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Mono- and Dinuclear Vanadium Complexes with the Pentadentate Schiff Base 2,6-Diacetylpyridine Bis(nicotinylhydrazone): Synthesis and Structures

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Abstract—A reaction between $VOSO_4$, 2,6-diacetylpyridine, and nicotinohydrazide in a molar ratio of 1 : 1 : 2 afforded two complexes differing in both color and crystal shape as well as in chemical composition and molecular structure. The compositions and structures of the vanadium complexes were determined by IR spectroscopy and X-ray diffraction (CIF files CCDC nos. 1411235 (**I**) and 1411236 (**II**)). These complexes can be formulated as $[V_2^{II}(H_2L)_2](NO_3)_4 \cdot H_2O$ (**I**) and $[V^{IV}(=O)(H_2L)(SO_4)] \cdot 5H_2O$ (**II**), where H_2L is 2,6-diacetylpyridine bis(nicotinylhydrazone). Complex **I** consists of centrosymmetric dinuclear complex cations $[V_2(H_2L)_2]^{4+}$, NO_3^- anions, and crystal water molecules in a ratio of 1 : 4 : 1; complex **II** is built from molecular V(IV) complexes and crystal water molecules in a ratio of 1 : 5. The coordination polyhedron of the metal atom in **I** is a tetragonal pyramid made up of the electron-donating atoms N_3O_2 of two ligands H_2L. The coordination polyhedron of the metal atom in **II** is a pentagonal bipyramid made up of the electron-donating atoms N_3O_2 of one neutral five-coordinate ligand H_2L and two O atoms coming from the oxo ligand and the SO_4^{2-} anion coordinated in a monodentate fashion.

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INTRODUCTION

Transition metal complexes with polydentate Schiff bases are promising objects of coordination chemistry [1, 2]. The design of polydentate organic ligands is known to often involve activation of certain functional groups in molecules during their coordination, because chelation to a complexing ion is thermodynamically more favorable than monodentate coordination of individual ligands containing the same electron-donating atoms. Nitrogen-containing ligands are mostly synthesized by matrix-assisted reactions [3]. In our studies, we used vanadyl(II) as a central ion: vanadium still remains an attractive metal for coordination chemists, not least because this element is found at active sites of several enzymes (e.g., peroxidase [4]). To understand better the function of this metal in living organisms, the structures, reactivities, and spectroscopic and catalytic properties of many vanadium complexes are being investigated [5–10].

A reaction of vanadyl(II) sulfate ($VOSO_4$) with 2,6-diacetylpyridine and nicotinohydrazide in a molar ratio of 1 : 1 : 2 gave crystalline complexes of two types containing a ligand assembled by condensation of the two organic molecules. The compositions of the crystals were roughly determined by IR spectroscopy; their exact compositions and structures were identified by X-ray diffraction: $[V_2^{II}(H_2L)_2](NO_3)_4 \cdot H_2O$ (**I**) and $[V^{IV}(=O)(H_2L)(SO_4)] \cdot 5H_2O$ (**II**), where H_2L is the Schiff base 2,6-diacetylpyridine bis(nicotinylhydrazone).

A survey of the Cambridge Structural Database (CSD) [11] revealed several mononuclear transition metal complexes with a ligand of this class; they mainly feature benzoic [12–14] or picolinic acid hydrazones [15, 16] as terminal fragments. Note that the CSD contains only vanadium complexes with salicylaldehyde benzoylhydrazone and salicylaldehyde nicotinylhydrazone [17, 18].

EXPERIMENTAL

Synthesis of H_2L. A mixture of 2,6-diacetylpyridine and isonicotinohydrazide was refluxed in methanol for 3 h. The condensation product (ligand H_2L) was used for comparative analysis of vanadium complexes **I** and **II** by IR spectroscopy.

IR (cm^{-1}): 3400 br. w, 3182 m, 3100–2800 (seven bands) w, 1663 s, 1614 m, 1591 m, 1567 s, 1518 m, 1487 m, 1443 m, 1416 s, 1385 s, 1375 m, 1327 m, 1299 m, 1280 m, 1258 m, 1196 m, 1161 s, 1139 m, 1119 m, 1087 m, 1030 m, 994 w, 950 w, 931 w, 916 w, 864 w, 815 m,

Table 1. Crystallographic parameters and the data collection and refinement statistics for structures **I** and **II**

Parameter	Value	
	I	**II**
Molecular formula	$C_{42}H_{39}N_{18}O_{17}V_2$	$C_{21}H_{29}N_7O_{12}SV$
M	1169.79	654.51
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a, Å	17.1607(16)	10.7647(4)
b, Å	28.3964(13)	9.9740(5)
c, Å	14.1062(13)	25.4131(9)
β, deg	127.368(15)	91.485(3)
V, Å^3	5463.1(8)	2727.6(2)
Z	4	4
ρ_{calcd}, g/cm^3	1.422	1.594
μ, mm^{-1}	0.426	0.516
F(000)	2396	1356
Crystal dimensions, mm	0.2 × 0.12 × 0.08	0.15 × 0.12 × 0.09
θ Scan range, deg	2.99–25.00	3.02–25.05
Ranges of h, k, l indices	$-13 \leqslant h \leqslant 20$ $-27 \leqslant k \leqslant 33$ $-16 \leqslant l \leqslant 16$	$-12 \leqslant h \leqslant 12$ $-10 \leqslant k \leqslant 11$ $-30 \leqslant l \leqslant 29$
Number of measured/unique reflections (R_{int})	10020/4430 (0.0497)	8778/4798 (0.0576)
Number of reflections with $I > 2\sigma(I)$	1966	2872
Number of parameters refined	367	406
GOOF	1.008	1.014
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0808$, $wR_2 = 0.2013$	$R_1 = 0.0674$, $wR_2 = 0.1240$
R factor (for all reflections)	$R_1 = 0.1551$, $wR_2 = 0.2182$	$R_1 = 0.1242$, $wR_2 = 0.1481$
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.723, –0.538	0.405, –0.560

792 m, 766 w, 735 s, 701 s, 677 w, 667 w, 656 w, 642 m, 627 w, 598 w, 585 w, 536 w, 508 w, 432 w, 421 w.

