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# Synthesis and Structural Characterization of Oxovanadium(V) Complexes with Mixed Tridentate Benzohydrazone and Bidentate No Ligands[1]

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**Abstract**—New oxovanadium(V) complexes, [VO($L^1$)(Bha)] (**I**) and [VO($L^2$)(Qnl)] (**II**), were prepared by the reactions of [VO$(Acac)_2$] (Acac = acetylacetonate), (4-nitrophenoxy)acetic acid [1-(2-hydroxy-3-methylphenyl)methylidene]hydrazide ($H_2L^1$) and benzohydroxamic acid (HBha), and [VO$(Acac)_2$], *N*'-(2-hydroxy-5-methylbenzylidene)-3-methylbenzohydrazide ($H_2L^2$), and 8-hydroxyquinoline (HQnl) in methanol, respectively. Crystal and molecular structures of complexes **I** and **II** were determined by elemental analysis, infrared and UV-Vis spectra and single crystal X-ray diffraction (CIF files CCDC nos. 1000875 (**I**) and 1012028 (**II**)). The V atoms in the complexes are in octahedral coordination. Thermal stability of complex **I** was studied.

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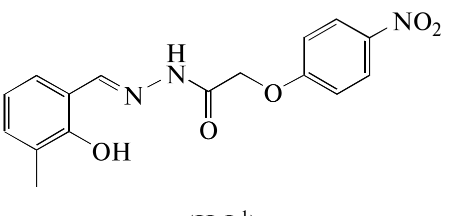
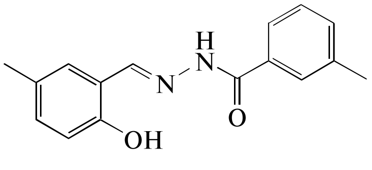
## INTRODUCTION

Two classes of vanadium enzymes, *viz.* vanadium-nitrogenases and vanadate-dependent haloperoxidases, have so far been found in nature, and their structures and properties have stimulated the search for structural and functional model compounds [1–5]. 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 [6–8]. The remarkable biological activity of acid hydrazides R–CO–NH–$NH_2$, their corresponding aroylhydrazones, R–CO–NH–N=CH–R', and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest [9–11]. Recently, our research group has reported a few metal complexes with biological activities [12–16]. Benzohydroxamic acid (HBha) and 8-hydroxyquinoline (HQnl) are typical bidentate ligands in coordination chemistry. The introduction of such ligands may introduce new vanadium complexes with novel catalytic or biological properties. In the present paper, new oxovanadium(V) complexes, [VO($L^1$)(Bha)] (**I**) and [VO($L^2$)(Qnl)] (**II**), where $L^1$ and $L^2$ are the deprotonated forms of (4-nitrophenoxy)acetic acid [1-(2-hydroxy-3-methylphenyl)methylidene]hydrazide ($H_2L^1$) and *N*'-(2-hydroxy-5-methylbenzylidene)-3-methylbenzohydrazide ($H_2L^2$), respectively, and Bha and Qnl are the deprotonated forms of benzohydroxamic acid and 8-hydroxyquinoline, respectively, are presented.



($H_2L^1$)



($H_2L^2$)

## EXPERIMENTAL

**Materials and methods.** Commercially available 3-methylsalicylaldehyde, 5-methylsalicylaldehyde, (4-nitrophenoxy)acetic acid hydrazide, and 3-methylbenzohydrazide were purchased from Sigma-Aldrich. Other solvents and reagents were made in China

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and used as received. C, H and N elemental analyses were performed with a PerkinElmer elemental analyser. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the (4000–400) cm$^{-1}$ region. UV-Vis spectrum was recorded on Lambda 900 spectrometer. Thermal stability analysis was performed on a PerkinElmer Pyris Diamond TGA–DTA thermal analyses system.

