ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 1, pp. 58–63. © Pleiades Publishing, Ltd., 2015.

Syntheses, Characterization, and Structures of Vanadium(V) Complexes with Similar Tridentate Hydrazone and Bidentate Benzohydroxamate Ligands[1]

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Received July 2, 2014

Abstract—New vanadium(V) complexes, [VO(L^1)(Bzh)] and [VO(L^2)(Bzh)] · CH_3OH, were prepared by the reaction of [VO$(Acac)_2$] (Acac = acetylacetonate) and benzohydroxamic acid (HBzh) with *N*'-(3-bromo-2-hydroxybenzylidene)-2-chlorobenzohydrazide (H_2L^1) and 2-chloro-*N*'-(2-hydroxy-5-methoxybenzylidene)benzohydrazide (H_2L^2), respectively, in methanol. Molecular component and structures of the complexes were determined by elemental analysis, infrared and UV-Vis spectra. Single crystal structures of the complexes were determined by X-ray diffraction (CIF file CCDC nos. 1006633 (**I**) and 1006634 (**II**)). The V atoms are in octahedral coordination. Thermal stability of the complexes was studied.

DOI: 10.1134/S107032841501008X

INTRODUCTION

Among versatile metal complexes, those derived from hydrazones have been 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 [5–7]. Ara and co-workers reported that some binuclear vanadium(IV) complexes possess interesting urease inhibitory activities [8]. Recently, our research group has reported a few vanadium complexes with biological properties [9, 10]. In order to explore new vanadium materials, in the present paper, two new oxidovanadium(V) complexes, [VO(L^1)(Bzh)] (**I**) and [VO(L^2)(Bzh)] · CH_3OH (**II**), where L^1, L^2, and Bzh are the deprotonated forms of *N*'-(3-bromo-2-hydroxybenzylidene)-2-chlorobenzohydrazide (H_2L^1) and 2-chloro-*N*'-(2-hydroxy-5-methoxybenzylidene)benzohydrazide (H_2L^2), and benzohydroxamic acid, respectively, are presented.

EXPERIMENTAL

Materials and measurements. Commercially available 3-bromosalicylaldehyde, 5-methoxybenzohydrazide, 2-chlorobenzohydrazide and benzohydroxamic acid were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. C, H, and N elemental analyses were performed with a Perkin-Elmer elemental analyser. 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 Lambda-900 spectrometer. Thermal stability analysis was performed on a PerkinElmer Pyris Diamond TG–DTA thermal analyses system.

Synthesis of I. 3-Bromosalicylaldehyde (1.0 mmol, 201 mg), 2-chlorobenzohydrazide (1.0 mmol, 171 mg) and benzohydroxamic acid (1.0 mmol, 137 mg) were dissolved in methanol (20 mL) and stirred at room temperature for 10 min. Then, 20 mL methanolic solution containing [VO$(Acac)_2$] (1.0 mmol, 265 mg) was added dropwise to the solution. The mixture was further stirred at room temperature for 10 min to give a deep brown solution. The solution was filtered to obtain clear filtrate, which was kept still at dark to slow evaporation. A few days later, well-shaped brown single crystals of the complex were formed and separated by filtration. The product was washed three times with cold methanol and dried in air. The yield was 53%.

UV-Vis (acetonitrile; λ_{max} (logε)): 240 (5.19); 269 (4.14); 341 (3.75); 455 (3.64) nm. IR (KBr; ν, cm^{-1}) 3534 m, 3135 w, 1609 v.s, 1554 m, 1517 w, 1468 m, 1401 s, 1346 s, 1266 m, 1235 w, 1162 w, 1118 m,

