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Synthesis and X-ray Structures of Di- and Mono-Nuclear Oxovanadium(V) Complexes Derived from Aroylhydrazones[1]

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Abstract—A new methanolato-bridged dinuclear oxovanadium(V) complex $[VO(L)(OMe)]_2$ (**I**) derived from *N*'-(2-hydroxy-5-methylbenzylidene)-2-methylbenzohydrazide (H_2L) and a new mononuclear oxovanadium(V) complex [VO(L')(OMe)(MeOH)] (**II**) derived from 3-chloro-*N*'-(2-hydroxy-3-methylbenzylidene)benzohydrazide (H_2L') were prepared and characterized by infrared spectra and single crystal X-ray determination (CIF files CCDC nos. 974793 (**I**) and 974792 (**II**)). Complex **I** crystallizes as triclinic space group $P\bar{1}$ with unit cell dimensions $a = 8.5063(4)$, $b = 9.5367(4)$, $c = 11.2445(5)$ Å, $\alpha = 71.740(1)°$, $\beta = 72.341(1)°$, $\gamma = 74.509(1)°$, $V = 810.37(6)$ Å^3, $Z = 1$, $R_1 = 0.0527$, $wR_2 = 0.1316$, $S = 0.969$. The complex possesses a crystallographic inversion center symmetry between two V atoms. Complex **II** crystallizes as triclinic space group $P\bar{1}$ with unit cell dimensions $a = 7.4257(3)$, $b = 9.9475(4)$, $c = 13.1021(5)$ Å, $\alpha = 71.954(1)°$, $\beta = 85.657(1)°$, $\gamma = 84.127(1)°$, $V = 914.38(6)$ Å^3, $Z = 2$, $R_1 = 0.0365$, $wR_2 = 0.0957$, $S = 1.039$. The tridentate aroylhydrazone ligands coordinate to the V center through azomethine nitrogen, phenolate oxygen, and enolate oxygen. The V atoms in the complexes are in octahedral coordination. Crystal structures of the complexes are stabilized by hydrogen bonds and $\pi\cdots\pi$ interactions.

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INTRODUCTION

Coordination chemistry of vanadium has attracted considerable attention due to its biochemical significance [1–3] as well as for the efficient catalytic properties in several organic synthesis procedures [4–7]. Aroylhydrazones are a kind of interesting ligand in coordination chemistry [8–10]. In recent years, a number of oxovanadium complexes with aroylhydrazones as ligands have been reported. During the search of literature, we found that most of the oxovanadium complexes with aroylhydrazone ligands are mononuclear, with solvent molecules or bidentate ligands completed the octahedral coordination [11–15]. Only a few examples are bridged by methanolate groups [16, 17]. Considering oxovanadium complexes with aroylhydrazone ligands have been reported to possess interesting biological activities [18, 19] and catalytic properties [20, 21], exploration of the synthesis and their detailed structures seems to be of particular importance. In this paper, a new methanolato-bridged dinuclear oxovanadium(V) complex $[VO(L)(OMe)]_2$ (**I**) and a new mononuclear oxovanadium(V) complex [VO(L')(OMe)(MeOH)] (**II**), where L and L' are the dianionic form of *N*'-(2-hydroxy-5-methylbenzylidene)-2-methylbenzohydrazide (H_2L) 3-chloro-*N*'-(2-hydroxy-3-methylbenzylidene)benzohydrazide (H_2L'), respectively, are presented.

EXPERIMENTAL

Materials and measurements. Commercially available 5-methylsalicylaldehyde, 3-methylsalicylaldehyde, 2-methylbenzohydrazide and 3-chlorobenzohydrazide were purchased from Aldrich and used without further purification. $[VO(Acac)_2]$ was purchased from Shenyang Haizhongtian Chemical Company. Other solvents and reagents were made in China and used as obtained. 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. Thermal stability analysis was performed on a PerkinElmer Pyris Diamond TG–DTA thermal analyses system.

Synthesis of H_2L. 5-Methylsalicylaldehyde (1.0 mmol, 0.14 g) and 2-methylbenzohydrazide (1.0 mmol, 0.15 g) were dissolved in methanol (30 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give colorless solution. The solution was left still in air to slow evaporate of most of the solvent, to give crystalline product of H_2L. The product was iso-

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lated by filtration and washed with cold methanol. The yield was 87%.

Selected IR data (KBr; ν, cm^{-1}): 3237 (N–H), 1641 (C=O), 1616 (C=N).