Synthesis of complexes I and II. Vanadyl sulfate trihydrate (0.11 g, 0.5 mmol) was dissolved in ethanol–water (5 : 2 v/v, 14 mL) (solution 1). 2,6-Diacetylpyridine (0.08 g, 0.5 mmol) was dissolved in ethanol (10 mL) (solution 2). Nicotinohydrazide (0.14 g, 1 mmol) was dissolved in ethanol (20 mL) (solution 3). Solutions 1 and 2 were simultaneously added to continuously stirred solution 3. The dark brown reaction mixture was heated (50°C) under reflux for 3 h, filtrated, and left for room-temperature crystallization in air. After 24 h, dark brown product **I** began to form as fine crystals and so did larger ruby crystals of complex **II** after two weeks; the latter were suitable for X-ray diffraction.

Complex **I**. IR (cm^{-1}): 3373 m, 3188 m, 3084 m, 2410 br. w, 1924: br. w, 1661 w, 1616 m, 1593 s, 1584 s, 1525 s, 1510 s, 1485 w, 1442 w, 1414 m, 1374 s, 1277 m, 1196 m, 1165 s, 1145 s, 1118 s, 1095 s, 1047 s, 1028 s, 1000 m, 968 s, 917 m, 868 w, 829 w, 810 m, 768 w, 715 s, 695 m, 642 m, 583 m, 553 m, 515 w, 505 w, 467 m, 457 m.

X-ray diffraction study. Experimental sets of reflection intensities for complexes **I** and **II** were collected at room temperature on an Xcalibur E diffractometer equipped with a CCD detector (MoK_α radiation, graphite monochromator). Structures **I** and **II** were solved by direct methods and refined by the least-squares method, mainly in an anisotropic full-matrix approximation for non-hydrogen atoms (SHELX-97) [19]. The hydrogen atoms of water molecules were located partially in difference electron-density maps and partially from theoretical considerations because the water molecules in both complexes are disordered over several positions. In structure **I**, the NO_3^- anions are also disordered. The other hydrogen atoms were located geometrically and refined isotropically using a rigid body model with $U_H = 1.2U_{equiv}$ or $1.5U_{equiv}$ (U_{equiv} relate to the parent O, N, and C atoms).

Crystallographic parameters and the data collection and refinement statistics for structures **I** and **II** are

Table 2. Selected bond lengths and bond angles in structures **I** and **II**

Bond	*d*, Å		Bond	*d*, Å	
	I	**II**		**I**	**II**
V(1)–O(1)	1.982(5)	1.985(3)	N(1)–C(5)	1.338(10)	1.329(5)
V(1)–O(2)	2.146(6)	1.971(3)	N(2)–N(3)	1.397(8)	1.394(5)
V(1)–O(3)		2.094(3)	N(3)–C(7)	1.284(8)	1.292(5)
V(1)–O(7)		1.594(3)	N(4)–C(8)	1.386(9)	1.334(6)
V(1)–N(3)	1.918(6)	2.125(4)	N(4)–C(12)	1.349(9)	1.338(6)
V(1)–N(4)	2.138(6)	2.129(4)	N(5)–C(13)	1.312(9)	1.288(5)
V(1)–N(5)	1.986(7)	2.122(4)	N(5)–N(6)	1.386(9)	1.368(5)
O(1)–C(6)	1.290(8)	1.288(5)	N(6)–C(14)	1.328(10)	1.292(5)
O(2)–C(14)	1.278(10)	1.291(5)	N(7)–C(18)/C(16)	1.15(3)	1.335(6)
N(1)–C(4)	1.319(12)	1.334(7)	N(7)–C(19)/C(17)	1.27(1)	1.342(6)

