Journal of Structural Chemistry. Vol. 54, No. 3, pp. 581-585, 2013
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CRYSTAL STRUCTURES OF NEW ISOSTRUCTURAL OXOVANADIUM(V) COMPLEXES WITH HYDRAZONE LIGANDS

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UDC 548.73:541.49:546.88

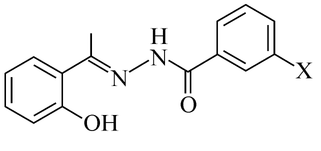
Two new isostructural methoxide-bridged dimeric oxovanadium(V) complexes $[VO(L^1)(OMe)]_2$ (**1**) and $[VO(L^2)(OMe)]_2$ (**2**), where L^1 and L^2 are the deprotonated forms of 3-bromo-*N*′-[1-(2-hydroxyphenyl)×ethylidene]benzohydrazide (H_2L^1) and 3-chloro-*N*′-[1-(2-hydroxyphenyl)ethylidene]benzohydrazide (H_2L^2) respectively, are synthesized and characterized by elemental analyses, IR spectra, and single crystal X-ray determination. Both crystals crystallize in the triclinic space group P-1. For **1**, $a = 7.5237(15)$ Å, $b = 10.846(3)$ Å, $c = 11.195(3)$ Å, $\alpha = 84.143(3)°$, $\beta = 72.244(3)°$, $\gamma = 77.869(3)°$, $V = 849.9(4)$ Å^3, $Z = 1$, $R_1 = 0.0634$, $wR_2 = 0.1373$. For **2**, $a = 7.493(2)$ Å, $b = 10.740(3)$ Å, $c = 11.109(3)$ Å, $\alpha = 84.569(2)°$, $\beta = 71.783(2)°$, $\gamma = 79.822(2)°$, $V = 835.0(4)$ Å^3, $Z = 1$, $R_1 = 0.0511$, $wR_2 = 0.1076$. Each V atom in the complexes is octahedrally coordinated.

DOI: 10.1134/S0022476613030177

Keywords: oxovanadium complex, synthesis, crystal structure, hydrazone.

INTRODUCTION

Oxovanadium complexes with multi-dentate ligands have been extensively investigated in recent years with respect to their remarkable efficiency as insulin mimetic compounds [1–3]. Their usage as orally active medicaments would represent an important advance in the treatment of human *diabetes mellitus* [4]. Hydrazones as well as their metal complexes are of current interest for the pharmacological properties [5-7]. In recent years, a number of oxovanadium complexes with hydrazones have been reported for their insulin mimetic properties [8, 9]. As an extension work on the construction of new oxovanadium complexes with potential insulin mimetic properties, two isostructural oxovanadium(V) complexes derived from the similar hydrazone ligands 3-bromo-*N*′-[1-(2-hydroxyphenyl)ethylidene]benzohydrazide (H_2L^1; Scheme 1) and 3-chloro-*N*′-[1-(2-hydroxyphenyl)ethylidene]benzohydrazide (H_2L^2; Scheme 1) were synthesized and characterized.



Scheme 1. Hydrazone ligands. X = Br for H_2L^1, X = Cl for H_2L^2.

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EXPERIMENTAL

Materials and methods. 1-(2-Hydroxyphenyl)ethanone, 3-bromobenzohydrazide, and 3-chlorobenzohydrazide were obtained from Lancaster. VO(acac)$_2$ and other chemicals (analytical grade) were purchased and used as received. IR spectra were recorded on a Nicolet 170SX spectrophotometer using KBr as support. Elemental analyses were performed on an Italy 1106 apparatus.

Synthesis of H_2L^1. A mixture of 3-bromobenzaldehyde (0.215 g, 1 mmol) and 1-(2-hydroxyphenyl)ethanone (0.136 g, 1 mmol) in 50 ml of methanol was stirred at room temperature for 1 h. 80% of the solvent was evaporated by distillation, and the mixture was cooled to room temperature, giving colorless microcrystals. The product was filtered out and washed with methanol. Yield, 85%. Anal. Calcd. (%) for $C_{15}H_{13}BrN_2O_2$: C, 54.1; H, 3.9; N, 8.4. Found (%): C, 53.9; H, 4.0; N, 8.5.