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

Parameter	Value	
	I	**II**
Formula weight	554.65	537.82
Crystal color; habit	Brown; block	Brown; block
Crystal size, mm	0.20 × 0.17 × 0.17	0.20 × 0.20 × 0.16
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*C*2/*c*
Unit cell parameters:		
a, Å	14.094(2)	36.084(2)
b, Å	13.891(2)	10.285(3)
c, Å	22.398(3)	14.198(3)
β, deg		112.429(2)
V, Å^3	4385.2(10)	4870.6(18)
Z	8	8
ρ_{calcd}, g cm^{-3}	1.680	1.467
μ, mm^{-1}	2.435	0.565
F(000)	2208	2208
Number of unique data	4065	3715
Number of observed data, $I > 2\sigma(I)$	2655	1432
Number of parameters refined	292	319
Number of restraints	1	0
Final R indices, $I > 2\sigma(I)$	0.0650, 0.1483	0.0911, 0.1113
R indices (all data)	0.1084, 0.1811	0.2770, 0.1557
Goodness of fit on F^2	1.116	1.049
Largest diff. peak/hole, e Å^{-3}	1.022 and –0.701	0.436 and –0.494

1039 w, 965 m, 910 w, 825 m, 776 w, 739 w, 696 m, 579 s, 450 w.

For $C_{21}H_{14}N_3O_5ClBrV$ (**I**)

anal. calcd., %:	C, 45.47;	H, 2.54;	N, 7.58.
Found, %:	C, 45.32;	H, 2.63;	N, 7.50.

Synthesis of II was carried out by the same method as that described for **I** with 3-bromosalicylaldehyde replaced by 5-methoxybenzohydrazide (1.0 mmol, 166 mg). The yield was 45%.

UV-Vis (acetonitrile); λ_{max} (logε): 270 (5.08); 333 (4.70); 443 (4.56) nm. IR (KBr; ν, cm^{-1}): 3430 w, 3130 m, 1609 v.s, 1529 m, 1480 m, 1426 s, 1395 s, 1346 s, 1278 m, 1229 w, 1143 m, 1038 w, 965 m, 910 w, 850 w, 781 w, 738 m, 685 m, 592 s, 487 w, 439 w.

For $C_{23}H_{21}N_3O_7ClV$ (**II**)

anal. calcd., %:	C, 51.36;	H, 3.94;	N, 7.81.
Found, %:	C, 51.49;	H, 4.08;	N, 7.73.

X-ray crystallography. Diffraction intensities for the complex 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 [11], and multi-scan absorption corrections were performed using the SADABS program [12]. The structure was solved by direct method and refined against F^2 by full-matrix least-squares method using the SHELXTL [13]. All of the non-hydrogen atoms were refined anisotropically. The amino H atom in **I** was located from a difference Fourier map and refined isotropically with N–H distance restrained to 0.90(1) Å. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 1006633 (**I**) and 1006634 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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

Bond	*d*, Å	Bond	*d*, Å
I			
V(1)–O(1)	1.871(4)	V(1)–O(2)	1.969(4)
V(1)–O(3)	2.176(5)	V(1)–O(4)	1.860(4)
V(1)–O(5)	1.577(5)	V(1)–N(1)	2.086(5)
II			
V(1)–O(1)	1.862(5)	V(1)–O(2)	1.957(6)
V(1)–O(3)	2.170(6)	V(1)–O(4)	1.878(5)
V(1)–O(5)	1.606(5)	V(1)–N(1)	2.073(6)
Angle	*d*, deg	Angle	*d*, deg
I			
O(5)V(1)O(4)	93.4(2)	O(5)V(1)O(1)	98.6(2)
O(4)V(1)O(1)	109.3(2)	O(5)V(1)O(2)	99.8(2)
O(4)V(1)O(2)	88.6(2)	O(1)V(1)O(2)	153.4(2)
O(5)V(1)N(1)	98.4(2)	O(4)V(1)N(1)	160.3(2)
O(1)V(1)N(1)	84.6(2)	O(2)V(1)N(1)	73.9(2)
O(5)V(1)O(3)	169.2(2)	O(4)V(1)O(3)	75.9(2)
O(1)V(1)O(3)	85.1(2)	O(2)V(1)O(3)	80.4(2)
N(1)V(1)O(3)	92.0(2)		
II			
O(5)V(1)O(4)	93.0(3)	O(5)V(1)O(1)	98.9(3)
O(4)V(1)O(1)	107.5(2)	O(5)V(1)O(2)	101.4(3)
O(4)V(1)O(2)	91.1(2)	O(1)V(1)O(2)	151.5(2)
O(5)V(1)N(1)	96.9(3)	O(4)V(1)N(1)	163.8(3)
O(1)V(1)N(1)	83.6(3)	O(2)V(1)N(1)	74.4(3)
O(5)V(1)O(3)	169.6(3)	O(4)V(1)O(3)	76.8(2)
O(1)V(1)O(3)	82.4(2)	O(2)V(1)O(3)	81.1(2)
N(1)V(1)O(3)	93.5(2)		