Angle	ω, deg		Angle	ω, deg	
	I	**II**		**I**	**II**
O(1)V(1)O(2)	106.2(2)	72.1(1)	C(8)N(4)C(12)	117.6(6)	120.0(4)
O(1)V(1)O(3)		87.5(1)	C(8)N(4)V(1)	108.3(5)	120.2(3)
O(1)V(1)O(7)		97.7(2)	C(12)N(4)V(1)	130.6(5)	119.8(3)
O(1)V(1)N(3)	80.3(2)	72.2(1)	C(13)N(5)N(6)	118.6(7)	119.2(4)
O(1)V(1)N(4)	156.6(2)	142.5(1)	C(13)N(5)V(1)	125.4(5)	123.6(3)
O(1)V(1)N(5)	95.5(3)	144.0(2)	N(6)N(5)V(1)	115.9(6)	117.2(3)
O(2)V(1)O(3)		89.0(1)	C(14)N(6)N(5)	111.6(8)	108.8(4)
O(2)V(1)O(7)		97.3(2)	C(6)O(1)V(1)	109.5(4)	118.4(3)
O(2)/O(2)$^{\#}$V(1)N(3)	114.0(2)	144.1(1)	C(14)O(2)V(1)	107.8(6)	119.3(3)
O(2)/O(2)$^{\#}$V(1)N(4)	90.6(2)	143.3(2)	N(1)C(4)C(3)	120.9(10)	119.9(5)
O(2)/O(2)$^{\#}$V(1)N(5)	77.7(3)	72.4(1)	N(1)C(5)C(1)	121.0(9)	119.8(5)
O(3)V(1)O(7)		172.9(1)	O(1)C(6)N(2)	125.3(7)	124.7(4)
O(3)V(1)N(3)		85.7(1)	O(1)C(6)C(1)	118.4(7)	116.5(4)
O(3)V(1)N(4)		82.9(1)	N(2)C(6)C(1)	116.3(7)	118.8(4)
O(3)V(1)N(5)		85.4(1)	N(3)C(7)C(8)	112.9(7)	111.4(4)
O(7)V(1)N(3)		91.2(2)	N(3)C(7)C(21)	124.7(7)	124.2(5)
O(7)V(1)N(4)		90.0(2)	N(4)C(8)C(9)	121.2(7)	121.2(5)
O(7)V(1)N(5)		93.1(2)	N(4)C(8)C(7)	114.6(6)	113.7(4)
N(3)V(1)N(4)	78.0(3)	71.1(2)	N(4)C(12)C(11)	123.4(7)	121.1(5)
N(3)V(1)N(5)	168.2(3)	142.1(2)	N(4)C(12)C(13)	117.6(7)	113.8(4)
N(4)V(1)N(5)	104.3(3)	71.3(2)	N(5)C(13)C(12)	115.0(7)	111.4(4)
C(4)N(1)C(5)	121.4(10)	122.4(5)	N(5)C(13)C(20)/C(21)	121.2(8)	125.2(5)
C(6)N(2)N(3)	108.3(6)	105.6(4)	O(2)C(14)N(6)	125.5(8)	121.8(5)
C(7)N(3)N(2)	121.2(6)	117.8(4)	O(2)C(14)C(15)	121.1(10)	117.6(4)
C(7)N(3)V(1)	122.3(5)	123.5(3)	N(6)C(14)C(15)	113.4(10)	120.6(5)
N(2)N(3)V(1)	116.3(5)	118.7(3)			

Table 3. Geometrical parameters of the intermolecular hydrogen bonds in structures **I** and **II**

D–H···A	Distance, Å			Angle DHA, deg	Symmetry operation for A
			I		
N(1)–H(1)···O(2N)	0.86	1.86	2.72(2)	171	*x*, *y*, *z* + 1
N(1)–H(1)···O(2N*A*)	0.86	1.78	2.60(2)	161	*x*, *y*, *z* + 1
N(1)–H(1)···O(1N*B*)	0.86	2.07	2.84(3)	150	*x*, *y*, *z* + 1
N(1)–H(1)···O(3N*B*)	0.86	2.14	2.85(4)	139	*x*, *y*, *z* + 1
N(7)–H(1)···O(4N)	0.86	2.24	3.08(3)	165	*x*, *y*, *z*
N(7)–H(1)···O(4N*A*)	0.86	1.86	2.63(2)	149	*x*, *y*, *z*
O(3*w*)–H(1)···O(4N)	0.84	2.01	2.85(6)	174	*x* + 1/2, –*y* + 1/2, *z* – 1/2
O(3*w*)–H(21)···O(1N)	0.79	2.03	2.81(6)	172	*x*, *y*, *z*
			II		
N(1)–H(1)···O(4)	0.86	1.89	2.734(6)	168	–*x* + 1, –*y* + 1, –*z* + 1
O(1*w*)–H(1)···O(5)	0.85	2.00	2.850(5)	175	–*x* + 3/2, *y* – 1/2, –*z* + 1/2
O(1*w*)–H(2)···O(7*w*)	0.86	2.42	3.20(2)	152	–*x* + 3/2, *y* – 1/2, –*z* + 1/2
O(2*w*)–H(1)···O(6)	0.85	2.05	2.842(6)	152	*x*, *y*, *z*
O(2*w*)–H(2)···O(4)	0.86	2.10	2.928(5)	161	–*x* + 1/2, *y* – 1/2, –*z* + 1/2
O(3*w*)–H(1)···O(2*w*)	0.86	2.07	2.898(6)	160	*x* – 1/2, –*y* + 1/2, *z* + 1/2
O(3*w*)–H(2)···N(7)	0.85	1.96	2.810(6)	176	*x*, *y*, *z*
O(4*w*)–H(1)···O(2*w*)	0.84	2.03	2.86(1)	167	*x*, *y*, *z*
O(4*w*)–H(2)···O(1*w*)	0.85	2.17	2.966(9)	156	*x*, *y*, *z*
O(5*w*)–H(1)···O(5)	0.86	2.06	2.83(5)	149	–*x* + 3/2, *y* – 1/2, –*z* + 1/2
O(5*w*)–H(2)···O(7*w*)	0.85	2.20	3.02(5)	165	*x*, *y*, *z*
O(5*w*)–H(2)···O(4*w*)	0.85	2.20	3.01(4)	161	*x*, *y*, *z*
O(6*w*)–H(1)···O(5)	0.85	2.03	2.85(3)	162	–*x* + 3/2, *y* – 1/2, –*z* + 1/2
O(6*w*)–H(2)···O(7*w*)	0.86	2.16	2.94(4)	152	*x*, *y*, *z*
O(6*w*)–H(2)···O(4*w*)	0.86	2.06	2.90(3)	165	*x*, *y*, *z*
O(7*w*)–H(1)···O(1*w*)	0.88	1.81	2.42(2)	125	*x*, *y*, *z*
O(7*w*)–H(1)···O(6*w*)	0.81	2.21	2.94(4)	151	*x*, *y*, *z*
O(8*w*)–H(1)···O(1)	0.88	2.50	3.17(3)	134	*x* + 1/2, –*y* + 1/2, *z* – 1/2
O(8*w*)–H(2)···O(5)	0.89	2.09	2.77(3)	133	–*x* + 3/2, *y* – 1/2, –*z* + 1/2