Synthesis of H_2L^2. The preparation of colorless microcrystals of H_2L^2 was analogous to that of H_2L^1, but with 3-bromobenzohydrazide replaced by 3-chlorobenzohydrazide (0.186 g, 1 mmol). Yield, 93%. Anal. Calcd. (%) for $C_{15}H_{13}ClN_2O_2$: C, 62.4; H, 4.5; N, 9.7. Found (%): C, 62.1; H, 4.5; N, 9.8.

Synthesis of $[VO(L^1)(OCH_3)]_2$ (1). VO(acac)$_2$ (52.6 mg, 0.2 mmol) dissolved in 10 ml of methanol was added dropwise to a methanol solution of H_2L^1 (66.6 mg, 0.2 mmol) with continuous stirring for 30 min to give a reddish-brown solution. Evaporation of the solution at room temperature yielded deep brown block-shaped single crystals after a few days. The crystals were isolated by filtration, and dried in air. Yield, 78%. Anal. Calcd. (%) for $C_{32}H_{28}Br_2N_4O_8V_2$: C, 44.8; H, 3.3; N, 6.5. Found (%): C, 45.0; H, 3.4; N, 6.3.

Synthesis of $[VO(L^2)(OCH_3)]_2$ (2). The preparation of deep brown block-shaped single crystals of **2** was analogous to **1**, but with H_2L^1 replaced by H_2L^2 (57.6 mg, 0.2 mmol). Yield, 82%. Anal. Calcd. (%) for $C_{32}H_{28}Cl_2N_4O_8V_2$: C, 50.0; H, 3.7; N, 7.3. Found (%): C, 49.7; H, 3.6; N, 7.1.

X-ray crystallography. The suitable single crystals of the complexes were carefully selected under a polarizing microscope and glued at the top of thin glass fibers for data collection performed on a Bruker SMART APEX II CCD area diffractometer (graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å)) using an ω-scan mode at 298(2) K. The structures were solved by the direct method and refined with SHELXTL [10] by the full-matrix least-squares technique on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the final refinement on the calculated positions riding on their parent atoms. The crystallographic data of the complexes are summarized in Table 1, and the selected bond lengths and bond angles are listed in Table 2. CIF files containing complete information on the studied structures were deposited with CCDC, deposition numbers 800890 (**1**) and 800891 (**2**), and are freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Synthesis. The two oxovanadium(V) complexes were readily synthesized by the reaction of VO(acac)$_2$ with hydrazone ligands in methanol. The deep brown single crystals were obtained by recrystallization of the complexes in methanol. The crystals are soluble in polar organic solvents such as DMF, DMSO, acetonitrile, methanol, and ethanol, but insoluble in water. From the literature search it can be seen that most of the crystal structures of oxovanadium complexes contain methanol molecules as coligands, instead of ethanol molecules [11-14]. It should be pointed out that vanadium in the starting material is in the V(IV) oxidation state, while it appears to be V(V) in both complexes, indicating that it was oxidized by air during the preparation and crystallization procedures.

Crystal structure description. The molecular structures including the atomic numbering scheme of the complexes **1** and **2** are shown in Figs. 1 and 2 respectively. The two structures are isostructural methoxide-bridged centrosymmetric dimeric oxovanadium(V) complexes with the V···V distances of 3.400(1) Å for **1** and 3.369(1) Å for **2**. The tridentate hydrazone ligands coordinate to the V atoms through the phenolate O, imino N, and enolic O atoms. The two VOL groups are linked by two methoxide bridges, forming a dimer. The V atom is in an octahedral coordination with three donor atoms of the