For $C_{16}H_{16}N_2O_2$

anal. calcd., %:	C, 71.62;	H, 6.01;	N, 10.44.
Found, %:	C, 71.53;	H, 6.12;	N, 10.55.

Synthesis of H_2L'. 3-Methylsalicylaldehyde (1.0 mmol, 0.14 g) and 3-chlorobenzohydrazide (1.0 mmol, 0.17 g) were dissolved in methanol (30 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give colorless solution. The solution was left still in air to slow evaporate of most of the solvent, to give crystalline product of H_2L. The product was isolated by filtration and washed with cold methanol. The yield was 81%.

Selected IR data (KBr; ν, cm^{-1}): 3228 (N–H), 1645 (C=O), 1613 (C=N).

For $C_{15}H_{13}ClN_2O_2$

anal. calcd., %:	C, 62.40;	H, 4.54;	N, 9.70.
Found, %:	C, 62.23;	H, 4.65;	N, 9.82.

Synthesis of I. A methanolic solution (10 mL) of [VO(Acac)$_2$] (0.1 mmol, 27.0 mg) was added to a methanolic solution (10 mL) of H_2L (0.1 mmol, 26.8 mg) with stirring. The mixture was stirred for 30 min 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 analysis were formed 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 67%.

Selected IR data (KBr; ν, cm^{-1}): 1607 (C=N), 976 (V=O).

For $C_{34}H_{34}N_4O_8V_2$

anal. calcd., %:	C, 56.05;	H, 4.70;	N, 7.69.
Found, %:	C, 55.89;	H, 4.77;	N, 7.54.

Synthesis of II. A methanolic solution (10 mL) of [VO(Acac)$_2$] (0.1 mmol, 27.0 mg) was added to a methanolic solution (10 mL) of H_2L (0.1 mmol, 28.9 mg) with stirring. The mixture was stirred for 30 min 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 analysis were formed 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 55%.

Selected IR data (KBr, ν, cm^{-1}): 1608 (C=N), 974 (V=O).

For $C_{34}H_{34}N_4O_8V_2$

anal. calcd., %:	C, 49.00;	H, 4.35;	N, 6.72.
Found, %:	C, 48.82;	H, 4.51;	N, 6.63.

X-ray diffraction. Diffraction intensities for the complexes **I**, **II** 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 SAINT [22], and multi-scan absorption corrections were performed using SADABS [23]. Structures of the complexes were solved by direct method and refined against F^2 by full-matrix least-squares methods using SHELXTL [24]. All of the non-hydrogen atoms were refined anisotropically. The methanol H atom in complex **II** was located from a difference Fourier map and refined isotropically with N–H distance restrained to 0.90 Å. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data for the complex 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 (CCDC nos. 974793 (**I**) and 974792 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The aroylhydrazone compounds were readily prepared by reaction of 5-methylsalicylaldehyde with 2-methylbenzohydrazide, and 3-methylsalicylaldehyde with 3-chlorobenzohydrazide in methanol. Replacement of two acetylacetonate ligands in [VO(Acac)$_2$] by aroylhydrazone ligands resulted in the oxovanadium(V) complexes. The dinegative aroylhydrazone ligands coordinated to the V atoms through the azomethine nitrogen, phenolate oxygen and enolate oxygen. The complexes are soluble in methanol, ethanol and acetonitrile. Molar conductance of complexes **I** and **II** at concentration of 10^{-4} mol/L are 45 and 30 Ω^{-1} cm^2 mol^{-1}, indicating their non-electrolyte nature [25].

Molecular structure and atom numbering scheme of complex **I** are shown in Fig. 1a. The complex possesses a crystallographic inversion center symmetry between two V atoms. The V atom in the complex is in octahedral coordination, with the azomethine N, phenolate O, and enolate O atoms of the aroylhydrazone ligand, as well as one methanolate O atom defining the equatorial plane, and with the other methanolate O atom and an oxo O atom locating at the axial positions. The V atoms deviate from the least-squares planes defined by the equatorial atoms by 0.333(1) Å. Coordinate bond lengths in complex **I** are similar to those observed in vanadium complexes with aroylhy-