summarized in Table 1; selected bond lengths and bond angles are listed in Table 2. The geometrical parameters of intermolecular hydrogen bonds are given in Table 3. The atomic coordinates and thermal parameters for structures **I** and **II** have been deposited with the Cambridge Structural Database (CCDC nos. 1411235 (**I**) and 1411236 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In the IR spectrum of H_2L, an easily identified medium-intensity band at 3182 cm^{-1} is due to the NH stretching vibrations [20]. This band is of importance in determining the state of the ligand H_2L in complexes **I** and **II** because the migration of the labile H atom to the carbonyl group changes the ligand from the ketone tautomer to an enol and its further migration to the heterocyclic N atom of the hydrazine fragment changes the ligand to the zwitterionic form. A set of seven bands with different (from medium to weak) intensities at 3100–2800 cm^{-1} are due to the C–H stretching vibrations. A band at 1663 cm^{-1} (ν(C=O) stretches, amide I), which is the most intense and informative in the spectrum, shows whether this carbonyl group is involved in the coordination to the metal center or/and is enolized to form a C–O bond. The medium-intensity band at 1614 cm^{-1} is indicative of the ν(CN) vibrations of the heterocycle. The vibrations of the pyridine ring are manifested as a set of bands at 1617 cm^{-1} (complex-shaped), 1567 (complex-shaped), 1486, and 792 cm^{-1} [21]. The medium-intensity bands at 1591 cm^{-1} are due to the ν(C=N) stretching vibrations of the azomethine group. The vibrations of the group amide II (δ(NH) + ν(C=N)) appear as a complex-shaped intense band at 1567 cm^{-1}. The medium- and high-intensity bands at 1443 and 1385 cm^{-1} are due to the bending vibrations of the Me groups (δ_{as}(Me) and δ_s(Me), respectively). An intense band at 1299 cm^{-1} (ν(C–N)) and a medium-intensity band at 1258 cm^{-1} (amide III) were also identified. The intense band at 1416 cm^{-1} can be assigned to the vibrations produced by interactions of the groups ν(C=N) and ν(C=C) [21]. The N–N stretching vibrations are manifested as an intense band at 1161 cm^{-1}. In the spectrum of H_2L, the in-plane C–H bending vibrations for substitution of the types 1, 2, 3 (central pyridine ring) and 1, 3 (terminal pyridine rings) appear at 1139, 1087, and 1030 cm^{-1}; the out-of-plane C–H bending vibrations for three adjacent and one isolated H atom appear at 766 and 864 cm^{-1}, respectively [21].

The IR spectrum of complex **I** shows no absorption band characteristic of V=O, which is most often very intense and appears at 930–1020 cm^{-1} for monomeric compounds and at 840–890 cm^{-1} for polymers [22, 23]. This provides evidence for the absence of the V=O group from complex **I**. Nor does the spectrum of complex **I** contain the ν(C=O) band, which appears as an intense signal at 1663 cm^{-1} in the spectrum of free H_2L. Therefore, the ligand H_2L is coordinated to the metal center in the enol form resulting from the proton migration =N–NH–C(=O)– → =N–N=C(–OH)–. The wide bands of medium and weak intensities at 2409 and 1924 cm^{-1} are probably due to proton migration to the heterocyclic N atoms of the terminal pyridine rings to give PyH^+ [21]. The wide bands at 3373 and 3188 cm^{-1} relate to the OH stretching vibrations and the ν(N–H) of the hydrogen bond N–H···O. The wide intense band at 3084 cm^{-1} is partially contributed by the C–H stretching vibrations of the complex. The most intense band in the spectrum at 1374 cm^{-1} can be assigned to the δ_s(Me) vibrations [24] as well as to the vibrations of free NO_3^- anions [24, 25]. Another medium-intensity band at 810 cm^{-1} is also attributable to the NO_3^- vibrations [26]. The spectrum of complex **I** shows new absorption bands at 600–400 cm^{-1}, which are not characteristic of free H_2L and are due to the V–N (552 and 515 cm^{-1}) and V–O vibrations (467 and 457 cm^{-1}).

