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Synthesis, Characterization, and X-ray Crystal Structures of Oxovanadium(V) Complexes with Hydrazone and 8-Hydroxyquinoline Ligands[1]

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Abstract—Three new oxovanadium(V) complexes with the general formula $[VO(L)^n(HQ)]$ ($n = 1–3$) were prepared by the reaction of $[VO(Acac)_2]$ (Acac = acetylacetonate) and 8-hydroxyquinoline with similar benzohydrazide ligands in methanol. Crystal and molecular structures of the complexes were determined by elemental analysis, infrared and UV-Vis spectra and single crystal X-ray diffraction (CIF file CCDC nos. 1004087 (**I**), 1004088 (**II**), and 1004089 (**III**)). The V atoms are in octahedral coordination. Thermal stability of the complexes were studied.

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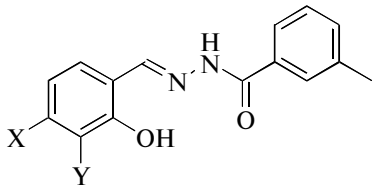
INTRODUCTION

Vanadium plays an important role in biological processes [1–3]. In human beings, vanadium complexes have shown promising activity for the treatment of diabetes [4, 5]. In recent years, a large number of vanadium complexes with various ligands have been prepared [6–10]. Among the complexes, those derived from hydrazones have been received particular attention in biological and medicinal chemistry [11–15]. 8-Hydroxyquinoline is a widely used bidentate ligand. As a continuation of the work to extend vanadium complexes, in the present paper, three new hydrazone oxovanadium(V) complexes $[VO(L^1)(HQ)]$ (**I**), $[VO(L^2)(HQ)]$ (**II**), and $[VO(L^3)(HQ)]$ (**III**) (H_2L^1 = *N*'-(2-hydroxybenzylidene)-3-methylbenzohydrazide, H_2L^2 = *N*'-(2-hydroxy-4-methoxybenzylidene)-3-methylbenzohydrazide, H_2L^3 = *N*'-(2-hydroxy-3-methoxybenzylidene)-3-methylbenzohydrazide), bearing 8-hydroxyquinoline (HHQ) ligands, have been presented. The hydrazone ligands are the following:



H_2L^1: X = Y = H; H_2L^2: X = OMe, Y = H;
H_2L^3 : X = H, Y = OMe

[1] The article is published in the original.

EXPERIMENTAL

Materials and measurements. Commercially available salicylaldehyde, 3-methoxysalicylaldehyde, 4-methoxysalicylaldehyde and 3-methylbenzohydrazide were purchased from Aldrich and used without further purification. C, H, and N elemental analyses were performed with a Perkin-Elmer elemental analyzer. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region. UV-Vis spectra were recorded on a Lambdar 900 spectrometer with acetonitrile as the solvent. Thermal stability analysis was performed on a PerkinElmer Pyris Diamond TG–DTA thermal analyses system.

Synthesis of the complexes. The three complexes were prepared by the similar method. Equimolar quantities (0.1 mmol each) of 3-methylbenzohydrazide and various aldehydes were reacted at room temperature in methanol (15 mL) for 30 min. Then, the solid of 8-hydoxyquinoline (0.1 mmol) and $[VO(Acac)_2]$ (0.1 mmol) were added to the mixture. The final mixture was further stirred for 30 min at room temperature to give a deep brown solution. The resulting solution was allowed to stand in air for a few days. Brown block-shaped crystals suitable for X-ray single crystal diffraction were formed at the bottom of the vessel. The isolated products were washed three

Table 1. Crystallographic data and refinement parameters for complexes **I**–**III**

Parameter	Value		
	I	**II**	**III**
Formula weight	463.3	493.4	493.4
Crystal color; habit	Brown; block	Brown; block	Brown; block
Crystal size, mm	0.22 × 0.21 × 0.17	0.20 × 0.17 × 0.17	0.32 × 0.27 × 0.26
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/n$	$P2_1/c$
Unit cell parameters:			
a, Å	13.071(1)	15.805(1)	8.006(1)
b, Å	14.476(1)	8.157(1)	31.065(3)
c, Å	22.918(2)	18.084(2)	9.341(1)
β, deg	90	100.512(2)	106.217(2)
V, Å^3	4336.4(5)	2292.2(3)	2230.6(3)
Z	8	4	4
ρ_{calcd}, g cm^{-3}	1.419	1.430	1.469
Temperature, K	298(2)	298(2)	298(2)
μ, mm^{-1}	0.494	0.475	0.488
F(000)	1904	1016	1016
Number of unique data	3857	4082	3979
Number of observed data ($I > 2\sigma(I)$)	2269	2414	2895
Number of parameters	290	309	309
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0763$, $wR_2 = 0.1307$	$R_1 = 0.0621$, $wR_2 = 0.1139$	$R_1 = 0.056$, $wR_2 = 0.1188$
R indices (all data)	$R_1 = 0.1404$, $wR_2 = 0.1592$	$R_1 = 0.1319$, $wR_2 = 0.1387$	$R_1 = 0.0868$, $wR_2 = 0.1308$
Goodness of fit on F^2	1.104	1.042	1.071
Highest peak and deepest hole, *e* Å^{-3}	0.441, –0.320	0.503, –0.338	0.469, –0.286

times with cold methanol and dried in air. The yields were 65 (**I**), 73 (**II**), 77% (**III**).

