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TWO ISOMERIC STRUCTURES OF OXOVANADIUM(V) COMPLEXES
WITH HYDRAZONE AND 8-HYDROXYQUINOLINE LIGANDSG.-H. Sheng¹, X.-S. Cheng², Z.-L. You², H.-L. Zhu¹¹School of Life Sciences, Shandong University of Technology, Zibo, P. R. China

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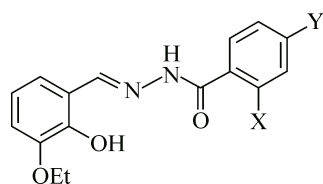
Two new oxovanadium(V) complexes [VOL¹(HQ)] (**1**) and [VOL²(HQ)] (**2**) are prepared by the reaction of [VO(acac)₂] (where acac = acetylacetonate), 8-hydroxyquinoline (HHQ) with 4-bromo-*N'*-(3-ethoxy-2-hydroxybenzylidene)benzohydrazide (H₂L¹) and 2-bromo-*N'*-(3-ethoxy-2-hydroxybenzylidene)benzohydrazide (H₂L²), respectively, in methanol. Crystal and molecular structures of the complexes are determined by elemental analysis, infrared spectroscopy, and single crystal X-ray diffraction. Complex **1** crystallizes in the monoclinic space group *P*2₁/*c*, with unit cell dimensions *a* = 12.5236(13) Å, *b* = 22.5260(15) Å, *c* = 16.7029(13) Å, β = 90.054(2)°, *V* = 4712.0(7) Å³, *Z* = 8, GOOF = 1.024, *R*₁ = 0.0586 and *wR*₂ = 0.0835. Complex **2** crystallizes in the triclinic space group *P*-1, with unit cell dimensions *a* = 7.4344(12) Å, *b* = 10.8677(16) Å, *c* = 14.687(2) Å, α = 85.327(5)°, β = 77.357(5)°, γ = 84.896(5)°, *V* = 1150.9(3) Å³, *Z* = 2, GOOF = 1.153, *R*₁ = 0.0917 and *wR*₂ = 0.3014. The V atoms are in the octahedral coordination. Thermal stability of the complexes is also studied.

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INTRODUCTION

Metal complexes with hydrazones have received particular attention in biological and medicinal chemistry [1–4]. In recent years, vanadium complexes have been reported to have interesting biological activities such as normalizing the high blood glucose levels and acting as models of haloperoxidases [5–9]. It is notable that Ara and co-workers reported that some binuclear vanadium(IV) complexes possess interesting urease inhibitory activities [10]. Aslam and co-workers reported that the Schiff bases of hydrazone type also possess urease inhibitory activities [11]. Recently, our research group has reported a few vanadium complexes with biological activities [12, 13]. 8-Hydroxyquinoline (HQ) is a widely known bidentate ligand in coordination chemistry [14–16], however, only two HQ coordinated oxovanadium complexes with hydrazone ligands have been reported so far [17, 18]. In the present paper, two new oxovanadium(V) complexes with hydrazone and HQ ligands, [VOL¹(HQ)] (**1**) and [VOL²(HQ)] (**2**) (H₂L¹ = 4-bromo-*N'*-(3-ethoxy-2-hydroxybenzylidene)benzohydrazide, H₂L² = 2-bromo-*N'*-(3-ethoxy-2-hydroxybenzylidene)benzohydrazide; Scheme 1), have been presented.



Scheme 1. Hydrazone ligands
 H_2L^1 : X=H, Y=Br; H_2L^2 : X=Br, Y=H

EXPERIMENTAL

Materials and measurements. Commercially available 3-ethoxysalicylaldehyde, 4-bromobenzohydrazide, and 2-bromobenzohydrazide were purchased from Sigma-Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. H_2L^1 and H_2L^2 were prepared according to the literature method [19, 20]. C, H, and N elemental analyses were performed with a Perkin-Elmer elemental analyzer. Infrared spectra were measured on a Nicolet AVATAR 360 spectrometer as KBr pellets in the range 4000–400 cm^{-1} . Thermal stability analysis was performed on a Perkin-Elmer Pyris Diamond TGA-DTA thermal analysis system.