**Synthesis of I.** 3-Methylsalicylaldehyde (1.0 mmol, 0.136 g) and (4-nitrophenoxy)acetic acid hydrazide (1.0 mmol, 0.201 g) were mixed in 20 mL methanol and refluxed for 30 min. To the solution was added dropwise a methanolic solution (20 mL) of [VO(Acac)$_2$] (1.0 mmol, 0.265 g) and HBha (1.0 mmol, 0.137 g). The color of the reaction mixture changed from colorless to dark brown. The final mixture was further stirred at reflux for 30 min and cooled to room temperature. The filtrate 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 times with cold methanol and dried in air. The yield was 46%.

For $C_{23}H_{19}N_4O_8V$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 52.1; | H, 3.6; | N, 10.6. |
| Found, %: | C, 51.9; | H, 3.7; | N, 10.5. |

**Synthesis of II.** 5-Methylsalicylaldehyde (1.0 mmol, 0.136 g) and 3-methylbenzohydrazide (1.0 mmol, 0.150 g) were mixed in 20 mL methanol and refluxed for 30 min. To the solution was added dropwise a methanolic solution (20 mL) of [VO(Acac)$_2$] (1.0 mmol, 0.265 g) and HQnl (1.0 mmol, 0.145 g). The color of the reaction mixture changed from colorless to dark brown. The final mixture was further stirred at reflux for 30 min and cooled to room temperature. The filtrate 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 times with cold methanol and dried in air. The yield was 40%.

For $C_{25}H_{20}N_3O_4V$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 62.9; | H, 4.2; | N, 8.8. |
| Found, %: | C, 62.7; | H, 4.3; | N, 8.9. |

**X-ray crystallography.** Diffraction intensities for the complexes **I**, **II** were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). The collected data were reduced using the SAINT program [17], and multi-scan absorption corrections were performed using the SADABS program [18]. The structures were solved by direct methods and refined against $F^2$ by full-matrix least-squares methods using the SHELXTL [19]. All of the non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material for complexes **I**, **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 1000875 (**I**) and 1012028 (**II**); 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 Bha or Qnl ligands in methanol resulted in the formation of the complexes. The complexes are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. Molar conductance of the complexes at the concentration of 10$^{-4}$ mol L$^{-1}$ are 18 and 31 $\Omega^{-1}$ cm$^2$ mol$^{-1}$, indicating their non-electrolyte nature [20].

The molecular structure and atom numbering scheme of complex **I** is shown in Fig. 1a. The V atom in the complex is in octahedral coordination with the three donor atoms of the hydrazone ligand and the hydroxy O atom of the Bha ligand defining the equatorial plane, and with one oxo O atom and the carbonyl O atom of the Bha ligand occupying the axial positions. The distance V(1)–O(8) is 1.584(3) Å, indicating it is a typical V=O double bond. The bond lengths in complex Imare similar to those observed in the mononuclear oxovanadium(V) complexes with octahedral coordination [21, 22]. The angular distortion in the octahedral environment around V comes from the five- and six-membered chelate rings taken by the hydrazone ligand. 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 74.5(1)° to 106.2(1)° for the perpendicular angles and from 152.1(1)° to 172.1(1)° for the diagonal angles. The displacement of the V atom from the equatorial plane is 0.285(1) Å. The dihedral angle between the two benzene rings of the hydrazone ligand is 14.8(3)°. In the crystal structure of complex **I**, two adjacent molecules are linked through intermolecular hydrogen bonds of type N–H···O (N(4)–H(4*A*)···O(2): N(4)–H(4*A*) 0.90(1), H(4*A*)···O(2) 2.03(2), N(4)···O(2) 2.896(4) Å, N(4)–H(4*A*)···O(2) 161(5)°; N(4)–H(4*A*)···O(3): N(4)–H(4*A*) 0.90(1), H(4*A*)···O(3) 2.58(4), N(4)···O(3) 3.196(4) Å, N(4)–H(4*A*)···O(3) 126(4)°) to form dimers (Fig. 2).

The molecular structure and atom numbering scheme of complex **II** are shown in Fig. 1b. The V atom in complex **II** is in octahedral coordination, with the three donor atoms of the hydrazone ligand and the hydroxy O atom of the Qnl ligand defining the equatorial plane and with one oxo O atom and the pyridine N atom of the Qnl ligand occupying the axial positions.