TABLE 1. Crystallographic and Experimental Data for the Complexes

	1	**2**
Chemical formula	$C_{32}H_{28}Br_2N_4O_8V_2$	$C_{32}H_{28}Cl_2N_4O_8V_2$
Fw	858.3	769.4
Crystal shape/colour	Block/deep brown	Block/deep brown
Crystal size, mm^3	0.27×0.26×0.26	0.17×0.15×0.13
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a, b, c, Å	7.5237(15), 10.846(3), 11.195(3)	7.493(2), 10.740(3), 11.109(3)
α, β, γ, deg	84.143(3), 72.244(3), 77.869(3)	84.569(2), 71.783(2), 79.822(2)
V, Å^3	849.9(4)	835.0(4)
Z	1	1
μ(MoK_α), cm^{-1}	2.956	0.776
$T_{\min}/T_{\max}$	0.5024/0.5136	0.8794/0.9058
Measured/Unique refl.	5624/3554	6246/3522
Observed refl. [$I \geq 2\sigma(I)$]	1771	2515
Parameters/restraints	219 / 0	219 / 0
$GOOF$ on F^2	1.018	1.030
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0634, 0.1373	0.0511, 0.1076
R_1, wR_2 (all data)^a	0.1373, 0.1644	0.0780, 0.1209

$^a R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

TABLE 2. Selected Bond Lengths (Å) and Bond Angles (deg) for the Complexes

			1		
V1–O1	1.823(4)	O4–V1–O1	101.35(19)	O4–V1–O3	103.95(18)
V1–O3	1.826(3)	O1–V1–O3	105.52(15)	O4–V1–O2	99.76(19)
V1–N1	2.121(4)	O1–V1–O2	151.14(17)	O3–V1–O2	88.10(15)
V1–O2	1.927(4)	O4–V1–N1	96.79(18)	O1–V1–N1	83.20(17)
V1–O4	1.580(4)	O3–V1–N1	155.19(17)	O2–V1–N1	74.94(17)
V1–O3A	2.428(4)	O4–V1–O3A	178.69(16)	O1–V1–O3A	79.14(15)
		O3–V1–O3A	74.75(15)	O2–V1–O3A	80.20(14)
		N1–V1–O3A	84.46(14)		
			2		
V1–O1	1.818(2)	O4–V1–O1	101.21(11)	O4–V1–O3	103.30(10)
V1–O3	1.8191(19)	O1–V1–O3	106.20(9)	O4–V1–O2	99.70(11)
V1–N1	2.111(3)	O1–V1–O2	151.21(10)	O3–V1–O2	87.86(9)
V1–O2	1.917(2)	O4–V1–N1	96.70(11)	O1–V1–N1	83.17(10)
V1–O4	1.583(2)	O3–V1–N1	155.55(10)	O2–V1–N1	74.90(10)
V1–O3A	2.400(2)	O4–V1–O3A	178.13(10)	O1–V1–O3A	79.23(9)
		O3–V1–O3A	74.85(8)	O2–V1–O3A	80.51(8)
		N1–V1–O3A	85.14(8)		

hydrazone ligand and one methoxide O atom defining the equatorial plane, and with one oxo O and one methoxide O atom occupying two axial positions. The mean deviations of the four basal donor atoms from the least-squares planes are 0.0014 Å for **1** and 0.0054 Å for **2**. The displacement of the V atoms toward the oxo groups from the planes are 0.357(2) Å for **1** and 0.347(2) Å for **2**. The coordinate bond lengths and angles in the complexes are comparable to each other and are also

