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КРАТКИЕ СООБЩЕНИЯ

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SUBSTITUENT GROUP EFFECTS ON THE SELF-ASSEMBLY OF OXOVANADIUM(V) COMPLEXES WITH HYDRAZONE LIGANDS BEARING BENZOIC ACID (1-METHYL-3-OXOBUTYLIDENE)HYDRAZIDE BACKBONES

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An oxo-bridged dinuclear oxovanadium(V) complex, $[V_2O_2(\mu\text{-}O)(L^1)_2]$ (**1**) [H_2L^1 = 3-nitrobenzoic acid (1-methyl-3-oxobutylidene)hydrazide], and a mononuclear oxovanadium(V) complex, $[VO(OMe)(L^2)]$ (**2**) [H_2L^2 = 3-hydroxynaphthalene-2-carboxylic acid (1-methyl-3-oxobutylidene)hydrazide], were prepared by the reactions of $[VO(acac)_2]$ with H_2L^1 and H_2L^2, respectively, in methanol. Both complexes were characterized by elemental analysis, IR spectra, and single crystal X-ray crystallography. The crystal of **1** crystallizes in the monoclinic space group $P2/n$, with $a = 13.116(3)$, $b = 7.597(2)$, $c = 13.927(2)$ Å, $\beta = 104.851(2)°$, $V = 1341.4(5)$ Å^3, $Z = 2$. The crystal of **2** crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.897(2)$, $b = 9.690(2)$, $c = 11.576(3)$ Å, $\alpha = 86.405(2)°$, $\beta = 70.597(2)°$, $\gamma = 85.991(2)°$, $V = 832.7(3)$ Å^3, $Z = 2$. The V atoms in the complexes have square pyramidal environment. The substituent groups attached to the aromatic rings can influence the self-assembly of the complexes.

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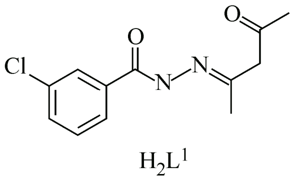
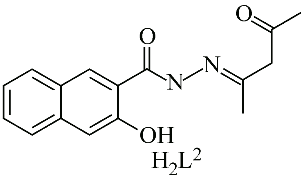
Vanadium complexes have received considerable attention in coordination chemistry [1—5]. The interest to the study of the oxovanadium complexes stems from the discovery of two kinds of vanadium enzymes, vanadium-nitrogenases and vanadate-dependent haloperoxidases [6, 7]. The insulin-like effect of vanadium complexes is another intriguing and promising feature that has further stimulated the vanadium coordination chemistry [8—10]. In addition, a number of vanadium complexes have shown effective catalytic properties on sulfoxidation and epoxidation of olefins [11—16]. It is well known that all the properties of vanadium complexes are based on the specific structures. So, exploration of the rules of the self-assembly of such complexes seems to be of major importance. In the present paper, an oxo-bridged dinuclear oxovanadium(V) complex, $[V_2O_2(\mu\text{-}O)(L^1)_2]$ (**1**) (H_2L^1 = = 3-nitrobenzoic acid (1-methyl-3-oxobutylidene)hydrazide; Scheme 1 (left)), and a mononuclear



H_2L^1



H_2L^2

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oxovanadium(V) complex, [VO(OMe)(L^2)] (**2**) (H_2L^2 = 3-hydroxynaphthalene-2-carboxylic acid (1-methyl-3-oxobutylidene)hydrazide; Scheme 1 (right)), were prepared and characterized.

Experimental. Materials and methods. 3-Nitrobenzohydrazide and 2-hydroxy-1-naphthohydrazide were purchased from Alfa Aesar. [VO(acac)$_2$] was prepared according to the literature method [17]. All chemicals and solvents were of analytical grade and used as obtained. Microanalyses of the complexes were performed with a Vario EL III CHNOS elemental analyzer. Infrared spectra were recorded as KBr pellets with an FTS-40 spectrophotometer.

Crystal structure determination. Data were collected on a Bruker SMART 1000 CCD area diffractometer using a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 298(2) K. The data were corrected with SADABS program and refined on F^2 with Siemens SHELXL software [18, 19]. The structures were solved by the direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included in the last cycles of the refinement. Crystal data and details of the data collection and refinement are listed in Table 1. Selected bond lengths and angles within the coordination sphere of vanadium are listed in Table 2.

Preparation. [V_2O_2(μ-O)(L^1)$_2$] (**1**). A stirred solution of 3-nitrobenzohydrazide (0.181 g, 1 mmol) in absolute methanol (20 mL) was mixed with [VO(acac)$_2$] (0.265 g, 1 mmol), and the resulting reaction mixture was refluxed on a water bath for 1 h, and then cooled to room temperature, yielding a deep brown solution. The solution was kept still at ambient temperature for slow evaporation of the solvent, yielding brown crystals of **1**. Yield 0.178 g (53 %). Anal. Calcd. for $C_{24}H_{22}N_6O_{11}V_2$ (%): C 42.9, H 3.3, N 12.5. Found: C 42.8, H 3.4, N 12.3. IR (KBr, ν_{max}, cm^{-1}): 1621 (C=N), 1536 (C—O, enolic), 972 and 870 (V=O).