For $C_{24}H_{18}N_3O_4V$ (**I**)

anal. calcd., %: C, 62.21; H, 3.92; N, 9.07.

Found, %: C, 62.38; H, 4.03; N, 8.92.

For $C_{25}H_{20}N_3O_5V$ (**II**) and (**III**)

anal. calcd., %: C, 60.86; H, 4.09; N, 8.52.

Found, %: C, 60.77; H, 4.20; N, 8.41 (**II**).

Found, %: C, 60.72; H, 4.14; N, 8.65 (**III**).

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 (λ = 0.71073 Å). The collected data were reduced using the SAINT program [16], and multi-scan absorption corrections were performed using the SADABS program [17]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL [18]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed

Table 2. Selected bond distances and angles for the complexes

Bond	*d*, Å	Bond	*d*, Å
	I		
V(1)–O(1)	1.839(4)	V(1)–O(2)	1.924(4)
V(1)–O(3)	1.838(4)	V(1)–O(4)	1.580(4)
V(1)–N(1)	2.074(5)	V(1)–N(3)	2.344(4)
	II		
V(1)–O(1)	1.848(3)	V(1)–O(2)	1.933(2)
V(1)–O(4)	1.838(2)	V(1)–O(5)	1.587(3)
V(1)–N(1)	2.071(3)	V(1)–N(3)	2.359(3)
	III		
V(1)–O(1)	1.849(2)	V(1)–O(2)	1.936(2)
V(1)–O(4)	1.847(2)	V(1)–O(5)	1.578(2)
V(1)–N(1)	2.076(3)	V(1)–N(3)	2.380(3)
Angle	ω, deg	Angle	ω, deg
	I		
O(4)V(1)O(3)	101.8(2)	O(4)V(1)O(1)	99.5(2)
O(3)V(1)O(1)	103.5(2)	O(4)V(1)O(2)	99.0(2)
O(3)V(1)O(2)	90.3(2)	O(1)V(1)O(2)	154.0(2)
O(4)V(1)N(1)	97.6(2)	O(3)V(1)N(1)	157.5(2)
O(1)V(1)N(1)	84.3(2)	O(2)V(1)N(1)	75.3(2)
O(4)V(1)N(3)	176.8(2)	O(3)V(1)N(3)	76.5(2)
O(1)V(1)N(3)	83.6(2)	O(2)V(1)N(3)	78.3(2)
N(1)V(1)N(3)	83.5(2)		
	II		
O(5)V(1)O(4)	98.7(1)	O(5)V(1)O(1)	99.7(1)
O(4)V(1)O(1)	104.3(1)	O(5)V(1)O(2)	97.4(1)
O(4)V(1)O(2)	91.1(1)	O(1)V(1)O(2)	154.8(1)
O(5)V(1)N(1)	100.0(1)	O(4)V(1)N(1)	157.9(1)
O(1)V(1)N(1)	84.0(1)	O(2)V(1)N(1)	75.0(1)
O(5)V(1)N(3)	174.5(1)	O(4)V(1)N(3)	75.7(1)
O(1)V(1)N(3)	82.0(1)	O(2)V(1)N(3)	82.7(1)
N(1)V(1)N(3)	85.4(1)		
	III		
O(5)V(1)O(4)	99.2(1)	O(5)V(1)O(1)	100.2(1)
O(4)V(1)O(1)	105.2(1)	O(5)V(1)O(2)	100.7(1)
O(4)V(1)O(2)	90.2(1)	O(1)V(1)O(2)	151.5(1)
O(5)V(1)N(1)	96.8(1)	O(4)V(1)N(1)	159.8(1)
O(1)V(1)N(1)	83.8(1)	O(2)V(1)N(1)	74.7(1)
O(5)V(1)N(3)	174.5(1)	O(4)V(1)N(3)	75.4(1)
O(1)V(1)N(3)	82.3(1)	O(2)V(1)N(3)	78.6(1)
N(1)V(1)N(3)	88.3(1)		

in idealized positions and constrained to ride on their parent atoms. The crystallographic data for the complexes **I**–**III** are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material for structures **I**–**III** has been deposited with the Cambridge Crystallographic Data Centre (nos. 1004087 (**I**), 1004088 (**II**), and 1004089 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk

RESULTS AND DISCUSSION

Replacement of two acetylacetonate ligands of $[VO(Acac)_2]$ by hydrazone and 8-hydroxyquinoline ligands in methanol resulted in the formation of three structurally similar complexes. The complexes are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. Molar conductance of the complexes at the concentrations of 10^{-4} mol L^{-1} are in the range 20–50 Ω^{-1} cm^2 mol^{-1}, indicating they are non-electrolytes [19].

