text{Mo } K\alpha) / \text{nm}$	0.071 073	0.071 073
$\theta_{\min}, \theta_{\max} / (^{\circ})$	1.62, 25.04	1.73, 25.07
Reflections collected	4 918	5 999
Unique reflections	3 317	3 374
Observed reflections [$I > 2\sigma(I)$]	2 851	2 367
Parameters	254	254
R_{int}	0.021 4	0.036 4
$(\Delta/\sigma)_{\max}$	0.000	0.000
GOF on F^2	1.031	1.027
Max / min $\Delta\rho_{\min} / (\text{e} \cdot \text{nm}^{-3})$	617/-554	486/-400
R^a	0.040 2	0.056 7
wR^b	0.106 2	0.143 8

$$^a R = \sum (|F_o| - |F_c|) / \sum |F_o|, ^b wR = \{ \sum w[(F_o^2 - F_c^2)^2] / \sum w[(F_o^2)^2] \}^{1/2}, w = 1 / [\sigma^2(F_o^2) + (AP)^2 + BP], P = (F_o^2 + 2F_c^2) / 3.$$

For **1**: $A = 0.0810$, $B = 0.7037$; for **2**: $A = 0.0989$, $B = 1.5908$.

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) for complex **1**

Mo(1)-O(5)	0.169 3(3)	Mo(1)-O(4)	0.169 8(3)	Mo(1)-O(1)	0.193 1(3)
Mo(1)-O(2)	0.201 2(3)	Mo(1)-N(2)	0.222 0(3)	Mo(1)-O(3)	0.234 8(3)
O(1)-C(18)	0.134 0(6)	O(2)-C(1)	0.131 9(5)	N(1)-C(1)	0.130 9(5)
N(1)-N(2)	0.140 4(5)	N(2)-C(8)	0.129 9(5)		
O(5)-Mo(1)-O(4)	106.10(18)	O(5)-Mo(1)-O(1)	99.37(16)	O(4)-Mo(1)-O(1)	103.25(15)
O(5)-Mo(1)-O(2)	96.06(15)	O(4)-Mo(1)-O(2)	97.19(14)	O(1)-Mo(1)-O(2)	149.73(13)
O(5)-Mo(1)-N(2)	95.17(15)	O(4)-Mo(1)-N(2)	157.17(15)	O(1)-Mo(1)-N(2)	80.86(12)
O(2)-Mo(1)-N(2)	71.91(12)	O(5)-Mo(1)-O(3)	169.12(15)	O(4)-Mo(1)-O(3)	84.29(13)
O(1)-Mo(1)-O(3)	80.94(13)	O(2)-Mo(1)-O(3)	79.13(12)	N(2)-Mo(1)-O(3)	74.09(11)

Symmetry transformation used to generate equivalent atoms: #1: x, y, z ; #2: $-x, -y, -z$.

Table 3 Selected bond lengths (nm) and angles ($^{\circ}$) for complex **2**

V-O(5)	0.158 3(3)	V-O(4)	0.176 1(3)	V-O(1)	0.186 2(3)
V-O(2)	0.195 5(3)	V-N(2)	0.210 8(3)	V-O(3)	0.232 3(3)
N(1)-C(1)	0.131 8(5)	N(1)-N(2)	0.139 7(4)	N(2)-C(8)	0.128 4(5)
C(1)-O(2)	0.130 2(4)	C(18)-O(1)	0.133 0(5)		

Continued Table 3

O(5)-V-O(4)	102.60(14)	O(5)-V-O(1)	98.92(15)	O(4)-V-O(1)	101.30(14)
O(5)-V-O(2)	98.06(15)	O(4)-V-O(2)	95.95(13)	O(1)-V-O(2)	152.45(12)
O(5)-V-N(2)	95.47(14)	O(4)-V-N(2)	160.71(13)	O(1)-V-N(2)	82.27(12)
O(2)-V-N(2)	74.64(11)	O(5)-V-O(3)	175.04(13)	O(4)-V-O(3)	81.60(12)
O(1)-V-O(3)	82.69(13)	O(2)-V-O(3)	78.75(12)	N(2)-V-O(3)	80.06(11)

Symmetry transformation used to generate equivalent atoms: #1: x, y, z ; #2: $-x+1/2, y+1/2, -z+1/2$; #3: $-x, -y, -z$; #4: $x-1/2, -y-1/2, z-1/2$.

2 Results and discussion

2.1 IR spectra

The IR spectrum of the ligand (H_2L) shows stretching bands at 1 644, 3 176 and 3 467 cm^{-1} , which should be attributed to C=O, naphthyl O-H and N-H bonds, respectively^[14-16]. However, a stretching vibration of naphthyl O-H at 3 176 cm^{-1} disappears in the two complexes, which indicate the PhO-H has been deprotonated and coordinated to the metals. The band of complex **1** at 912 cm^{-1} can be assigned to antisymmetric vibration of the O=Mo=O core^[3], and the band of complex **2** at 975 cm^{-1} is assigned to the vibration of V=O.