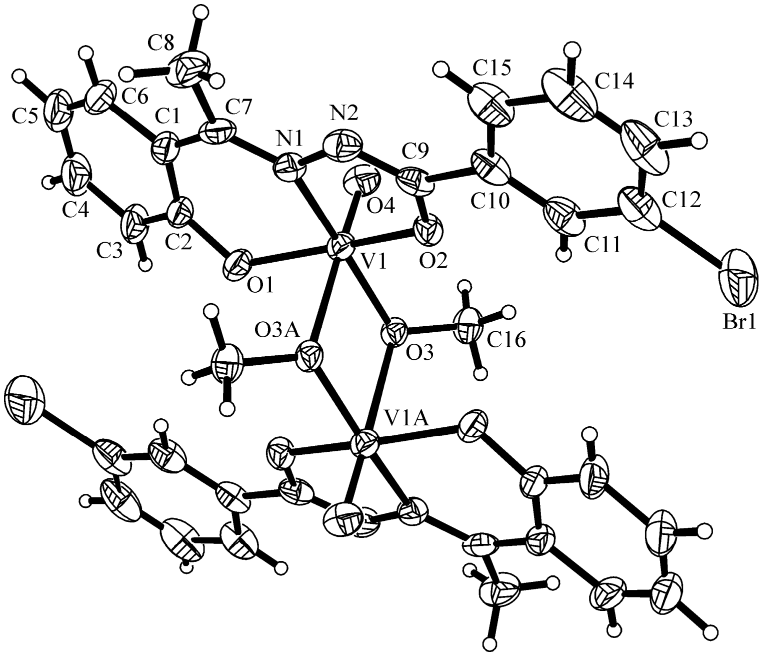

Fig. 1. ORTEP drawing of **1** with 30% probability thermal ellipsoids. Unlabeled atoms and those labeled with the suffix A are at the symmetry position 1–*x*, 1–*y*, 2–*z*.

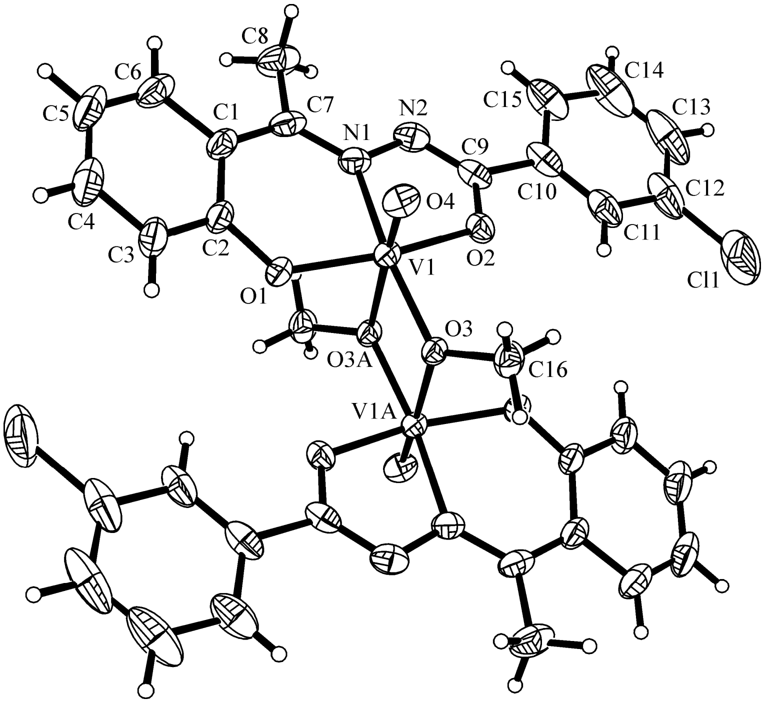

Fig. 2. ORTEP drawing of **2** with 30% probability thermal ellipsoids. Unlabeled atoms and those labeled with the suffix A are at the symmetry position –*x*, 1–*y*, –*z*.

comparable to those observed in other similar oxovanadium(V) complexes [11-18]. The V–O_{oxo} bonds are shorter in both complexes than the other coordinate bonds, indicating that they are typical double bonds.

IR spectra. The IR spectra of the hydrazone compounds exhibit two absorption bands in the regions 3200-3230 cm^{-1} and 1650-1660 cm^{-1} due to the ν(N–H) and ν(C=O) stretches. The absence of these bands in the spectra of the two oxovanadium(V) complexes is consistent with the enolization of the amide functionality and subsequent proton replacement by the V atom. The strong bands at about 1610 cm^{-1} in both complexes are assigned to the conjugated C=N–N=C moieties. The intense absorption bands in the spectra of both complexes corresponding to ν(V=O) are observed at about 983 cm^{-1} and 950 cm^{-1} for both complexes [4].

CONCLUSIONS

In summary, the present paper reports the synthesis and characterization of two new isostructural centrosymmetric dimeric oxovanadium(V) complexes with similar hydrazone compounds. Single crystal X-ray diffraction indicates that the hydrazone ligands coordinate to the V atoms through the phenolate O, imino N, and enolic O atoms. Methanol, which readily adopts the deprotonated bridging form, is the preferred solvent for the synthesis and crystallization of such complexes. Further work can be carried out to investigate their insulin mimetic activities.

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