ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 7, pp. 442–446. © Pleiades Publishing, Ltd., 2015.

Synthesis, Crystal Structure, and Preliminary Antibacterial Activity of Oxovanadium(V) Complex with Hydrazone Ligand[1]

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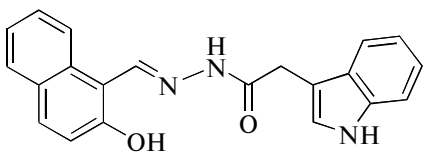
Received January 12, 2015

Abstract—A new mononuclear oxovanadium(V) complex, [VOL(OMe)(MeOH)] (**I**), where L is the dianionic form of (1*H*-indol-3-yl)acetic acid [1-(2-hydroxynaphthalen-1-yl)methylidene]hydrazine, has been synthesized and characterized by physico-chemical methods and single crystal X-ray determination, (CIF file CCDC no. 858861). The complex crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 10.117(1)$, $b = 10.609(2)$, $c = 11.454(2)$ Å, $\alpha = 99.228(2)°$, $\beta = 112.250(2)°$, $\gamma = 100.561(2)°$, $V = 1082.3(3)$ Å^3, $Z = 2$, $R_1 = 0.0512$, and $wR_2 = 0.1045$. The V atom in complex **I** is in an octahedral coordination. Thermal analysis and preliminary antibacterial activity of complex **I** were studied.

DOI: 10.1134/S1070328415070040

INTRODUCTION

Schiff base complexes play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [1–4]. Hydrazone compounds, bearing –CH=N–NH–C(O)– functional groups, are a special kind of Schiff bases, which have extensive biological properties [5–8]. In recent years, some metal complexes with hydrazone ligands have been reported [9, 10]. But when compared to the general Schiff base complexes, the number of hydrazone-type complexes is much less. Considering that vanadium ion plays important role in biological processes [11–13], the present work designed, synthesized and studied on the antibacterial activity of a new oxovanadium(V) complex [VOL(OMe)(MeOH)] (**I**) with the hydrazone ligand (1*H*-indol-3-yl)acetic acid [1-(2-hydroxynaphthalen-1-yl)methylidene]hydrazine (H_2L).



(H_2L)

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EXPERIMENTAL

Materials and measurements. Commercially available 2-hydroxy-1-naphthyaldehyde, (1*H*-indol-3-yl) acetic acid hydrazide and $VO(Acac)_2$ were purchased from Lancaster and used without further purification. Other solvents and reagents were made in China and were used as obtained. C, H and N elemental analyses were performed with a PerkinElmer 240C elemental analyser. IR spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region. Thermal analysis was carried out on PerkinElmer Pyris Diamond TG–DTA thermal analyses system at a temperature range of 30–1000°C.

Synthesis of H_2L. The Schiff base ligand H_2L was prepared by the condensation of 2-hydroxy-1-naphthaldehyde (1.0 mmol, 172 mg) with (1*H*-indol-3-yl)acetic acid hydrazide (1.0 mmol, 189 mg) in methanol (20 cm^3) at room temperature. The yield was 78%.

For $C_{21}H_{17}N_3O_2$			
anal. calcd., %:	C, 73.4;	H, 5.0;	N, 12.2.
Found, %:	C, 73.6;	H, 5.0;	N, 12.1.

Synthesis of complex I. A methanol solution (5 cm^3) of $VO(Acac)_2$ (0.1 mmol, 26.5 mg) was added to a methanol solution (10 cm^3) of H_2L (0.1 mmol, 34.3 mg) with continuous stirring. The mixture was

Table 1. Crystallographic data and structure refinement for complex **I**

Parameter	Value
Crystal shape/colour	Block/brown
Crystal size, mm	0.32 × 0.30 × 0.27
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	10.117(1)
b, Å	10.609(2)
c, Å	11.454(2)
α, deg	99.228(2)
β, deg	112.250(2)
γ, deg	100.561(2)
V, Å^3	1082.3(3)
Z	2
λ(MoK_α), Å	0.71073
μ(MoK_α), cm^{-1}	0.499
T_{min}/T_{max}	0.8567/0.8771
Measured reflections	8147
Independent reflections	4566
Observed reflections ($I \geq 2\sigma$, I)	3102
Number of refinement parameters	296
Restraints	2
Goodness of fit on F^2	1.035
R_1, wR_2 ($I \geq 2\sigma$, (I))*	0.0512, 0.1045
R_1, wR_2 (all data)*	0.0847, 0.1170

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o)^2 + (0.0449(F_o^2 + 2F_c^2)/3)^2 + 0.2273(F_o^2 + 2F_c^2)/3]^{-1}$.

stirred for 20 min at room temperature to give a deep brown solution. Upon keeping the solution in air for several days, brown block-like single crystals suitable for X-ray diffraction were deposited at the bottom of the vessel. The isolated product was washed three times with cold methanol and dried in a vacuum over anhydrous $CaCl_2$. The yield was 53%.