2.2 UV-Vis spectra

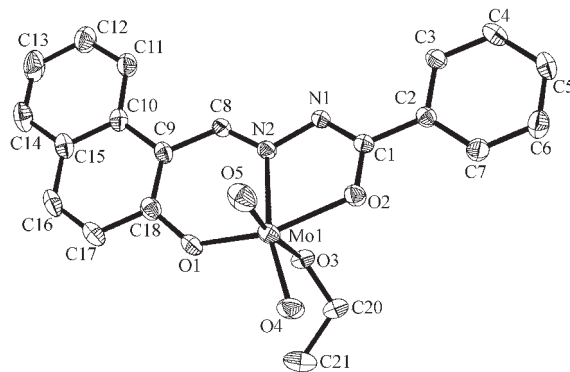
The electronic spectra were recorded in ethanol solution for the free ligand and the complexes **1** and **2**, in which all display two strong absorptions locating in the range of 208~261 and 312~362 nm, except a shoulder in the 425~440 nm region for the free ligand. The range of 208~261 nm can be attributed to $n-\pi^*$ transitions of the naphthyl ring and π conjugation^[14], and 312~362 nm to intraligand transitions. The bands in the region of 425~440 nm are feature peaks for the title complexes, and may be assigned to the ligand to metal charge transfer (LMCT) transitions^[3,17].

2.3 Crystal structures

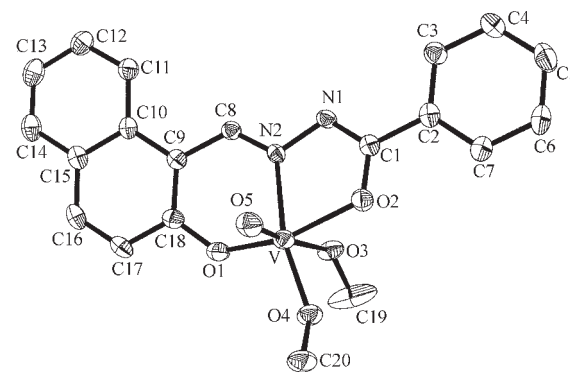
The naphthaldehyde benzoylhydrazone, H_2L , was used as a dianionic tridentate O and N donors ligand in this work. The molecular structures and the atom numbering schemes of the two complexes **1** and **2** are given in Figs.1 and 2, respectively.

The coordination geometries around the metal cores in the two complexes can be described as distorted octahedral. In complex **1**, the L ligand is bonded to the *cis*- MoO_2^{2+} ion in a planar fashion (in the xy -

plane) through the naphtholate oxygen O(1), the enolate O(2) and the imine nitrogen atom N(2). And an ethanol molecule completes the distorted octahedral coordination sphere. The Mo-O(3) bond [0.234 8(3) nm] is much more longer than that of other Mo-O bonds [0.169 3(3)~0.222 0(3) nm], indicating that the alcohol molecule is weakly bonded to the MoO_2^{2+} -core and this position can be a potential substitute-binding site. The C(1)-O(2) bond distance is 0.131 9(5) nm, which is nearer to a C-O single bond than to a C-O double bond distance. However, it is shorter than a classic C-O single bond (0.142 nm). The reason for



The solvent ethanol molecule is omitted for clarity
Fig.1 ORTEP draw of $[MoO_2(EtOH)L]$ (**1**) showing the atomic labeling scheme (30% probability ellipsoids)



The solvent methanol molecule is omitted for clarity
Fig.2 ORTEP draw of $[VO(OMe)L(MeOH)]$ (**2**) showing the atomic labeling scheme (30% probability ellipsoids)

such shortening distance may be attributed to electron delocalization in the coordinated ligand^[3]. The adjacent C(1)-N(1) bond length is 0.130 9(5) nm, which is very close to the normal C=N length^[3]. The N(2)-Mo-O (1) and N(2)-Mo-O(2) bond angles are 80.86(12) and 71.91(12)°, respectively. There are intramolecular hydrogen bonds between the OH group of the weak coordinated CH₃CH₂OH and the nitrogen atom of the hydrazone ligand (symmetry code: $-x-1, -y-1, -z$), show in Fig.3 and Table 4.

Complex **2** displays the analogous structure to that of the complex **1**. The VO₃⁺ core in **2** is coordi-

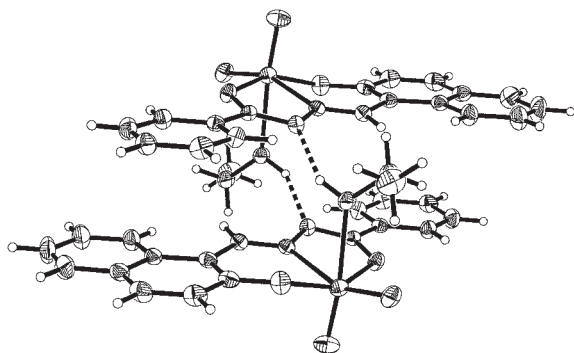


Fig.3 Packing diagram of complex **1** showing H-bonding as broken lines

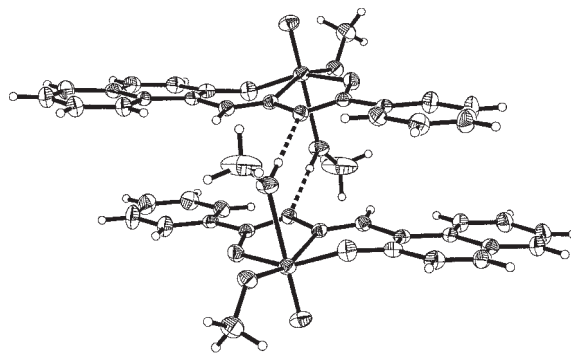


Fig.4 Packing diagram of complex **2** showing H-bonding as broken lines

Table 4 Hydrogen bonding data for complexes **1** and **2**

	D-H...A	Distance of D...A /nm	Angle of D-H-A /(°)
Complex 1	O(3)-H(3B)...N(1)#1 ^a	2.782(5)	149.8
Complex 2	O(3)-H(3B)...N(1)#1 ^b	2.800(4)	171.6

Symmetry transformation used to generate equivalent atoms: ^a: $-x-1, -y-1, -z$; ^b: $-x+1, -y+2, -z+1$.

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