[VO(OMe)(L^2)] (**2**). A stirred solution of 2-hydroxy-1-naphthohydrazide (0.202 g, 1 mmol) in absolute methanol (20 mL) was mixed with [VO(acac)$_2$] (0.265 g, 1 mmol), and the resulting reaction

Table 1

Crystallographic data for the complexes

Parameter	**1**	**2**
Formula	$C_{24}H_{22}N_6O_{11}V_2$	$C_{17}H_{17}N_2O_5V$
Formula weight	672.4	380.3
Crystal system	Monoclinic	Triclinic
Space group	$P2/n$	$P\overline{1}$
a, b, c, Å	13.116(3), 7.597(2), 13.927(2)	7.897(2), 9.690(2), 11.576(3)
α, β, γ, deg.	104.851(2)	86.405(2), 70.597(2), 85.991(2)
V, Å^3	1341.4(5)	832.7(3)
Z	2	2
T, K	298(2)	298(2)
λ, Å	0.71073	0.71073
ρ_{calcd}, g/cm^3	1.665	1.517
μ, mm^{-1}	0.770	0.626
Measured / independent / observed ($I > 2\sigma(I)$) reflections	5276 / 2310 / 1092	4333 / 3065 / 2226
R_1[a] / wR_2[b]	0.0696 / 0.1615	0.0517 / 0.1434
GOOF on F^2	1.079	1.011

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[a] $R_1 = \sum(||F_0| - |F_c||)/\sum|F_0|$.

[b] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$, $w_{(1)} = 1/[\sigma^2(F_0^2) + (0.109P)^2]$, $w_{(2)} = 1/[\sigma^2(F_0^2) + (0.1019P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$.

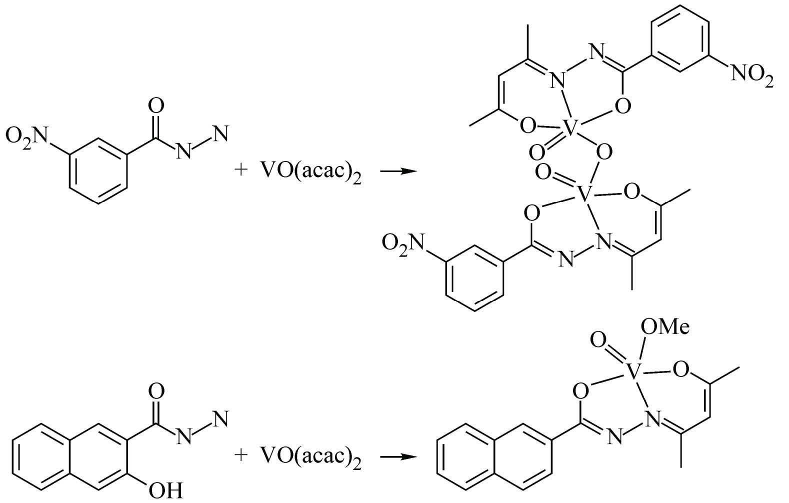
Table 2

Selected bond lengths (Å) *and angles* (deg.) *for the complexes*

1				2			
V1—O1	1.939(6)	O3—V1—O4	109.1(2)	V1—O2	1.918(2)	O4—V1—O5	106.04(14)
V1—O3	1.558(5)	O3—V1—N1	103.5(2)	V1—O4	1.580(3)	O4—V1—O2	108.15(12)
V1—N1	2.062(6)	O4—V1—O2	101.48(18)	V1—N2	2.065(3)	O5—V1—O3	98.58(11)
V1—O2	1.843(8)	O2—V1—O1	152.2(2)	V1—O3	1.847(2)	O3—V1—O2	142.65(11)
V1—O4	1.787(3)	O2—V1—N1	83.8(3)	V1—O5	1.762(3)	O3—V1—N2	84.05(11)
		O3—V1—O2	102.0(3)			O4—V1—O3	105.19(13)
		O3—V1—O1	100.9(3)			O4—V1—N2	98.54(13)
		O4—V1—O1	85.55(18)			O5—V1—O2	88.04(11)
		O4—V1—N1	144.9(2)			O5—V1—N2	153.53(13)
		O1—V1—N1	75.7(2)			O2—V1—N2	74.89(10)

mixture was refluxed on a water bath for 1 h, and then cooled to room temperature, yielding a deep brown solution. The solution was kept still at ambient temperature for slow evaporation of the solvent yielding brown crystals of **2**. Yield 0.133 g (35 %). Anal. Calcd. for $C_{17}H_{17}N_2O_5V$ (%): C 53.7, H 4.5, N 7.4. Found: C 53.5, H 4.5, N 7.2. IR (KBr, ν_{max}, cm^{-1}): 3336 (OH), 1625 (C=N), 1537 (C—O, enolic), 967 (V=O).