For $C_{23}H_{22}N_3O_5V$ ($Fw = 471.4$)

anal. calcd., %:	C, 58.6;	H, 4.7;	N, 8.9.
Found, %:	C, 58.4;	H, 4.6;	N, 9.0.

X-ray structure determination. Diffraction intensities for complex **I** were collected at 298(2) K using a Bruker APEX II area-detector with MoK_α radiation. The collected data were reduced using SAINT program [14], and multiscan absorption corrections were performed using SADABS program [15]. The structure was solved by direct methods and refined against F^2 by full-matrix least-squares methods using SHELXTL program [16]. All of the non-hydrogen atoms were refined anisotropically. H(5) and H(3) atoms were located from a difference Fourier map and refined isotropically with O–H and N–H distances restrained to 0.85(1) and 0.90(1) Å, respectively. The remaining hydrogen atoms in the complex were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

The supplementary crystallographic data for complex **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 858861; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam. ac.uk).

RESULTS AND DISCUSSION

Facile condensation of 2-hydroxy-1-naphthyaldehyde with (1*H*-indol-3-yl)acetic acid hydrazide in an 1 : 1 molar ratio furnished the ligand H_2L. Complex **I** was formed in methanol solution containing equimolar quantities of H_2L and $VO(Acac)_2$:

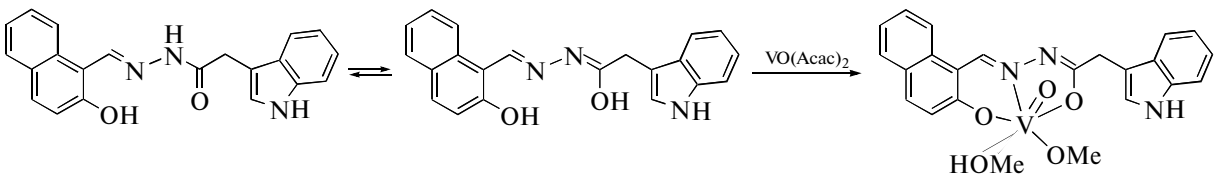

Table 2. Selected bond lengths (Å) and bond angles (deg) for **I**

Bond	*d*, Å	Bond	*d*, Å
V(1)–O(1)	1.853(2)	V(1)–O(2)	1.953(2)
V(1)–O(3)	1.574(2)	V(1)–O(4)	1.771(2)
V(1)–O(5)	2.466(2)	V(1)–N(1)	2.112(2)
Angle	ω, deg	Angle	ω, deg
O(3)V(1)O(4)	102.2(1)	O(3)V(1)O(1)	101.5(1)
O(4)V(1)O(1)	103.5(1)	O(3)V(1)O(2)	100.4(1)
O(4)V(1)O(2)	94.0(1)	O(1)V(1)O(2)	148.2(1)
O(3)V(1)N(1)	94.2(1)	O(4)V(1)N(1)	161.2(1)
O(1)V(1)N(1)	81.7(1)	O(2)V(1)N(1)	74.0(1)
O(3)V(1)O(5)	176.4(1)	O(4)V(1)O(5)	77.7(1)
O(1)V(1)O(5)	82.0(1)	O(2)V(1)O(5)	76.0(1)
N(1)V(1)O(5)	85.4(1)		

The crystals of **I** are soluble in most polar organic solvents, such as methanol, ethanol, DMF, and DMSO. Elemental analysis is in good agreement with the chemical formula proposed for the complex. In dry methanol, complex **I** behaves as a non-electrolyte as reflected in its Λ_M value of 31 Ω^{-1} cm^2 mol^{-1} [17].