**Table 1.** Crystallographic data and structure refinement for complexes **I** and **II**

| Parameter | Value | |
|---|---|---|
| | **I** | **II** |
| *Mr* | 530.36 | 477.38 |
| Crystal shape/color | Block/brown | Block/deep brown |
| Crystal size, mm | 0.18 × 0.17 × 0.15 | 0.23 × 0.23 × 0.22 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| $a$, Å | 9.7695(6) | 12.560(3) |
| $b$, Å | 10.9349(6) | 12.641(3) |
| $c$, Å | 12.4862(8) | 14.389(3) |
| $\alpha$, deg | 105.777(2) | 90 |
| $\beta$, deg | 107.229(2) | 93.015(2) |
| $\gamma$, deg | 103.199(2) | 90 |
| $V$, Å$^3$ | 1154.7(1) | 2281.4(8) |
| $Z$ | 2 | 4 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.525 | 1.390 |
| $\mu(\text{Mo}K_\alpha)$, mm$^{-1}$ | 0.488 | 0.471 |
| $F(000)$ | 544 | 984 |
| Measured reflections | 11207 | 7460 |
| Independent reflections | 4289 | 2524 |
| Observed reflections ($I \geq 2\sigma(I)$) | 3235 | 1532 |
| Min and max transmission | 0.9174 and 0.9305 | 0.8993 and 0.9034 |
| Number of refinement parameters | 329 | 287 |
| Restraints | 1 | 30 |
| Goodness-of-fit on $F^2$ | 1.057 | 1.019 |
| $R_1$, $wR_2$ ($I \geq 2\sigma(I)$)* | 0.0601, 0.1520 | 0.0604, 0.1555 |
| $R_1$, $wR_2$ (all data)* | 0.0839, 0.1674 | 0.1103, 0.1818 |

* $R_1 = F_o - F_c/F_o$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]^{1/2}$.

The distance V(1)–O(4) is 1.576(5) Å, indicating it is a typical V=O double bond. The V–N(Py) bond in complex **II** is significantly longer than the other coordinate bonds, yet it is not uncommon for such complexes [23, 24]. The bond lengths in complex **II** are comparable to those observed in the mononuclear oxovanadium(V) complexes with octahedral coordination [23, 24]. The angular distortion in the octahedral environment around the V comes from the five- and six-membered chelate rings taken by the hydrazone ligand. 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 75.1(2)° to 102.7(2)° for the perpendicular angles and from 155.4(2)° to 176.9(2)° for the diagonal angles. The displacement of the V atom from the equatorial plane is 0.318(1) Å. The dihedral angle between the two benzene rings of the hydrazone ligand is 13.2(5)°.