Table 1. Crystallographic and experimental data for complexes **I** and **II**

Parameter	Value	
	I	**II**
Fw	728.5	416.7
Crystal shape/color	Block/brown	Block/brown
Crystal size/mm	0.17 × 0.15 × 0.15	0.13 × 0.10 × 0.10
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.5063(4)	7.4257(3)
b, Å	9.5367(4)	9.9475(4)
c, Å	11.2445(5)	13.1021(5)
α, deg	71.740(1)	71.954(1)
β, deg	72.341(1)	85.657(1)
γ, deg	74.509(1)	84.127(1)
V, Å^3	810.37(6)	914.38(6)
Z	1	2
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	0.636	0.719
ρ, g cm^{-3}	1.493	1.514
Reflections/parameters	2912/220	3706/241
Independent reflections	2701	3453
Restraints	0	1
Index ranges h, k, l	$-9 \le h \le 10$, $-11 \le k \le 10$, $-13 \le l \le 13$	$-9 \le h \le 8$, $-12 \le k \le 12$, $-16 \le l \le 14$
F(000)	376	428
$T_{\mathrm{min}}/T_{\mathrm{max}}$	0.8996/0.9107	0.9123/0.9316
Goodness of fit on F^2	0.969	1.039
R_1, wR_2 ($I \ge 2\sigma(I)$)*	0.0527, 0.1316	0.0365, 0.0957
R_1, wR_2 (all data)*	0.0561, 0.1350	0.0392, 0.0983

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

drazone ligands [16, 17]. Distortion of the octahedral coordination can be observed from the coordinate bond angles, ranging from 73.9(1)° to 106.8(1)° for the perpendicular angles and from 150.3(1)° to 176.2(1)° for the diagonal angles. The dihedral angle between the aromatic rings of the aroylhydrazone ligand is 16.9(3)°. Weak coordination of the methanolate ligand at *trans* to the oxo group is not uncommon in the vanadium complexes with tridentate ligands when they are synthesized or crystallized in methanol [16, 17].

In the crystal structure of complex **I** (Fig. 2a), molecules are stacked along the y axis through π···π interactions (centroid to centroid distances: 2.695(3) Å (Cg1···Cg2), 4.361(3) Å (Cg2···Cg4$^{\mathrm{i}}$), 4.053(3) Å (Cg3···Cg4$^{\mathrm{ii}}$), 4.470(3) Å (Cg4···Cg4$^{\mathrm{i}}$); symmetry codes: $^{\mathrm{i}}$ $-x$, $-y$, $1 - z$; $^{\mathrm{ii}}$ x, $1 + y$, z; Cg1, Cg2, Cg3, and Cg4 are the centroids of V(1)–O(4)–V(1*A*)–O(4*A*), V(1)–O(2)–C(9)–N(2)–N(1), C(1)–C(2)–C(3)–C(4)–C(5)–C(6), and C(10)–C(11)–C(12)–C(13)–C(14)–C(15), respectively).

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 phenolate O, azomethine N, and enolate O atoms of the aroylhydrazone ligand as well as the methanolate O atom defining the equatorial plane, and with the methanol O atom and an oxo O atom locating at the axial positions. The V atom deviates from the least-squares plane defined by the equatorial atoms by 0.318(1) Å. The coordinate bond lengths in complex **II** are similar to those observed in vanadium complexes with hydrazone ligands [22–24]. The distortion of the octahedral coordination can be observed from the coordinate bond angles, ranging from 73.94(5)° to 102.80(7)° for the perpendicular angles, and from 151.19(6)° to 175.49(6)° for the diagonal angles. The dihedral angle