Complex **I** has an ionic structure. Its crystals are built from centrosymmetric dinuclear cations $[V_2(H_2L)_2]^{4+}$ (Fig. 1), the NO_3^- anions, and crystal water molecules in a ratio of 1 : 4 : 1. The initial reaction mixture contains no NO_3^- anions, so the formation of the latter most likely results from complex transformations (i.e., redox processes involving nicotinohydrazide and vanadium(IV) ions). The dinuclear complex cation $[V_2(H_2L)_2]^{4+}$ has a double helical structure in which two organic neutral ligands H_2L are coordinated to two metal atoms and lie along the axis V(1)–V(1)* ($-x + 1, y, -z + 3/2$). The V···V* distance in the dinuclear cation is 3.261 Å. Either ligand H_2L is coordinated to the V atom in a pentadentate-tridentate fashion through the electron-donating atoms N_2O and to the V* atom in a bidentate fashion through the atoms NO. A similar coordination has been found earlier in dinuclear Cu(II) complexes with diacetylpyridine bis(semicarbazone) [27]. The coordination polyhedron of the V atom in complex **I** is a tetragonal pyramid. Its base is made up of the O(1), N(3), and N(4) atoms of one H_2L molecule and the N(5) atom of the other molecule; the pyramid is completed with the O(2) atom of the latter as an apex (Fig. 1). The bond lengths in the coordination polyhedron are as follows: V–O(1), 1.982(5) Å; V–N(3), 1.918(6) Å; V–N(4), 2.138(6) Å; V–N(5)*, 1.986(7) Å; V–O(2)*, 2.146(6) Å (Table 2). The ligand H_2L is coordinated to the metal centers to form three five-membered chelate rings (the V atom is involved in the two rings and the V* atom, in the remaining one). The ligand H_2L is nonplanar; the dihedral angle between the former two chelate rings is 7.4°.

Analysis of the difference electron-density maps showed that the H atoms are located at the terminal N(1) and N(7) atoms, which is confirmed by the intermolecular hydrogen bonds N(1)/N(7)–H···O(NO_3^-) (N···O, 2.60(2)–3.08(3) Å; angles NHO, 141°–170°). In the crystal, the complex cations and the anions are linked by intermolecular hydrogen bonds as well as by electrostatic interactions (Fig. 2, Table 3).

Solvate water molecules act as proton donors in hydrogen bonds, with the O atoms of the NO_3^- anions as the proton acceptors (O(*w*)···O, 2.64(6)–3.27(6) Å). Since the H atoms of the water molecules are located for O(3*w*) only, the intermolecular hydrogen bonds involving only this molecule are presented in Table 3 and Fig. 2. Apart from the above intermolecular hydrogen bonds, structure **I** is additionally stabilized by weaker bonds C–H···O: C(4)–H···O(5N*A*) ($-x + 1/2, y - 1/2, -z + 3/2$); C···O, 3.279 Å; H···O, 2.55 Å; angle CHO, 171°; C(9)–H···O(5N*A*) ($x + 1/2, y - 1/2, z$); C···O, 3.032 Å; H···O, 2.24 Å; angle CHO, 143°; C(9)–H···O(6N) ($x + 1/2, y - 1/2, z$); C···O, 3.260 Å; H···O, 2.39 Å; angle CHO, 155°; C(18)–H···O(5N); C···O, 2.936 Å; H···O, 2.37 Å; angle CHO, 119°; C(18)–H···O(2N*A*) ($-x + 1/2, y + 1/2, -z + 1/2$); C···O, 3.064 Å; H···O, 2.29 Å; angle CHO, 140°.

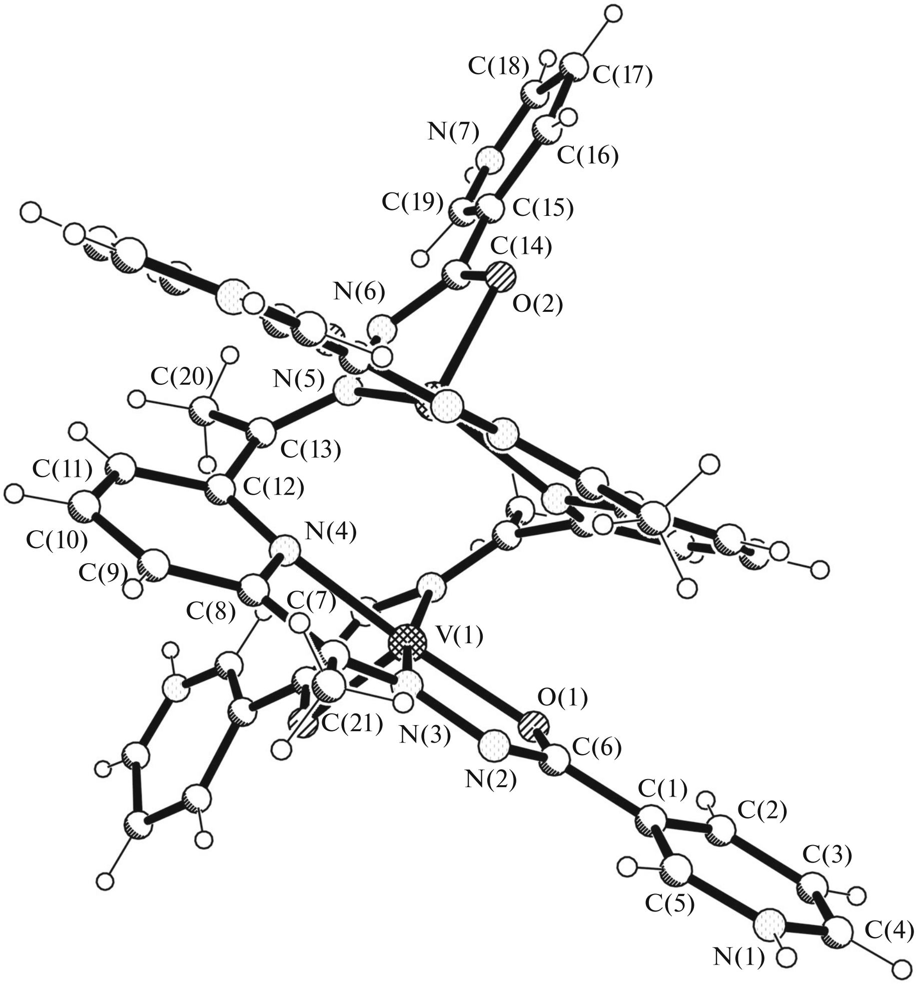

Fig. 1. Dinuclear complex cation $[V_2(H_2L)_2]^{4+}$ in structure **I**.