**Table 2.** Selected bond distances (Å) and angles (deg) for complexes **I**, **II**

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| | | **I** | |
| V(1)–O(1) | 1.859(3) | V(1)–O(2) | 2.006(2) |
| V(1)–O(6) | 2.223(3) | V(1)–O(7) | 1.863(2) |
| V(1)–O(8) | 1.584(3) | V(1)–N(1) | 2.051(3) |
| | | **II** | |
| V(1)–O(1) | 1.838(5) | V(1)–O(2) | 1.927(5) |
| V(1)–O(3) | 1.838(5) | V(1)–O(4) | 1.576(5) |
| V(1)–N(1) | 2.063(6) | V(1)–N(3) | 2.340(5) |
| **Angle** | **ω, deg** | **Angle** | **ω, deg** |
| | | **I** | |
| O(8)V(1)O(1) | 99.5(1) | O(8)V(1)O(7) | 96.7(1) |
| O(1)V(1)O(7) | 106.2(1) | O(8)V(1)O(2) | 100.5(1) |
| O(1)V(1)O(2) | 152.1(1) | O(7)V(1)O(2) | 90.5(1) |
| O(8)V(1)N(1) | 97.5(1) | O(1)V(1)N(1) | 83.8(1) |
| O(7)V(1)N(1) | 161.0(1) | O(2)V(1)N(1) | 74.5(1) |
| O(8)V(1)O(6) | 172.1(1) | O(1)V(1)O(6) | 84.8(1) |
| O(7)V(1)O(6) | 75.7(1) | O(2)V(1)O(6) | 77.7(1) |
| N(1)V(1)O(6) | 89.4(1) | | |
| | | **II** | |
| O(4)V(1)O(1) | 99.1(3) | O(4)V(1)O(3) | 102.6(2) |
| O(1)V(1)O(3) | 102.7(2) | O(4)V(1)O(2) | 98.1(2) |
| O(1)V(1)O(2) | 155.4(2) | O(3)V(1)O(2) | 90.5(2) |
| O(4)V(1)N(1) | 97.9(2) | O(1)V(1)N(1) | 85.3(2) |
| O(3)V(1)N(1) | 156.5(2) | O(2)V(1)N(1) | 75.1(2) |
| O(4)V(1)N(3) | 176.9(2) | O(1)V(1)N(3) | 84.1(2) |
| O(3)V(1)N(3) | 76.5(2) | O(2)V(1)N(3) | 78.9(2) |
| N(1)V(1)N(3) | 82.4(2) | | |