Synthesis of [VOL¹(HQ)] (1). A methanolic solution (10 ml) of [VO(acac)₂] (0.1 mmol, 26.5 mg) was added to a methanolic solution (10 ml) of H_2L^1 (0.1 mmol, 36.3 mg) and HHQ (0.1 mmol, 14.5 mg) with stirring. The mixture was stirred for 30 min at room temperature to give a deep brown solution. The resulting solution was allowed to stand in the air for a few days. Brown block-shaped crystals suitable for X-ray single crystal diffraction formed at the bottom of the vessel. The isolated products were washed three times with cold ethanol and dried in the air. Yield: 73 %; Anal. Calcd. (%) for C₂₅H₁₉BrN₃O₅V: C 52.5, H 3.3, N 7.3. Found (%): C 52.3, H 3.3, N 7.5.

Synthesis of [VOL²(HQ)] (2). This complex was prepared according to the same method as that described for **1**, with H_2L^1 replaced by H_2L^2 . Yield: 67 %; Anal. Calcd. (%) for C₂₅H₁₉BrN₃O₅V: C 52.5, H 3.3, N 7.3. Found (%): C 52.3, H 3.4, N 7.4.

X-ray crystallography. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The collected data were reduced using the SAINT program [21], and multi-scan absorption corrections were performed using the SADABS program [22]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using SHELXTL [23]. All of the non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized positions and constrained to ride on their parent atoms. [VOL¹(HQ)]: C₂₅H₁₉BrN₃O₅V, $FW = 572.3$, $T = 298(2) \text{ K}$, crystal size 0.30×0.30×0.27 mm, monoclinic, $P2_1/c$, $a = 12.5236(13)$, $b = 22.5260(15)$, $c = 16.7029(13) \text{ \AA}$, $\beta = 90.054(2)^\circ$, $V = 4712.0(7) \text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 1.613 \text{ g/cm}^3$, $\mu(\text{MoK}_\alpha) = 2.160 \text{ mm}^{-1}$, a total of 45065 ($\theta_{\text{min/max}} = 2.18 / 25.16^\circ$), 8400 unique ($R_{\text{int}} = 0.1337$), 3793 ($F > 4\sigma_F$), 633 parameters. GOOF = 1.024, $R_1 = 0.0586$, $wR_2 = 0.0835$ ($I > 2\sigma_I$), $R_1 = 0.1817$, $wR_2 = 0.1132$ (all data), max / min diff. peak 0.451 / -0.449 $e/\text{\AA}^{-3}$. [VOL²(HQ)]: C₂₅H₁₉BrN₃O₅V, $FW = 572.3$, $T = 298(2) \text{ K}$, crystal size 0.18×0.18×0.13 mm, triclinic, $P-1$, $a = 7.4344(12)$, $b = 10.8677(16)$, $c = 14.687(2) \text{ \AA}$, $\alpha = 85.327(5)^\circ$, $\beta = 77.357(5)^\circ$, $\gamma = 84.896(5)^\circ$, $V = 1150.9(3) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.651 \text{ g/cm}^3$, $\mu(\text{MoK}_\alpha) = 2.210 \text{ mm}^{-1}$, a total of 10802 ($\theta_{\text{min/max}} = 2.29 / 25.25^\circ$), 4110 unique ($R_{\text{int}} = 0.0486$), 2790 ($F > 4\sigma_F$), 317 parameters. GOOF = 1.153, $R_1 = 0.0917$, $wR_2 = 0.3014$ ($I > 2\sigma_I$), $R_1 = 0.1323$, $wR_2 = 0.3228$ (all data), max / min diff. peak 1.127 / -0.546 $e/\text{\AA}^{-3}$. Selected bond lengths and angles are given in Table 1.