Figure 1 gives perspective view of the complex together with the atomic labeling system. X-ray crystallography reveals that the compound is a mononuclear vanadium complex. The V atom in the complex is in an octahedral coordination, with the three donor atoms of L and one methanolato O atom defining the equatorial plane, and with one oxo O atom and one methanol O atom occupying the axial positions. The distance V(1)–O(3) is 1.574(2) Å, indicating it is a typical V=O bond. The coordinate bond lengths in the complex are comparable to those observed in mononuclear oxovanadium complexes with octahedral coordination [18–20]. The distortion of the octahedral coordination can be observed from the coordinate bond angles, ranging from 73.96(8)° to 103.50(8)° for the perpendicular angles, and from 148.25(9)° to 176.39(9)° for diagonal angles. The displacement of the V atom from the equatorial plane towards the axial oxo O atom is 0.328(1) Å. The formation of the coordinate bonds with the V atoms, together with the delocalization, lead to the planarity of the naphthylene ring and the V(1)–N(1)–N(2)–C(12)–O(2) chelate ring. The naphthylene ring forms dihedral angles of 18.2(3)° and 69.8(3)° with the V(1)–N(1)–N(2)–C(12)–O(2) chelate ring and the indole ring, respectively. In the crystal structure, adjacent two molecules are linked through intermolecular O(5)–H(5)···N(2) hydrogen bonds (O(5)–H(5) 0.85(1), H(5)···N(2)^{i} 1.88(1), O(5)···N(2)^{i} 2.727(3) Å, O(5)–H(5)···N(2)^{i} 177(3)°; symmetry code for i: $1-x, -y, 1-z$), forming a dimer. The dimers are further linked through intermolecular N(3)–H(3)···O(5) hydrogen bonds (N(3)–H(3) 0.90(1), H(3)···O(5)^{ii} 2.19(1), N(3)···O(5)^{ii} 3.084(3) Å, N(3)–H(3)···O(5)^{ii} 176(3)°;

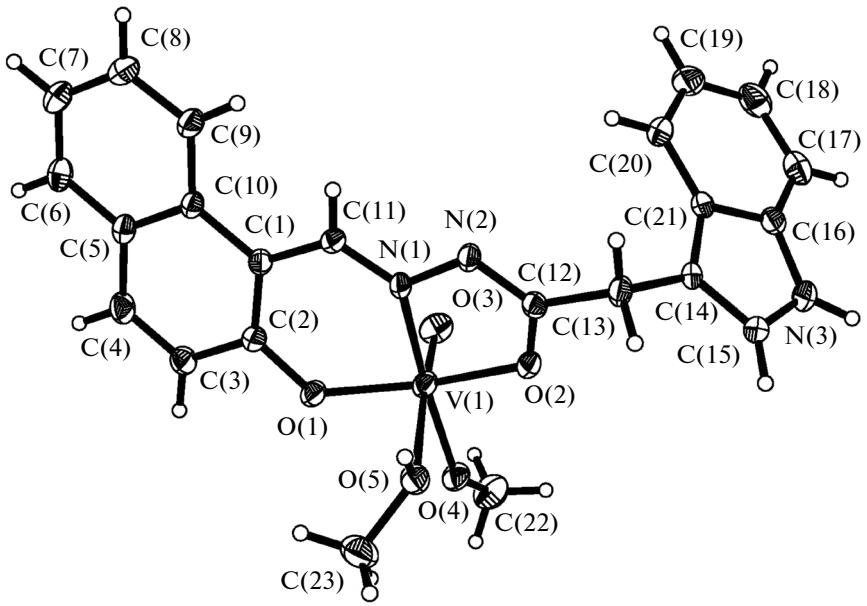

Fig. 1. The structure of complex **I**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

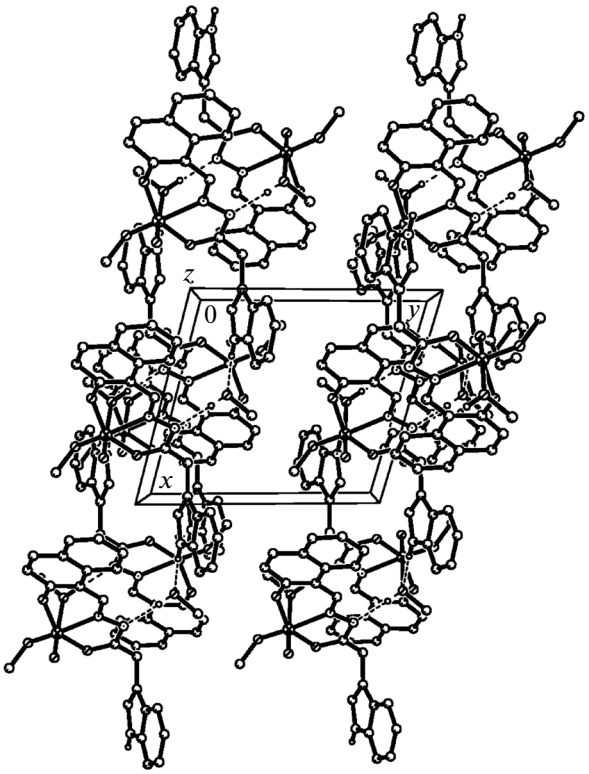

Fig. 2. Molecular packing of **I**, viewed down the *z* axis.