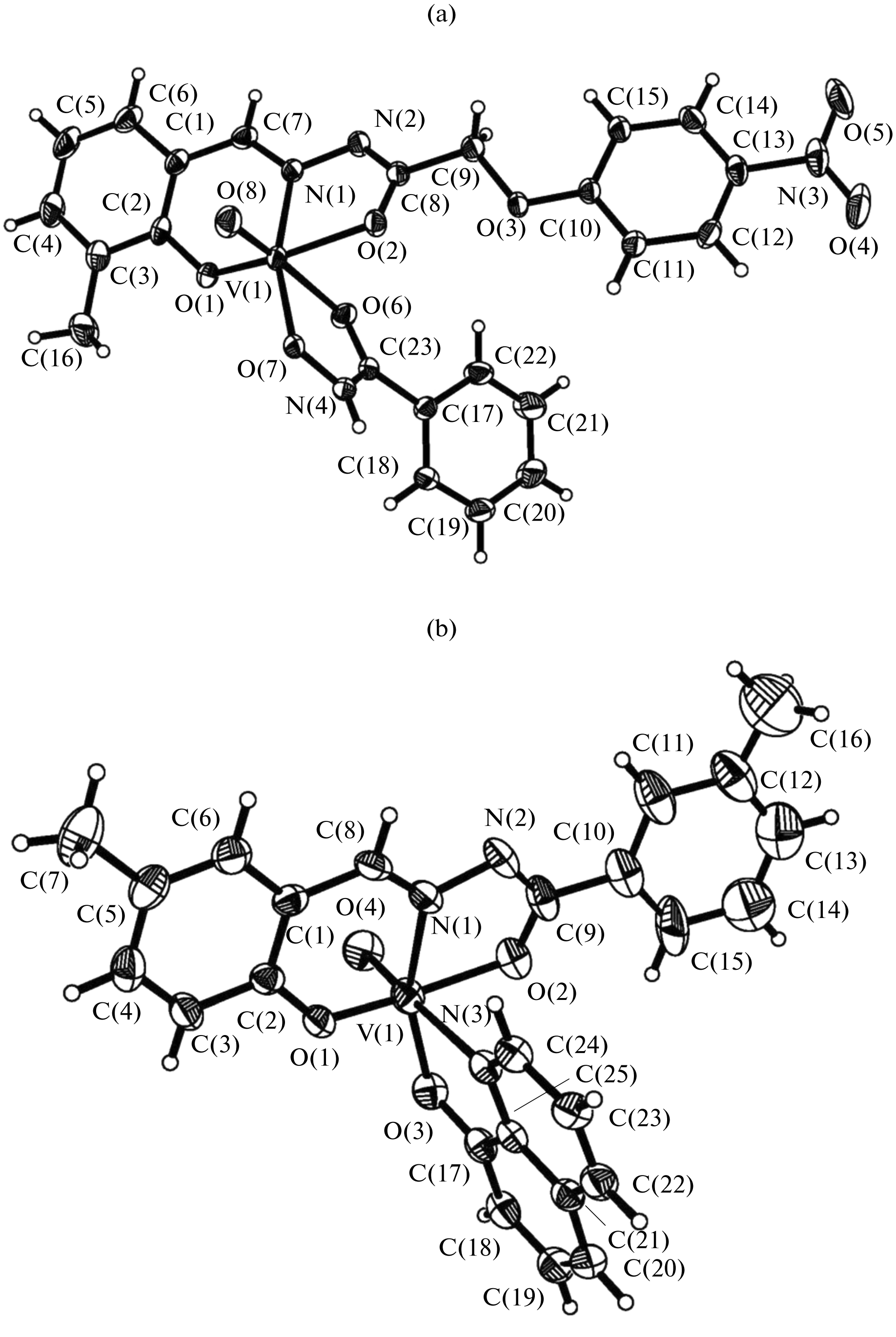

**Fig. 1.** The molecular structure of complex **I** (a) and **II** (b). Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level.

Complexes **I** and **II** exhibit typical bands at 979 and 973 $cm^{-1}$, respectively, which are assigned to the V=O vibrations. The bands due to ν(C=O) are absent in the complexes, but new C–O stretches appeared at 1257 $cm^{-1}$ for **I** and 1270 $cm^{-1}$ for **II**. This suggests occurrence of *keto*-imine tautomerization of the ligands during complexation. The intense ν(C=N) absorptions in both complexes are observed at 1605–1611 $cm^{-1}$. The weak peaks in the low wave numbers in the region (400–700 $cm^{-1}$) 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 of **I** and **II** (Fig. 3). For **I**, there are four bands with maximum absorptions at 203, 272, 340 and 445 nm. For **II**, there are four bands

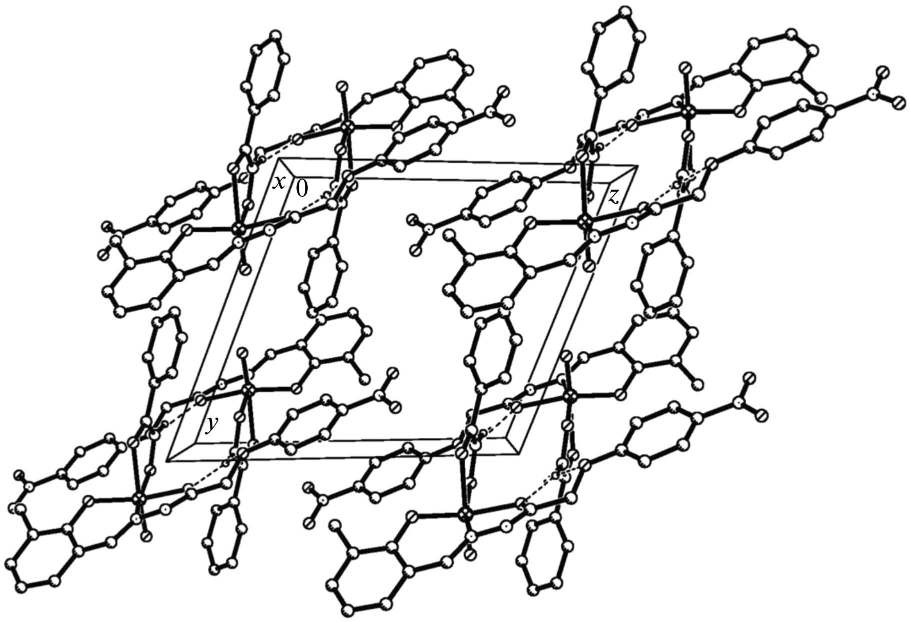

**Fig. 2.** The hydrogen linked dimeric structure of complex **I**. Hydrogen bonds are drawn as dashed lines.

with maximum absorptions at 240, 285, 337 and 512 nm. The absorptions in the visible region can be attributed to the ligand-to-metal charge transfer transition. The high energy absorptions are most likely due to the transition involving ligand orbitals only, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$.