RESULTS AND DISCUSSION

Replacement of two acetylacetonate ligands in $[VO(Acac)_2]$ by hydrazone and benzohydroxamate ligands in methanol resulted in the formation of the complexes, with similar structures. The complexes are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. Molar conductance of the complexes at a concentration of 10^{-4} mol/L is in the range of 20–35 Ω^{-1} cm^2 mol^{-1}, indicating they are non-electrolytes [14].

The molecular structures and atom numbering schemes of complexes **I** and **II** 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 benzohydroxamate ligands defining the equatorial plane and with one oxo O atom and the carbonyl O atom occupying the axial positions. The axial bond lengths of V(1)–O(5) for **I** and **II** are 1.57 and 1.61 Å, respectively, indicating they are typical V=O double bonds. The other axial bond lengths in the complexes are significantly longer than the remaining coordinate bonds, which might due to the *trans* effect of the V=O bonds. This is not uncommon for oxidovanadium complexes [9, 15]. In both complexes, the coordinate bond lengths are comparable to each other, and also similar to those observed in the mononuclear oxidovanadium(V) complexes with octahedral coordination [9, 15]. 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 73.9(2)° to 109.3(2)° for the perpendicular angles and from 153.4(2)° to 169.2(2)° for the diagonal angles for **I**, and from 74.4(3)° to 107.5(2)° for the perpendicular angles, and from 151.5(2)° to 169.6(3)° for the diagonal angles for **II**. The displacement of the V atoms from the equatorial planes are 0.244(1) Å for both complexes. The dihedral angles between the benzene rings of the hydrazone ligands are 60.4(4)° for **I** and 53.5(5)° for **II**.

The crystal structures of the complexes (Fig. 2) are stabilized by intermolecular hydrogen bonds (**I**: N(3)–H(3) 0.90(1), H(3)···N(2)^{i} 2.09(3), N(3)···N(2)^{i} 2.956(8) Å, angle N(3)–H(3)···N(2)^{i} 161(7)°; **II**: N(3)–H(3*A*) 0.86, H(3*A*)···O(7)^{ii} 1.97, N(3)···O(7)^{ii} 2.771(10) Å, angle N(3)–H(3*A*)···O(7)^{ii} 155°; O(7)–H(7) 0.82, H(7)···O(2)^{iii} 2.11, O(7)···O(2)^{iii} 2.883(8) Å, angle O(7)–H(7)···O(2)^{iii} 158°; symmetry codes: ^{i} $3/2 - x, -1/2 + y, z$; ^{ii} $1 - x, -y, -z$; ^{iii} $-1 + x, y, -1 + z$).

Both complexes exhibit similar absorption peaks in the infrared spectra. The typical absorption bands at 965 cm^{-1} can be assigned to the V=O vibrations [16]. The intense ν(C=N) absorptions are observed at 1609 cm^{-1} for both complexes. The weak peaks in the low wave numbers in the region 400–600 cm^{-1} may be attributed to the vibrations of the V–O and V–N bonds of 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. 3). There are absorptions within the range 550–330 nm in the complexes. This can be attributed to the ligand-to-metal charge transfer transitions. The high energy absorptions are most likely due to the transition involving ligand orbitals only.