Complex **II** was obtained in minor amounts, together with the crystals of major complex **I**. Because of this, we failed to isolate and properly purify a sufficient amount of complex **II** for elemental analysis and IR spectroscopic measurements. Its chemical composition and structure were determined by single-crystal X-ray diffraction.

The crystal structure of **II** is built from molecular mononuclear complexes $[V^{IV}(=O)(H_2L)(SO_4)]$ and solvate water molecules in a ratio of 1 : 5. The coordination polyhedron of the V^{4+} cation is a pentagonal bipyramid made up of the electron-donating atoms N_3O_2 of the pentadentate neutral ligand H_2L and two O atoms of the SO_4^{2-} anion and oxo ligand O^{2-} both coordinated in a monodentate fashion (Fig. 3). The equatorial bond lengths are as follows: V–N(3), 2.125(4) Å; V–N(4), 2.129(4) Å; V–N(5), 2.122(4) Å; V–O(1), 1. 985(3) Å; V–O(2), 1.971(3) Å. The axial bond lengths are as follows: V–O(3), 2.094(3) Å; V–O(7), 1.594(3) Å (Table 2). These bond lengths are typical of vanadyl complexes [17, 18, 28]. The ligand H_2L in structure **II** is nonplanar. The equatorial plane shows four fused five-membered chelate rings: two OCNNV and two NCCNV ones (Fig. 3). The dihedral angles between the chelate rings range from 3.2° to 7.2°. The same range holds for the dihedral angles between the planes passing through the coordinated atoms N_3O_2 of the ligand H_2L and the terminal pyridine rings as well as for the dihedral angles between the latter rings (4.5°, 3.2°, 3.2°, and 3.7°, respectively).

Analysis of the N–C bond lengths in H_2L revealed a tautomeric transformation in only one moiety of this ligand: the proton is unexpectedly located at the terminal N(1) atom rather than at N(2) atom. This is confirmed by the donor···acceptor distance in the intermolecular hydrogen bond N–H···O (Table 3) involving the N(1) atom as a proton donor as well as by the bond angle at the N(1) atom (122.4(5)°). Note that the angle CNC at N(7) (116.7(5)°) is much smaller than 120°, so the second proton is located at the N(6) rather than N(7) atom.

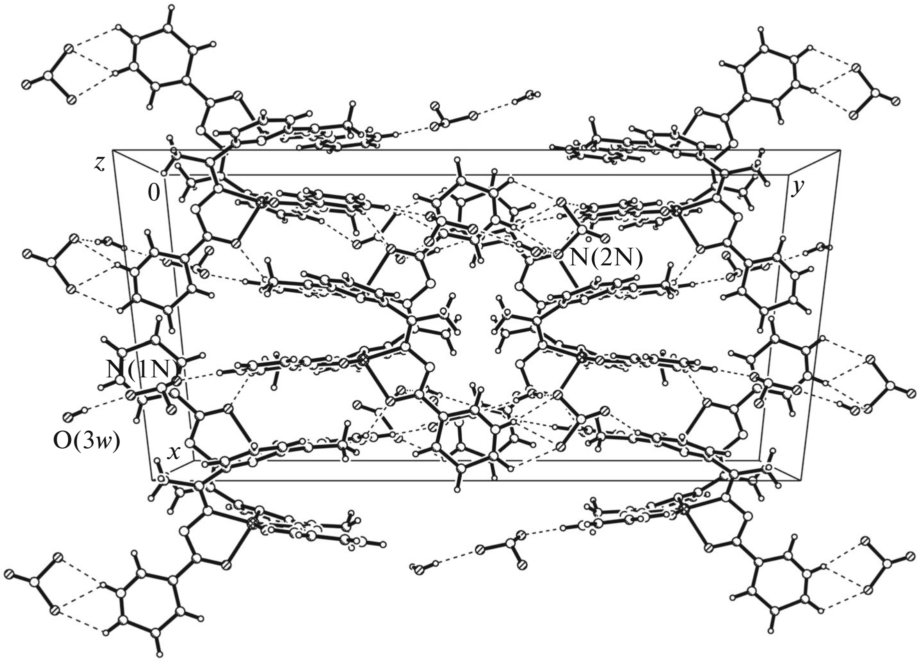

Fig. 2. Fragment of the packing pattern in the crystal of **I**.