RESULTS AND DISCUSSION

General. The replacement of two acetylacetonate ligands of [VO(acac)₂] by hydrazone and hydroxamate ligands in methanol resulted in the formation of two structurally similar complexes. The complexes are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. Molar conductances of complexes **1** and **2** at the concentrations of 10⁻⁴ mol·L⁻¹ are 25 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ and 33 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, respectively, indicating that they are non-electrolytes [24].

Crystal structure description of the complexes. The molecular structures and atom numbering schemes of complexes **1** and **2** are shown in Figs. 1a, b and 2, respectively. The asymmetric unit of **1**

Table 1

Selected bond distances (Å) and angles (deg.) for the complexes

Bond lengths		Bond angles		Bond lengths	
1					
V(1)—O(1)	1.850(3)	V(1)—O(2)	1.955(3)	O(1)—V(1)—O(2)	153.36(14)
V(1)—O(4)	1.833(3)	V(1)—O(9)	1.583(3)	O(9)—V(1)—N(3)	177.29(17)
V(1)—N(1)	2.067(4)	V(1)—N(3)	2.333(5)	O(8)—V(2)—N(4)	159.05(17)
V(2)—O(5)	1.853(3)	V(2)—O(6)	1.956(3)	O(4)—V(1)—N(1)	159.07(16)
V(2)—O(8)	1.827(3)	V(2)—O(10)	1.585(3)	O(5)—V(2)—O(6)	153.42(14)
V(2)—N(4)	2.056(4)	V(2)—N(6)	2.327(4)	O(10)—V(2)—N(6)	176.84(17)
2					
V(1)—O(1)	1.854(8)	V(1)—O(2)	1.950(8)	O(1)—V(1)—O(2)	153.3(4)
V(1)—O(4)	1.862(8)	V(1)—O(5)	1.582(9)	O(4)—V(1)—N(1)	157.6(4)
V(1)—N(1)	2.087(9)	V(1)—N(3)	2.320(10)	O(5)—V(1)—N(3)	174.8(4)