The molecular structures and atom numbering schemes of complexes **I**, **II**, and **III** are shown in Fig. 1. The V atoms in the complexes are in octahedral coordination, with the three donor atoms of the hydrazone ligands and the hydroxy O atom of the 8-hydroxyquinoline ligand defining the equatorial plane, and with one oxo O atom and the pyridine N atom of the 8-hydroxyquinoline ligand occupying the axial positions. The distances V(1)–O(4) in **I** and V(1)–O(5) in **II** and **III** are in the range 1.57–1.59 Å, indicating they are typical V=O double bonds. The V(1)–N(3) bonds in the complexes are significantly longer than the other coordinate bonds, yet, it is not uncommon for such complexes [20, 21]. The coordinate bond lengths in the complexes are comparable to each other and also similar to those observed in the mononuclear oxovanadium(V) complexes with octahedral coordination [20–23]. The angular distortion in the octahedral environment around V comes from the five– and sixmembered chelate rings taken by the hydrazone ligands. For the same reason, the *trans* angles significantly deviate from the ideal values of 180°. Distortion of the octahedral coordination can be observed from the coordinate bond angles, ranging from 75.3(2)° to 103.5(2)° for the perpendicular angles, and from 154.0(2)° to 176.8(2)° for the diagonal angles for **I**, and from 75.0(1)° to 104.3(1)° for the perpendicular angles, and from 154.8(1)° to 174.5(1)° for the diagonal angles for **II**, and from 74.7(1)° to 105.2(1)° for the perpendicular angles, and from 151.5(1)° to 174.5(1)° for the diagonal angles for **III**. The displacement of the V atoms from the equatorial plane are 0.319(1) Å for **I**, 0.298(1) Å for **II**, and 0.309(1) Å for **III**. The dihedral angle between the benzene rings of the hydrazone ligand are 7.7(5)° for **I**, 24.7(4)° for **II**, and 7.7(3)° for **III**.

The complexes exhibit typical V=O absorption bands at about 973 cm^{-1} [24]. The bands due to