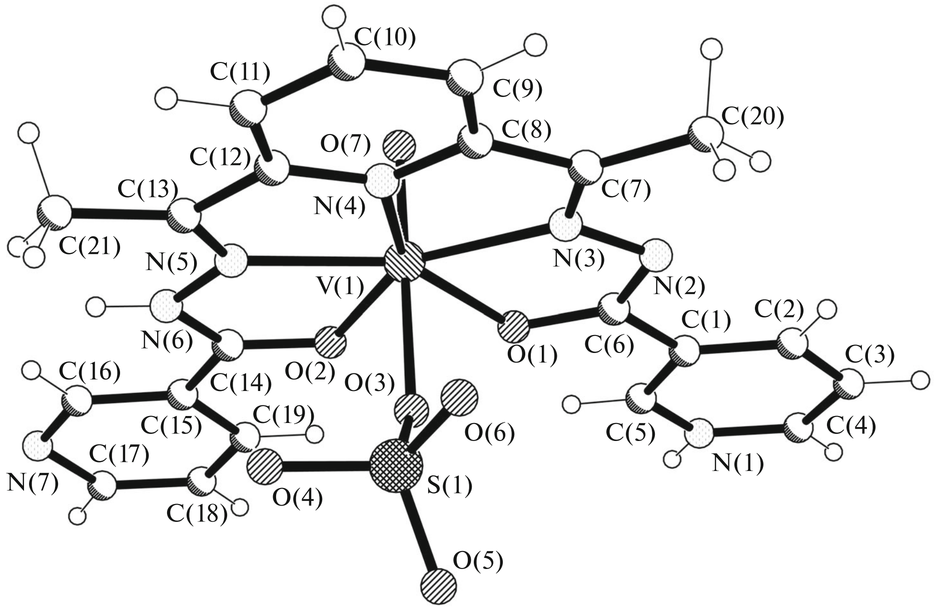

Fig. 3. Mononuclear molecular vanadyl(II) complex in structure **II**.

Analysis of intermolecular interactions in the crystal of **II** showed that the complexes $[V(=O)(H_2L)(SO_4)]$ are dimerized through the intermolecular hydrogen bonds N(1)–H···O(4) ($-x + 1$, $-y + 1$, $-z + 1$); N···O, 2.734(6) Å. The dimers are united into chains along the axis *z* through weak intermolecular hydrogen bonds C(9)–H···O(6) ($-x + 1/2$, $y - 1/2$, $-z + 1/2$); C···O, 3.490 Å; H···O(6), 2.57 Å; angle CHO, 173°. The intermolecular hydrogen bonds C(3)–H···O(7) ($-x + 1$, $-y$, $-z + 1$; C···O, 3.148 Å; H···O(7), 2.56 Å; angle CHO, 122°) serve to unite the chains into layers along the axis *x* (Fig. 4). Crystal water molecules in structure **II** form centrosymmetric chains along the axis *y*. These chains not only fill the

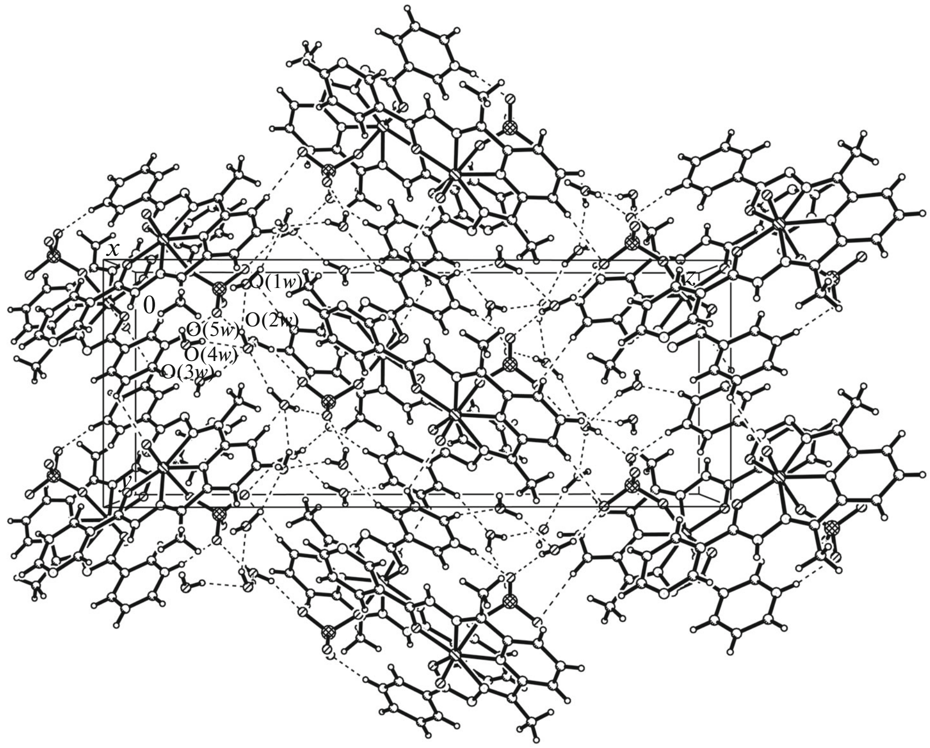

Fig. 4. Fragment of the packing pattern in the crystal of **II**.

intermolecular space in the crystal but also unite bulky complexes into a 3D framework. The parameters of a branched system of intermolecular hydrogen bonds involving water molecules as proton donors and acceptors (O(1*w*)–H···O(5) ($-x + 3/2, y - 1/2, -z + 1/2$); O···O, 2.850(5) Å; O(2*w*)–H···O(6) (x, y, z); O···O, 2.842(6) Å; O(3*w*)–H···N(7) (x, y, z); O···N, 2.810(6) Å; O(5*w*)–H···O(5) ($-x + 3/2, y - 1/2, -z + 1/2$); O···O, 2.83(5) Å, etc.) are given in Table 3. Structure **II** is additionally stabilized by weak intermolecular hydrogen bonds C–H···O(*w*): C(2)–H···O(5*w*) ($-x + 3/2, y - 1/2, -z + 1/2$); C···O, 3.139 Å; H···O, 2.32 Å; angle CHO, 147°; C(3)–H···O(3*w*) ($x + 1, y - 1, z$); C···O, 3.084 Å; H···O, 2.19 Å; angle CHO, 161°; C(11)–H···O(1*w*) ($-x + 1/2, y + 1/2, -z + 1/2$); C···O, 3.459 Å; H···O, 2.63 Å; angle CHO, 156°.