Differential thermal and thermal gravimetric analyses were conducted to examine the stability of the complexes under air atmosphere and with standard

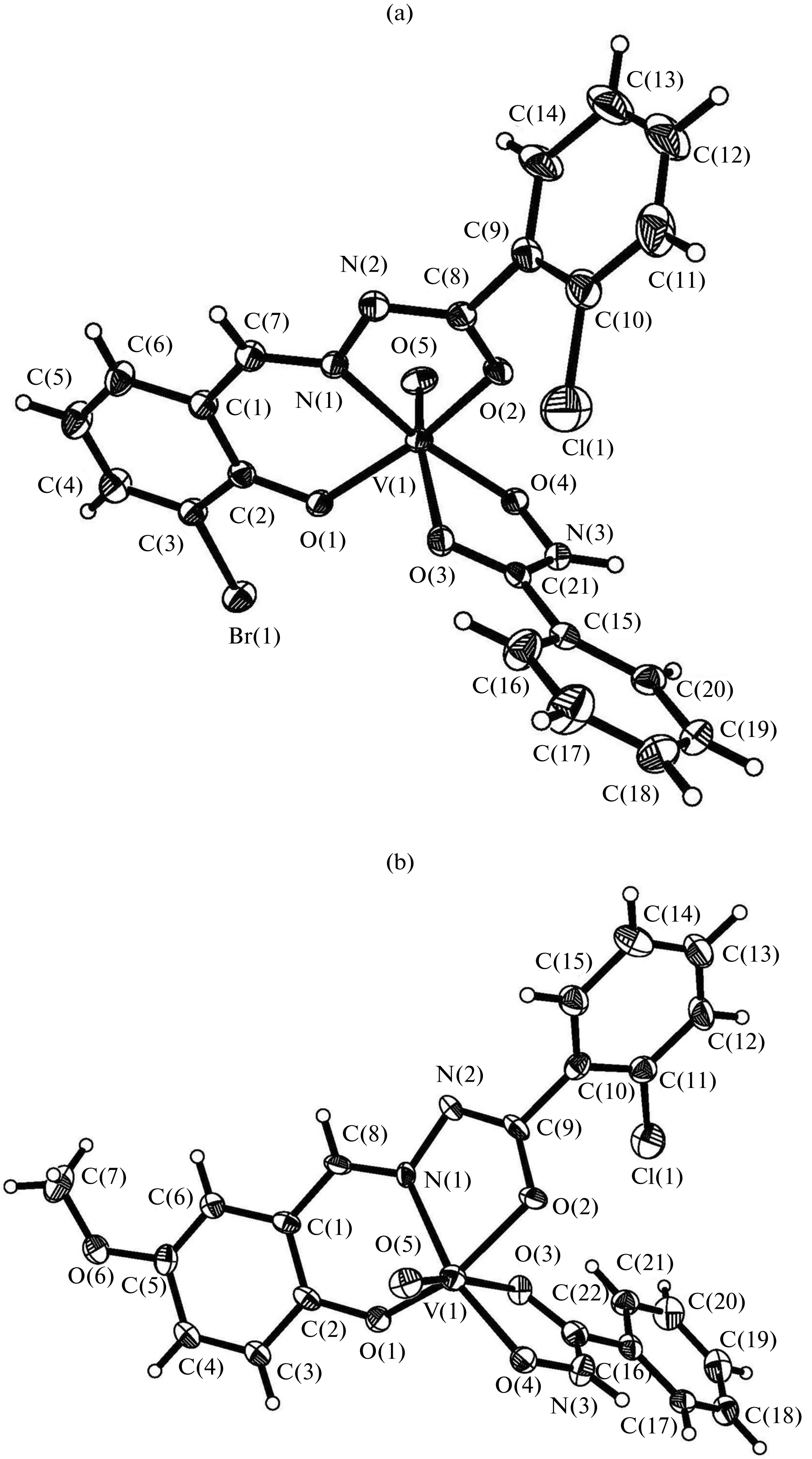

Fig. 1. ORTEP plot of the crystal structure of **I** (a) and **II** (b). Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level.