Results and discussion. The preparation of the two complexes is shown in Scheme 2. On aerial oxidation in methanol, the V^{IV} atom in VO(acac)$_2$ is changed to V^V in the complexes.



Scheme 2. The synthesis of the complexes

Structure description. $[V_2O_2(\mu\text{-}O)(L^1)_2]$ (**1**). The molecular structure of **1** with atom numbering scheme is shown in Fig. 1. The complex is an oxo-bridged dinuclear vanadium(V) complex, which possesses a crystallographic two-fold rotation axis symmetry. The V···V distance is 2.956(1) Å. The ligand L^1 forms five- and six-membered chelate rings with bite angles of 75.7(2) and 83.8(3)° at the V atoms. The V atom is in distorted square pyramidal coordination environment. The imino N and enolic O atoms of L^1, and the bridging oxo O atom constitute the equatorial plane. The V atom deviates from the least-squares plane defined by the basal donor atoms by 0.460(1) Å. The apical position is occupied by one oxo group. The square pyramidal geometry can be verified by the τ value [20] of 0.12. The *cis* and *trans* bond angles in the basal plane are in the range 75.7(2)—101.5(2)° and 144.9(2)—152.2(2)°, respectively. The angles between the apical and the basal donor atoms are in the range 100.9(3)—

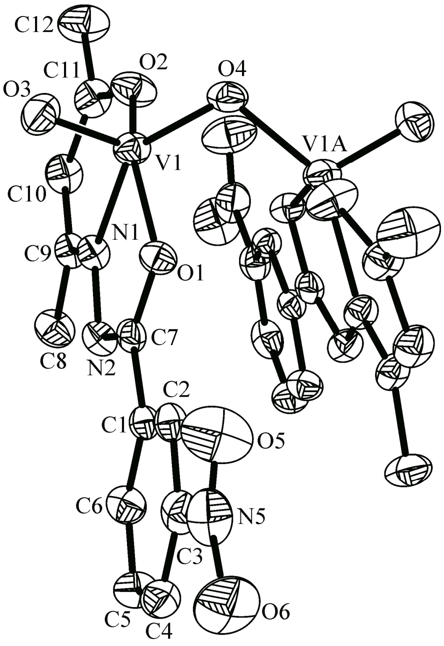


Fig. 1. ORTEP plots (30 % probability level) and numbering scheme for **1**

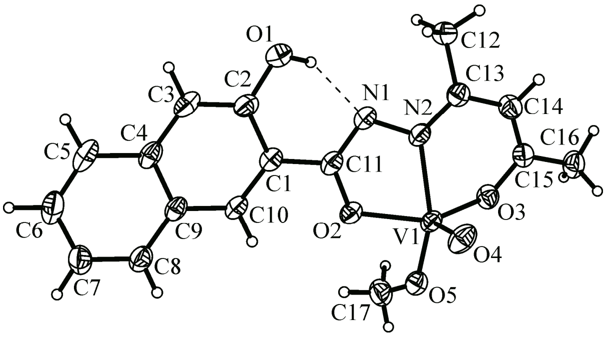


Fig. 2. ORTEP plots (30 % probability level) and numbering scheme for **2**. Hydrogen bond is indicated by a dashed line

109.1(2)°. The V—O and V—N bond lengths in the complex are comparable with the bond lengths reported for oxovanadium(V) complexes with hydrazone ligands [21, 22].

[VO(OMe)(L^2)] (**2**). The molecular structure of **2** with atom numbering scheme is shown in Fig. 2. Just as observed for **1**, the ligand L^2 in **2** also forms one five- and one six-membered chelate ring with bite angles of 74.9(1) and 84.0(1)° at the V atom. The V atom is in distorted square pyramidal coordination environment. The imino N and enolic O atoms of L^2, and the O atom of the deprotonated methanol ligand constitute the equatorial plane. The V atom deviates from the least-squares plane defined by the basal donor atoms by 0.476(1) Å. The apical position is occupied by one oxo group. The square pyramidal geometry can be verified by the τ value [20] of 0.18. The *cis* and *trans* bond angles in the basal plane are in the range 74.9(1)—98.6(1)° and 142.6(1)—153.5(1)°, respectively. The angles among the apical and the basal donor atoms are in the range 98.5(1)—108.2(1)°. The V—O and V—N bond lengths in the complex are comparable with those of **1** and other similar oxovanadium(V) complexes with hydrazone ligands [21, 22].

Conclusions. In summary, the present paper reports the synthesis and structures of two oxovanadium(V) complexes with similar tridentate hydrazone ligands. The self-assembly of 3-nitro substituted benzoic acid hydrazone with VO(acac)$_2$ afforded an oxido-bridged dinuclear vanadium(V) complex, while the self-assembly of 2-hydroxy-1-naphthyl substituted hydrazone ligand with VO(acac)$_2$ produced mononuclear vanadium(V) species. Thus, the electronic-withdrawing or electronic-donating effects of the substituent groups of the aromatic rings of hydrazone ligands can influence the self-assembly of the complexes.

CCDC 995562 and 995563 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* summary.ccdc.cam.ac.uk/structure-summary-form.

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