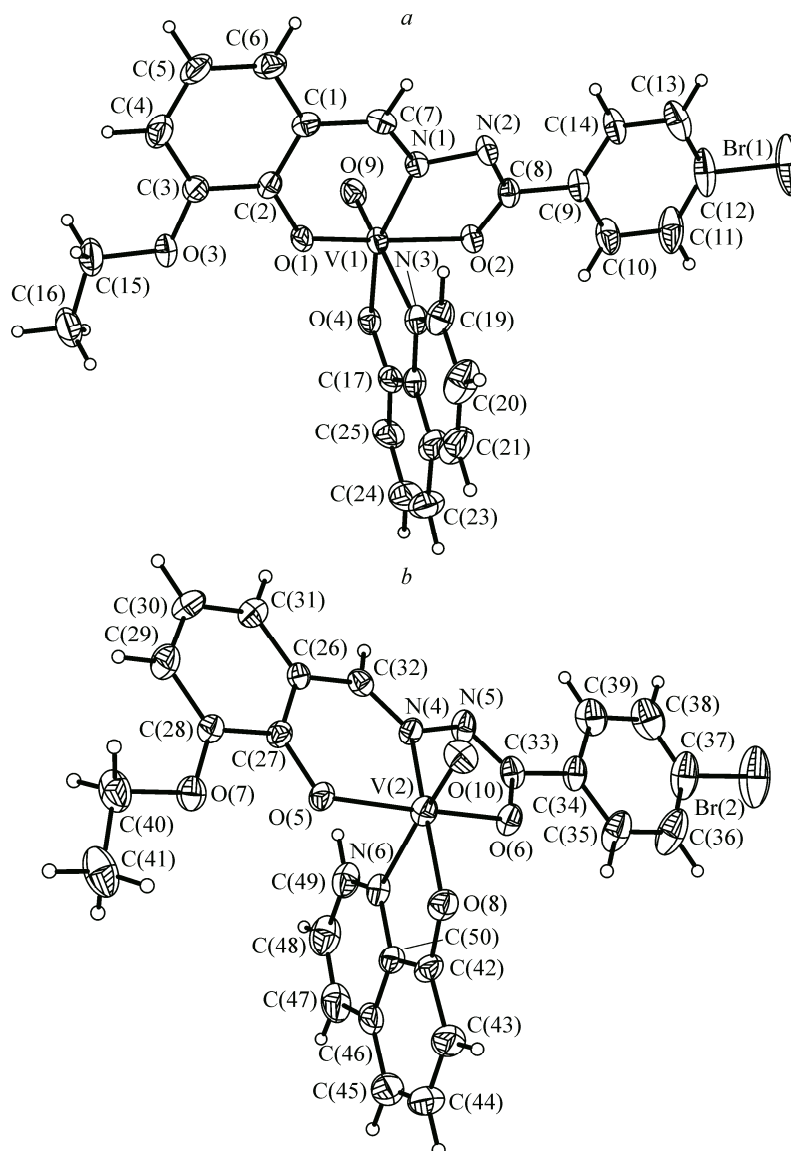


Fig. 1. ORTEP plot of the V1 (a) and V2 (b) molecule of **1**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30 % probability level

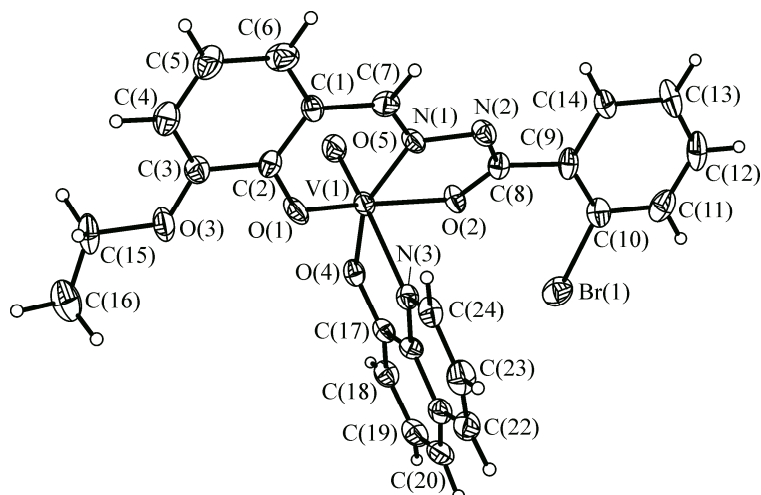


Fig. 2. ORTEP plot of the molecular structure of **2**.

Displacement ellipsoids of non-hydrogen atoms are drawn at the 30 % probability level

contains two independent molecules. The V atoms in the complexes are in the octahedral coordination, with three donor atoms of the hydrazone ligands and the hydroxy O atom of the HQ ligand defining the equatorial plane, and with one oxo O atom and the pyridine N atom of the HQ ligand occupying the axial positions. The distances between the V(1) and O(9), and V(2) and O(10) atoms in **1**, and V(1) and O(5) in **2** are 1.58 Å, indicating that they are typical V=O double bonds. The V—N_{pyridine} bonds in the complexes are significantly longer than the other coordinate bonds, yet, it is not uncommon for such complexes [17, 18]. In both complexes the bond lengths are comparable to each other, and also similar to those observed in the mononuclear oxovanadium(V) complexes with the octahedral coordination [17, 18]. The angular distortion in the octahedral environment around V comes from the five- and six-membered chelate rings taken by the hydrazone ligands. For the same reason, the *trans* angles significantly deviate from the ideal values of 180°. A distortion of the octahedral coordination can be observed from the coordinate bond angles, ranging from 74.88(14)° to 103.40(15)° for the perpendicular angles, and from 153.36(14)° to 177.29(17)° for the diagonal angles for **1**, and from 74.6(3)° to 107.5(4)° for the perpendicular angles, and from 157.6(4)° to 174.8(4)° for the diagonal angles for **2**. The displacement of the V atoms from the equatorial plane are 0.31 Å for **1** and 0.30 Å for **2**. The dihedral angles between the two benzene rings of the hydrazone ligands are 6.6(4)° and 6.4(4)° in **1** and 15.5(5)° in **2**.