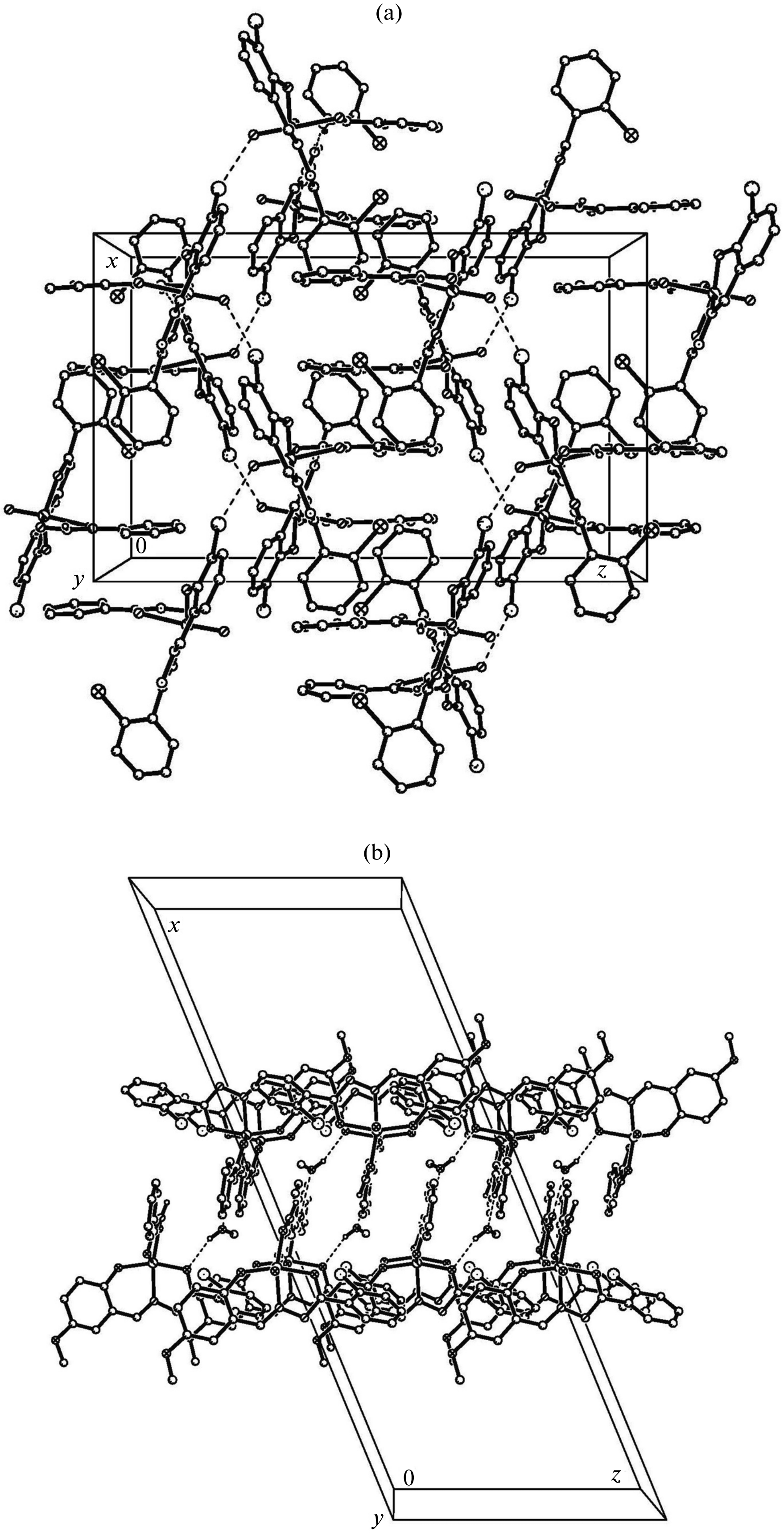

Fig. 2. Packing diagram of **I** (a) and **II** (b). Hydrogen bonds are shown as dashed lines.