symmetry code for ii: $-x$, $-y$, $1 - z$), to form 1D chains running along the *x* axis, as shown in Fig. 2.

The medium and broad absorption centered at 3320 cm^{-1} is assigned to the vibration of the hydroxyl groups of the coordinate methanol molecule. The weak and sharp absorption at 3135 cm^{-1} is assigned to the vibration of the N–H group. The typical strong ν(C=O) absorption band of the free hydrazone ligand is absent in complex **I**, indicating the enolisation of the amide functionality group. The strong absorption band at 1605 cm^{-1} is assigned to the vibration of the azomethine group, ν(C=N) [21]. The band indicative of the V=O vibration is at 960 cm^{-1} [22].

Table 3. Antibacterial screening results

Compound	Zone of inhibition, mm			
	E. coli	*P. aeruginosa*	*B. subtilis*	*S. aureus*
H_2L	15 ± 3.3	4 ± 3.3	*	*
Complex **I**	20 ± 5.8	13 ± 3.3	5 ± 3.3	9 ± 3.3
Penicillin G	31 ± 3.3	27 ± 3.3	29 ± 5.8	25 ± 3.3
DMSO	–	–	–	–

* Indicates that the bacteria are resistant to the compound.

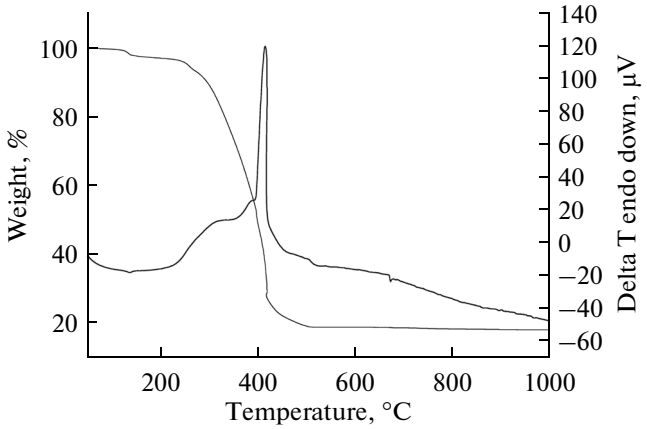

Fig. 3. TG–DTA curves of complex **I**.

Differential thermal (DTA) and thermal gravimetric analyses (TGA) were conducted to examine the stability of **I** (Fig. 3). The first step started at 120°C and completed at 165°C, which might due to the loss of the methanol ligand. The second step started at 240°C and completed at 513°C, corresponding to the loss of the ligands and the formation of the final product, V_2O_5. The total weight loss of 81.3% is close to the calculated value of 80.7%.

The antibacterial assay was performed according to the literature method [23]. Penicillin G was used as a standard drug. The zone of inhibition for the 5000 μg mL^{-1} test solutions (DMSO as the solvent) on the four bacteria, *Escherichia coli, Pseudomonas aeruginosa, Salmonella typhi* and *Staphylococcus aureus* is given in Table 3. The MIC values are given in Table 4. The results indicated that there was from weak to medium activity observed by H_2L against *E. coli* and *P. aeruginosa*, and negative activity against *B. subtilis* and *S. aureus*. It is noteworthy that the zones of inhibition areas are somewhat larger for the complex than the free hydrazone ligand. The trend in this work is accord with those reported earlier [24, 25], which have shown that metal complexes are more potent bactericidal than those of the corresponding Schiff bases. Complex **I** has much stronger activity against *E. coli* than the remaining bacteria strains.

Table 4. Antibacterial activities as MIC values (μg mL^{-1})

Compound	*E. coli*	*P. aeruginosa*	*B. subtilis*	*S. aureus*
H_2L	12.5	50	>100	>100
Complex **I**	6.25	12.5	50	50
Penicillin G	3.13	6.25	1.56	6.25

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