IR spectra. Complexes **1** and **2** exhibit typical bands at 963 cm⁻¹ and 965 cm⁻¹, respectively, assigned to the V=O vibration. The bands due to ν_{C=O} were absent in the complexes, but new C—O stretches appeared at 1266 cm⁻¹ for **1** and **2**. This suggests the occurrence of *keto*-imine tautomerization of the ligands during complexation. The intense ν_{C=N} absorptions are observed at 1602 cm⁻¹ for **1** and **2**. Weak peaks in the low wavenumber region (400—650 cm⁻¹) may be attributed to V—O and V—N bonds in the complexes.

Thermal property. Differential thermal (DTA) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complexes under the air atmosphere and with the standard corundum crucible sample holder (Fig. 3, *a* for **1** and Fig. 3, *b* for **2**). The gas flow rate is 20.0 cm³·min⁻¹. The sample masses are 2.193 mg for **1** and 2.660 mg for **2**. The heating rate is 10 °/min. For **1**, the complex decomposed from 270 °C to 500 °C, corresponding to the loss of the hydrazone and HQ ligands and the formation of V₂O₅. The total observed weight loss of 86.0 % is close to the calculated value of 84.5 %. For **2**, the complex decomposed from 230 °C to 510 °C, corresponding to the loss of the hydrazone and HQ ligands and the formation of V₂O₅. The total observed weight loss of 85.7 % is close to the calculated value of 84.5 %.

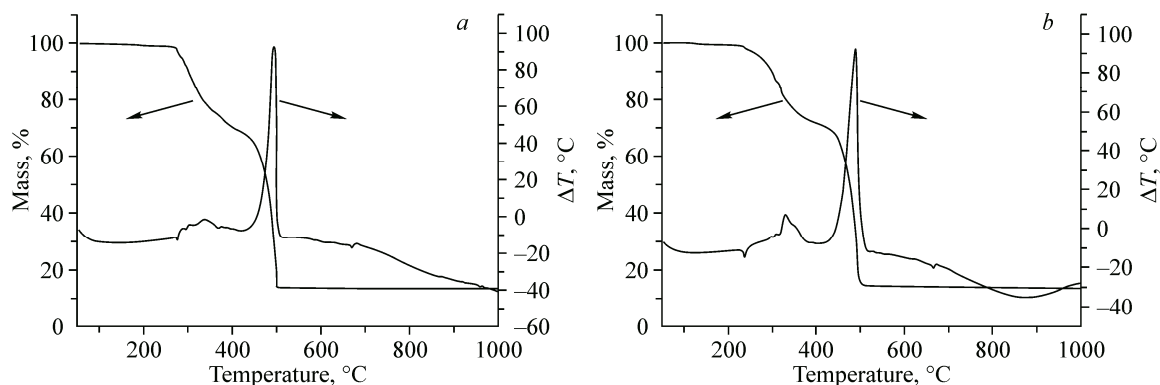


Fig. 3. DTA-TGA curve of **1** (a) and DTA-TGA curve of **2** (b)

CONCLUSIONS

In summary, two new 8-hydroxyquinoline coordinated oxovanadium(V) complexes with similar tridentate hydrazone ligands have been prepared and structurally characterized. The hydrazone ligands coordinate to the V atoms through the phenoalte O, imino N, and enolate O atoms. 8-Hydroxyquinoline coordinates to the V atom through the hydroxy O and pyridine N atoms. Thermal stability of the complexes was studied. The difference thermal properties (Figs. 3, a, b) point to the different structures of the compounds; there is no phase transformation (isomerization) on heating.

CCDC 979487 for **1** and CCDC 979488 for **2** contain the supplementary crystallographic data for these compounds. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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