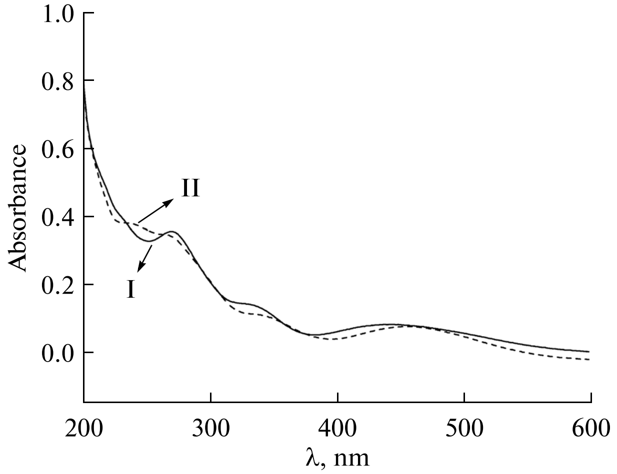

Fig. 3. UV-Vis spectra of the complexes.

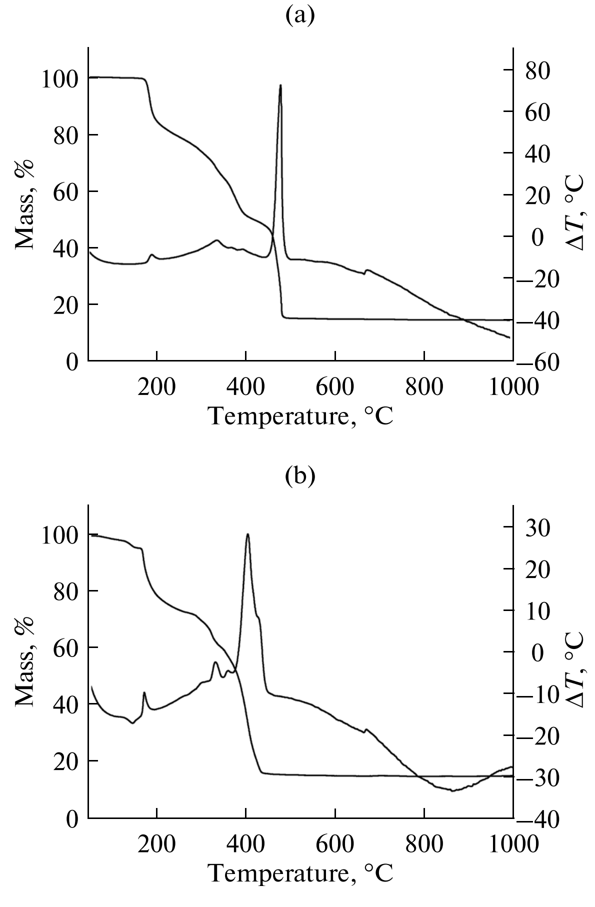

Fig. 4. DT–TGA curves of **I** (a) and **II** (b).

corundum crucible sample holder (Fig. 4). The rate of the gas flow is 20.0 cm^3 min^{-1}. The heating rate is 10°C min^{-1}. For **I**, the complex decomposed from 180 to 490°C, corresponding to the loss of the hydrazone and benzohydroxamate ligands and the formation of V_2O_5. The total observed weight loss of 84.0% is close to the calculated value of 83.5%. For **II**, the complex decomposed from 75 to 145°C, which might due to the lose of the methanol molecules. Then the complex decomposed gradually from 170 to 440°C, corresponding to the loss of the hydrazone and benzohydroxamate ligands and the formation of V_2O_5. The total observed weight loss of 83.6% is close to the calculated value of 83.1%.

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