Differential thermal (DTA) and thermal gravimetric analyses (TGA) were conducted to examine the stability of complex **I** under air atmosphere and with standard corundum crucible sample holder (Fig. 4). The rate of the gas flow is 20.0 $\text{cm}^3\ \text{min}^{-1}$. The sample mass is 2.543 mg. The heating rate is 10°C $\text{min}^{-1}$. The complex decomposed from 145 to 535°C, corresponding to the loss of the hydrazone and benzohy-

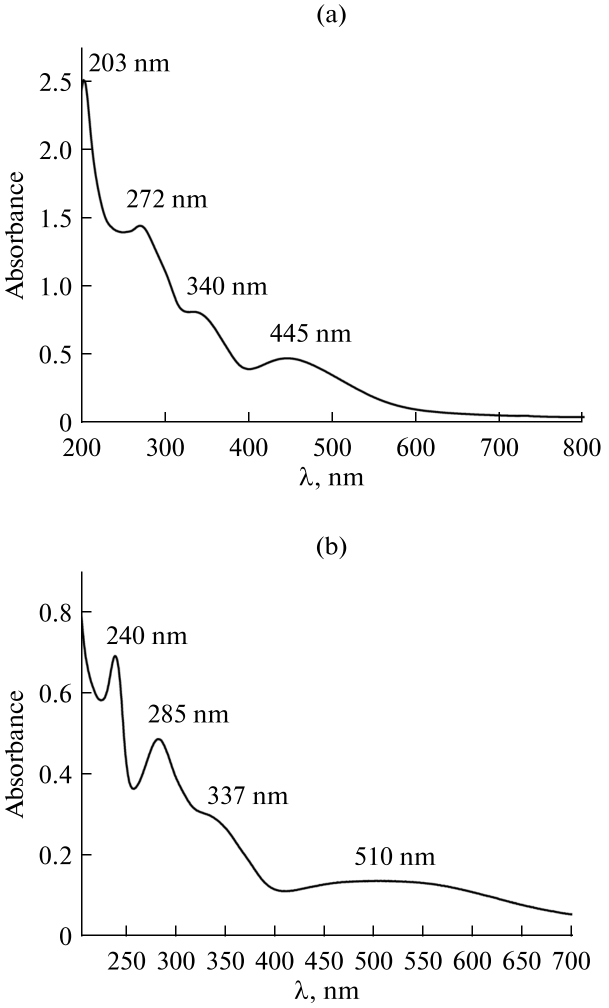

**Fig. 3.** UV-Vis spectrum of complex **I** (a) and **II** (b).

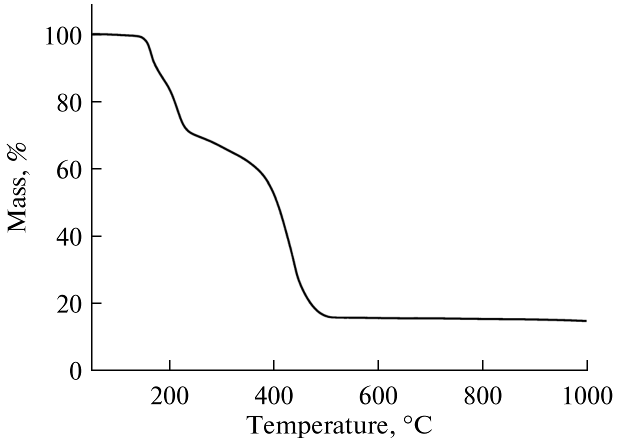

**Fig. 4.** TG curve of complex **I**.

droxamate ligands and the formation of $V_2O_5$. The total observed weight loss of 83.7% is close to the calculated value of 82.8%.

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