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

Bond	*d*, Å	Bond	*d*, Å
I			
V(1)–O(1)	1.836(2)	V(1)–O(2)	1.930(2)
V(1)–O(3)	1.581(2)	V(1)–O(4)	2.371(2)
V(1)–O(4*A*)	1.832(2)	V(1)–N(1)	2.105(2)
II			
V(1)–O(1)	1.845(1)	V(1)–O(2)	1.945(1)
V(1)–O(3)	2.401(1)	V(1)–O(4)	1.764(1)
V(1)–O(5)	1.587(1)	V(1)–N(1)	2.129(1)
Angle	ω, deg	Angle	ω, deg
I			
O(3)V(1)O(4*A*)	101.7(1)	O(3)V(1)O(1)	101.2(1)
O(4*A*)V(1)O(1)	106.8(1)	O(3)V(1)O(2)	100.1(1)
O(4*A*)V(1)O(2)	88.7(1)	O(1)V(1)O(2)	150.3(1)
O(3)V(1)N(1)	96.1(1)	O(4*A*)V(1)N(1)	157.1(1)
O(1)V(1)N(1)	83.4(1)	O(2)V(1)N(1)	73.9(1)
O(3)V(1)O(4)	176.2(1)	O(4)V(1)O(4*A*)	74.6(1)
O(1)V(1)O(4)	80.6(1)	O(2)V(1)O(4)	79.4(1)
N(1)V(1)O(4)	87.4(1)		
II			
O(5)V(1)O(4)	102.80(7)	O(5)V(1)O(1)	100.22(7)
O(4)V(1)O(1)	101.47(6)	O(5)V(1)O(2)	98.99(7)
O(4)V(1)O(2)	94.94(6)	O(1)V(1)O(2)	151.19(6)
O(5)V(1)N(1)	95.17(7)	O(4)V(1)N(1)	160.24(6)
O(1)V(1)N(1)	83.10(6)	O(2)V(1)N(1)	73.94(5)
O(5)V(1)O(3)	175.49(6)	O(4)V(1)O(3)	81.20(6)
O(1)V(1)O(3)	80.87(6)	O(2)V(1)O(3)	78.43(6)
N(1)V(1)O(3)	80.58(5)		

between the aromatic rings of the aroylhydrazone ligand is 12.7(2)°. Weak coordination of methanol at *trans* to the oxo group is not uncommon in the vanadium complexes with tridentate ligands when they are synthesized or crystallized in methanol [24].

In the crystal structure of complex **II**, molecules are linked through intermolecular O–H···N hydrogen bonds (O(3)–H(3) 0.85(1), H(3)···N(2)^i 2.06(1), O(3)···N(2)^i 2.898(2) Å, O(3)–H(3)···N(2)^i 171(3)°; symmetry code: ^{i} $2 - x, 2 - y, 1 - z$), to dimeric structure (Fig. 2b).

The non-observation of the ν(C=O) bands, presents in the free aroylhydrazones H_2L and H_2L' at 1641 and 1645 cm^{-1} [26], indicate the enolization of the amide functionality upon coordination to the V cen-