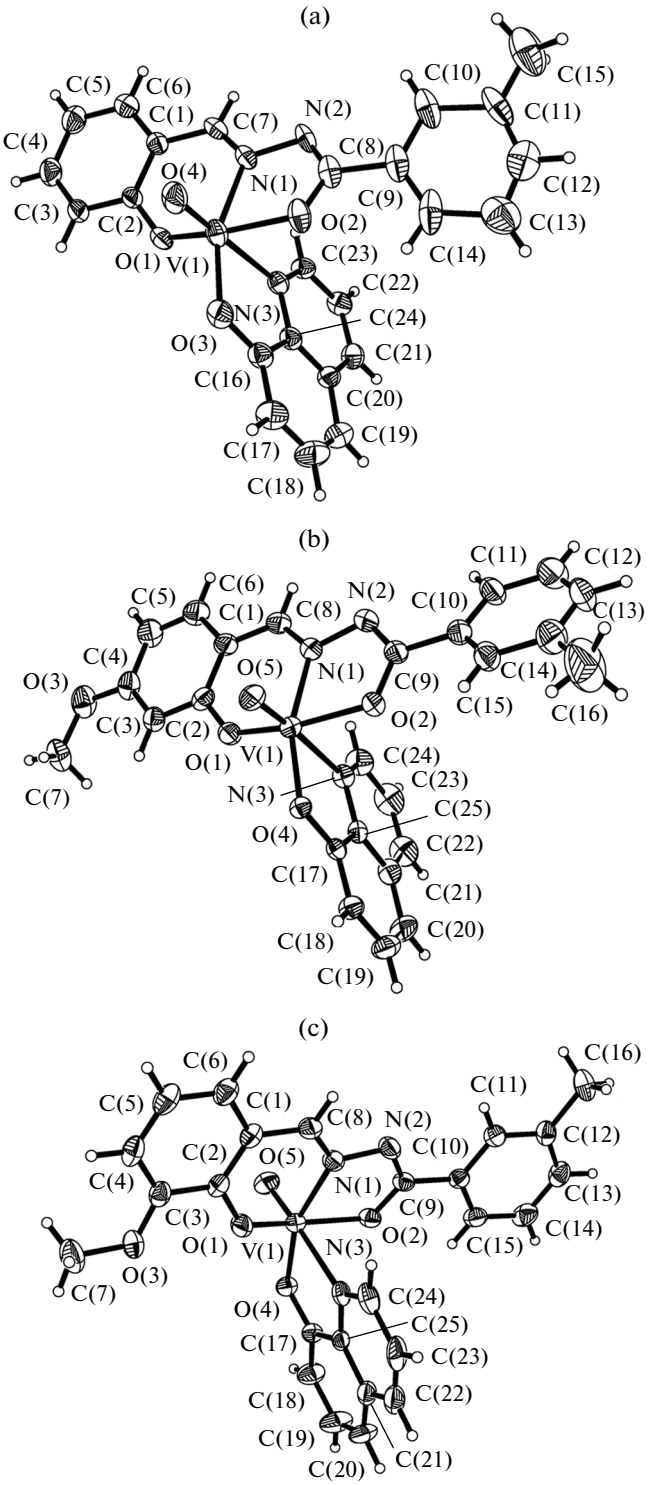


Fig. 1. ORTEP plot of the crystal structures of **I** (a), **II** (b), and **III** (c). Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level.

ν(C=O) were absent in the complexes, but new C–O stretches appeared at about 1230–1260 cm^{-1} for the complexes. This suggests occurrence of *keto*-imine tautomerization of the ligands during complexation.

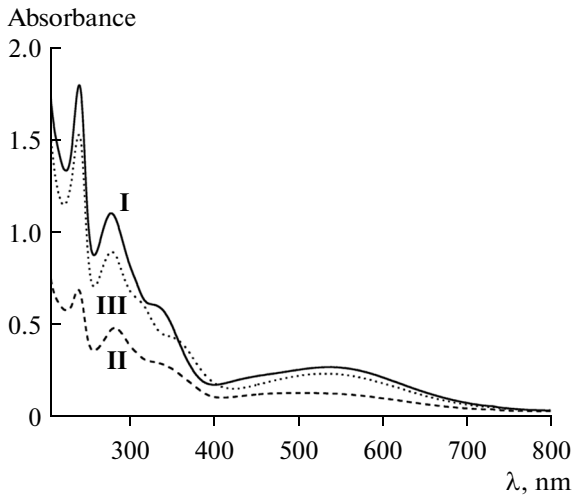


Fig. 2. UV-Vis spectra of complexes **I**–**III**.

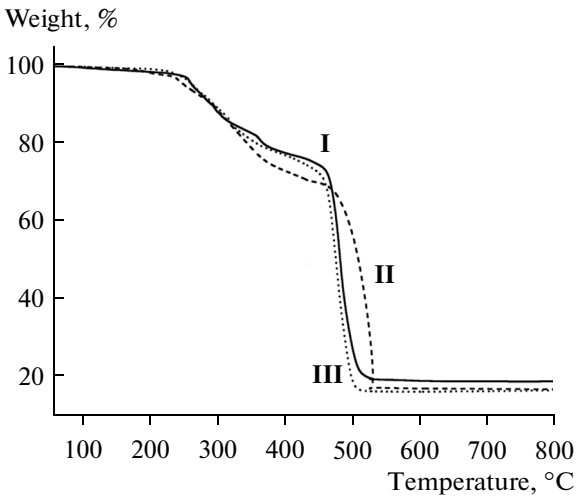


Fig. 3. TGA curves of complexes **I**–**III**.

The intense ν(C=N) absorptions are observed at 1610–1617 cm^{-1} for the complexes. The weak peaks in the low wave numbers in the region 400–690 cm^{-1} may be attributed to V–O and V–N bonds in the complexes.

The acetonitrile solutions of the complexes with concentration of 10^{-5} mol L^{-1} have been used to record the electronic spectra. The main features of all the spectra are quite similar (Fig. 2). There are absorptions within the range 700–400 nm in the complexes. This can be attributed to the ligand-to-metal charge transfer transitions (LMCT). The high energy absorptions at about 280 and 240 nm are most likely due to the transition involving ligand orbitals only.

Thermal gravimetric analyses (TGA) were conducted to examine the stability of the complexes (Fig. 3). The thermal behavior of the complexes is similar to each other. All the complexes decomposed from about 190°C and ended at about 530°C, corresponding to the loss of the hydrazone and 8-hydroxyquinoline ligands and the formation of V_2O_5. The total observed weight loss of 80.5% for **I**, and 82.5% for **II** and **III**, are close to the calculated values of 80.3% for **I**, and 81.6% for **II** and **III**.

In summary, three new structurally similar 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. Thermal behavior of the complexes was studied.

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