To sum up, reactions in the system $VOSO_4$–2,6-diacetylpyridine–nicotinohydrazide (1 : 1 : 2) gave two (mono- and dinuclear) vanadium complexes. 2,6-Diacetylpyridine bis(nicotinylhydrazone) was synthesized by condensation of 2,6-diacetylpyridine with nicotinohydrazide in a molar ratio of 1 : 2 using a metal ion matrix. The oxidation state +4 is retained for the vanadium ion in mononuclear complex **II**; in dinuclear complex **I**, vanadium is stabilized in the oxidation state +2. The outer-sphere anions in the latter complex are NO_3^- anions rather than the expected SO_4^{2-} ones. Apparently, the NO_3^- anions are produced by a complex redox process. Intermolecular hydrogen bonds are crucial for the crystal structures of complexes **I** and **II**; both anions and crystal water molecules act as proton acceptors in these bonds.

REFERENCES

1. Gupta, K.C. and Sutar, A.K., *Coord. Chem. Rev.*, 2008, vol. 252, nos. 12–14, p. 1420.
2. Smith, D.R., *Coord. Chem. Rev.*, 1998, vol. 172, p. 457.
3. Gerbeleu, N.V. and Arion, V.B., *Templatnyi sintez makrotsiklicheskikh soedinenii* (Template Synthesis of Macrocyclic Compounds), Chisinau: Shtiintsa, 1990.
4. De Boer, E., van Kooyk, Y., Tromp, M.G.M., et al., *Biochim. Biophys. Acta*, 1986, vol. 869, p. 48.
5. Auerbach, U., Della Vedova, B.S.P.C., Wieghardt, K., et al., *Chem. Commun.*, 1990, p. 1004.
6. Gerbeleu, N.V., Arion, V.B., Simonov, Yu.A., et al., *Zh. Neorg. Khim.*, 1990, vol. 35, no. 4, p. 918.
7. Vergopoulos, V., Jantzen, S., Julien, N., et al., *Z. Naturforsch. B: J. Chem. Sci.*, 1994, vol. 49, p. 1127.
8. Kopka, K. and Mattes R., *Z. Naturforsch. B: J. Chem. Sci.*, 1995, vol. 50, p. 1281.
9. Kravtsov, V.Kh., Belyaeva, K.F., Biyushkin, V.N., et al., *Koord. Khim.*, 1981, vol. 7, no. 10, p. 1569.
10. Arion, V.B., Kravtsov, V.Ch., Goddard, R., et al., *Inorg. Chim. Acta*, 2001, vol. 317, p. 33.
11. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, p. 380.

12. Abboud, K.A., Palenik, R.C., and Palenik, G.J., *Acta Crystallogr., Sect C: Cryst. Struct. Commun.*, 1996, vol. 52, p. 2994.
13. Thomas, J.E., Palenik, R.C., and Palenik, G.J., *Inorg. Chim. Acta*, 1979, vol. 37, p. L459.
14. Giordano, T.J., Palenik, G.J., Palenik, R.C., and Sullivan, D.A., *Inorg. Chem.*, 1979, vol. 18, p. 2445.
15. Pelizzi, C., Pelizzi, G., Predieri, G., and Resola, S., *J. Chem. Soc., Dalton Trans.*, 1982, p. 1349.
16. Pelizzi, C., Pelizzi, G., and Vitali, F., *Transition Met. Chem.* 1986, vol. 11, p. 401.
17. Gao, Sh., Huo, Li-H., Zhao, H., and Ng, S.W., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, vol. 60, p. m1757.
18. Sundheim, A., Theers, C., and Mattes R., *Z. Naturforsch., A: Phys. Sci.*, 1994, vol. 49, p. 176.
19. Sheldrick, G., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
20. Mazza, P., Zani, F., Orcesi, M., et al., *J. Inorg. Biochem.*, 1992, vol. 48, no. 4, p. 251.
21. Nakanishi, K., *Infrared Absorption Spectroscopy*, Tokyo: Nankodo, 1962.
22. Adams, D.M., *Metal—Ligand and Related Vibrations: A Critical Survey of the Infrared and Raman Spectra of Metallic and Organometallic Compounds*, London, 1967.
23. Nejati, K., Rezvani, Z., and Seyedahmadian, M., *Dyes and Pigments*, 2009, vol. 83, p. 304.
24. Nakamoto K., *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
25. Tarasevich, B.N., *IK-spektry osnovnykh klassov organicheskikh soedinenii. Spravochnye materialy* (IR Spectra of the Main Classes of Organic Compounds. Reference Data), Moscow, 2012.
26. Turte, K.I., Mereakre, V.M., Zubareva, V.E., et al., *Russ. J. Coord. Chem.*, 1996, vol. 22, no. 2, p. 125.
27. Koziol, A.E., Palenik, R.C., Palenik, G.J., and Wester, D.W., *Inorg. Chim. Acta.*, 2006. vol. 359, p. 2569.
28. Kopka, K. and Mattes R., *Z. Naturforsch., B: J. Chem. Sci.*, 1995, vol. 50, p. 281.

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