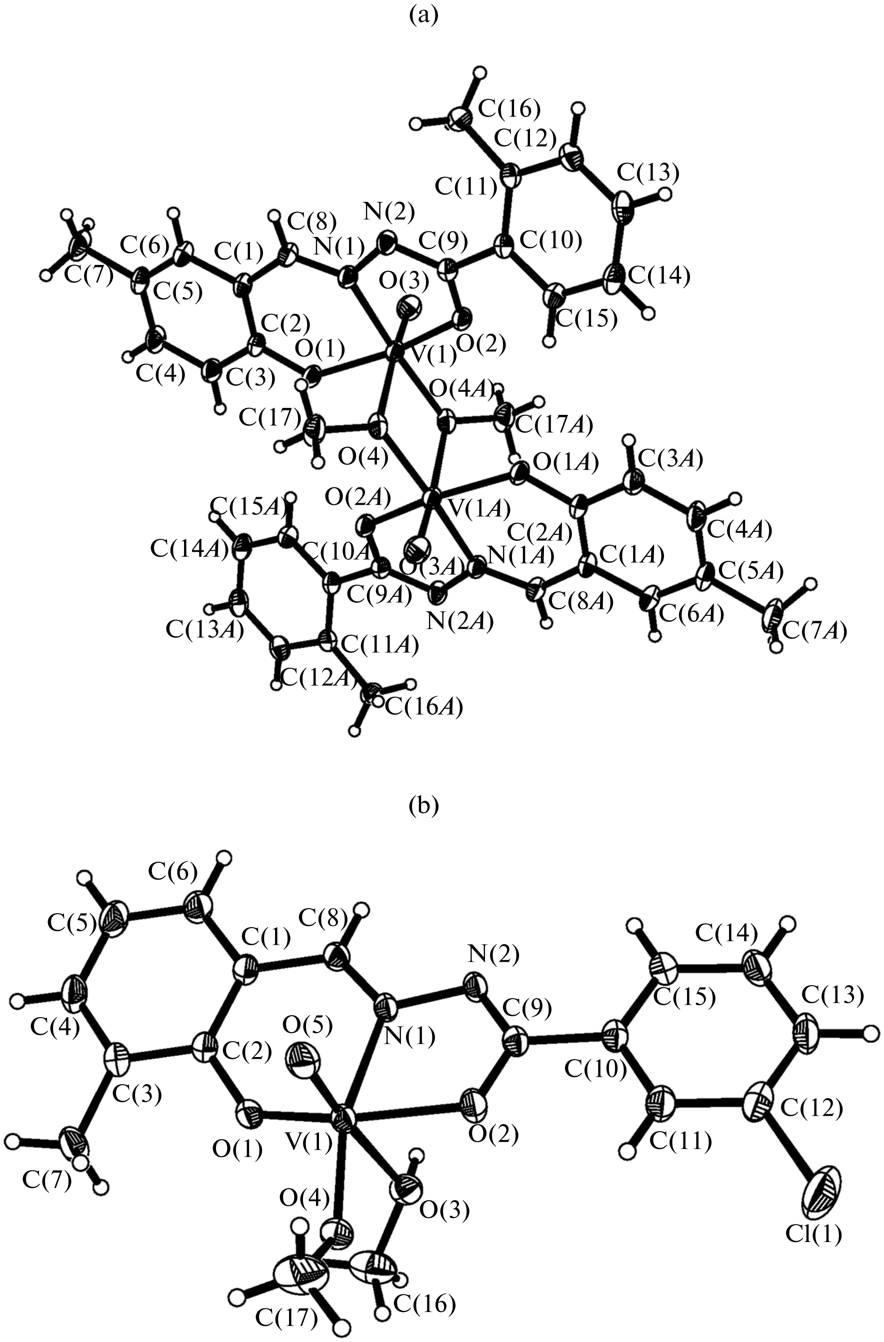

Fig. 1. Molecular structures of complexes **I** (a) and **II** (b) at 30% probability displacement. Code symmetry: (*A*) $-x, -y, 2-z$ for **I**.

ter. Instead strong bands at about 1607 cm^{-1} are observed, which can be attributed to the asymmetric stretching vibration of the conjugated CH=N–N=C groups, characteristic for the coordination of the enolate form of the aroylhydrazone ligands [27]. The shift of ν(C=N) and the disappearance of ν(N–H) are in agreement with tridentate coordination through the carbonylic oxygen, the azomethyne nitrogen and the phenolic oxygen. The strong ν(V=O) at about 975 cm^{-1} can be clearly identified for the complexes [28].

Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complexes. Complex **I** start to decompose at 140°C and completed at 505°C (Fig. 3a). The final product is in accordance with V_2O_5. The total weight loss of 75.9% is close to the calculated value of 75.1%.

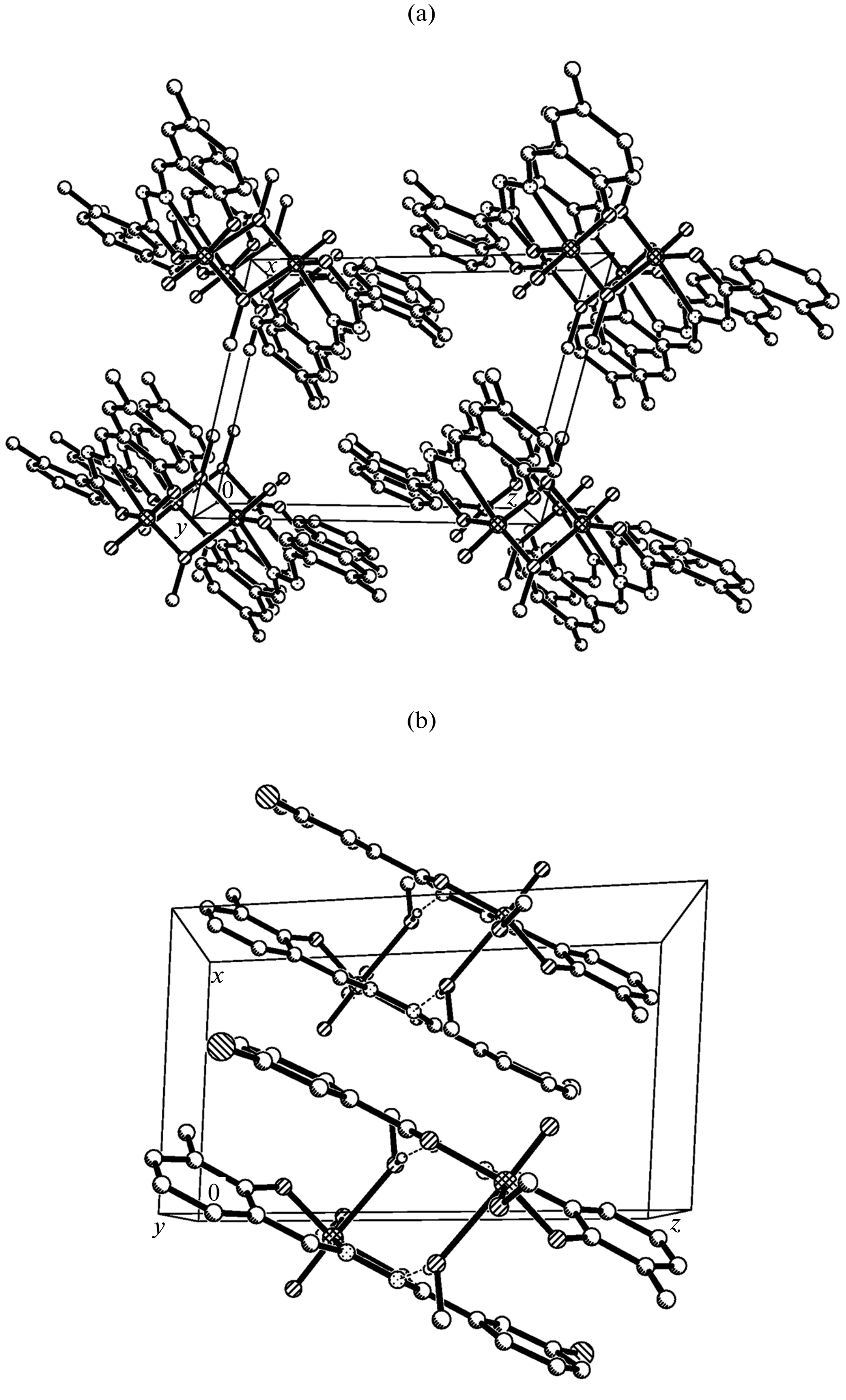

Fig. 2. Molecular packing structures of complexes **I** (a) and **II** (b). Hydrogen bonds in **II** are drawn as dashed lines. Hydrogen atoms not related to hydrogen bonds are omitted for clarity.

For complex **II** (Fig. 3b), the first step started from 85°C and ended at 125°C, corresponding to the loss of the methanol ligand. The observed weight loss of 7.6% is close to the calculated value of 7.7%. The second step started from 125°C and ended at 217°C, corresponding to the loss of the methanolate ligand. The observed weight loss of 7.3% is close to the calculated value of 7.4%. The last step, from 270 to 500°C, corresponds to the loss of the aroylhydrazone ligand, and the formation of the final product (V_2O_5). The total

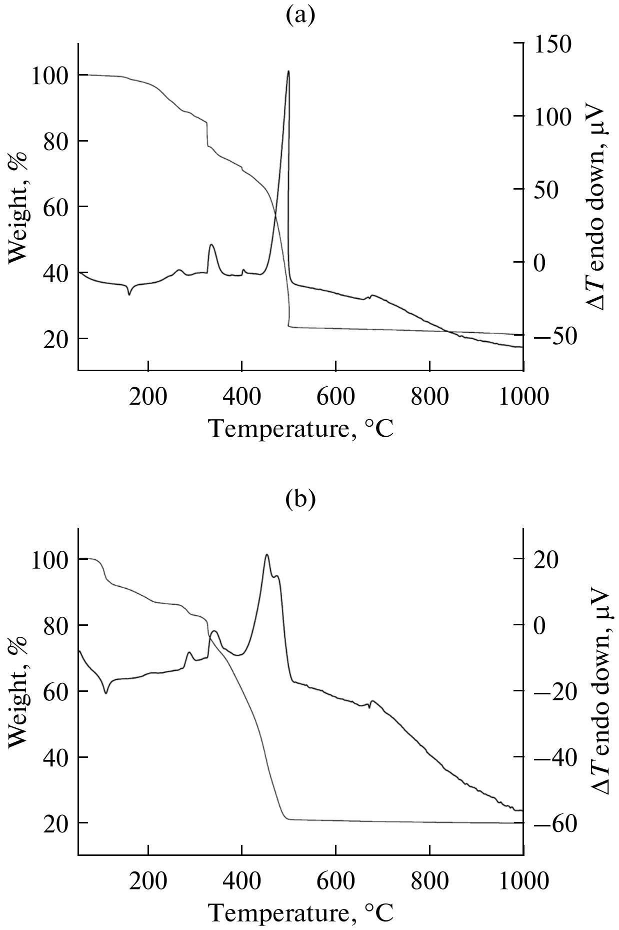

Fig. 3. DT–TGA curves of complexes **I** (a) and **II** (b).

weight loss of 78.5% is close to the calculated value of 78.2%.

REFERENCES

1. Guilherme, L.R., Massabni, A.C., Cuin, A., et al., *J. Coord. Chem.*, 2009, vol. 62, no. 10, p. 1561.
2. Ashiq, U., Ara, R., Mahroof-Tahir, M., et al., *Chem. Biodivers.*, 2008, vol. 5, no. 1, p. 82.
3. Monga, V., Thompson, K.H., Yuen, V.G., et al., *Inorg. Chem.*, 2005, vol. 44, no. 8, p. 2678.
4. Rostami, A. and Atashkar, B., *Catal. Commun.*, 2015, vol. 58, p. 80.
5. Pradhan, M., Roy, A., Sinha, A.K., et al., *Dalton Trans.*, 2015, vol. 44, no. 4, p. 1889.
6. Ebrahimipour, S.Y., Abaszadeh, M., Castro, J., et al., *Polyhedron*, 2014, vol. 79, p. 138.
7. Saha, U., Si, T.K., Nandi, P.K., et al., *Inorg. Chem. Commun.*, 2013, vol. 38, p. 43.
8. Adly, O.M.I. and Emara, A.A.A., *Spectrochim. Acta, A*, 2014, vol. 132, p. 91.
9. Alagesan, M., Sathyadevi, P., Krishnamoorthy, P., et al., *Dalton Trans.*, 2014, vol. 43, no. 42, p. 15829.
10. Vrdoljak, V., Pisk, J., Agustin, D., et al., *New J. Chem.*, 2014, vol. 38, no. 12, p. 6176.
11. Gao, S., Weng, Z.-Q., and Liu, S.-X., *Polyhedron*, 1998, vol. 17, no. 20, p. 3595.
12. You, Z.-L., Shi, D.-H., Zhang, J.-C., et al., *Inorg. Chim. Acta*, 2012, vol. 384, no. 1, p. 54.
13. Lalami, N.A., Monfared, H.H., Noei, H., et al., *Transition Met. Chem.*, 2011, vol. 36, no. 6, p. 669.
14. Sangeetha, N.R., Kavita, V., Wocadlo, S., et al., *J. Coord. Chem.*, 2000, vol. 51, no. 1, p. 55.
15. Mandal, T.N., Roy, S., Barik, A.K., et al., *Polyhedron*, 2008, vol. 27, no. 15, p. 3267.
16. Seena, E.B., Mathew, N., Kuriakose, M., et al., *Polyhedron*, 2008, vol. 27, no. 5, p. 1455.
17. Mondal, B., Drew, M.G.B., Banerjee, R., et al., *Polyhedron*, 2008, vol. 27, no. 15, p. 3197.
18. Nair, R.S., Kuriakose, M., Somasundaram, V., et al., *Life Sci.*, 2014, vol. 116, no. 2, p. 90.
19. Huo, Y., Ye, Y.-T., Cheng, X.-S., et al., *Inorg. Chem. Commun.*, 2014, vol. 45, p. 131.
20. Li, A.-M., *J. Coord. Chem.*, 2014, vol. 67, no. 12, p. 2076.
21. Yang, K.-H., *Acta Chim. Slov.*, 2014, vol. 61, no. 4, p. 629.
22. *SMART and SAINT*, Madison (WI, USA): Bruker AXS Inc., 2002.
23. Sheldrick, G.M., *SADABS, Program for Empirical Absorption Correction of Area Detector*, Göttingen (Germany): Univ. of Göttingen, 1996.
24. Sheldrick, G.M., *Acta Crystallogr., A*, 2008, vol. 64, no. 2, p. 112.
25. Geary, W.J., *Coord. Chem. Rev.*, 1971, vol. 7, no. 1, p. 81.
26. Galić, N., Perić, B., Kojić-Prodić, B., et al., *J. Mol. Struct.*, 2001, vol. 559, nos. 1–3, p. 187.
27. Sarkar, A. and Pal, S., *Inorg. Chim. Acta*, 2008, vol. 361, no. 8, p. 2296.
28. Sarkar, A. and Pal, S., *Polyhedron*, 2006, vol. 25, no. 7, p. 1689.