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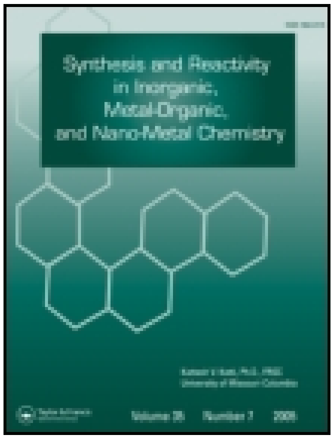

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Synthesis, Crystal Structure, and Thermal Property of [N′-(2-hydroxy-3-methoxybenzylidene)-2-methoxybenzohydrazonato](methanol)(methoxy)oxovanadium(V)

Jun-Min Wang[a], Hui-Min Liu[a], Dong-Nuan Zhang[a], Peng-Lei Cui[a] & Jing-Jun Ma[a]
[a] Hebei Key Laboratory of Bioinorganic Chemistry, College of Sciences, Agricultural University of Hebei, Baoding, P. R. China

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Synthesis, Crystal Structure, and Thermal Property of [*N*′-(2-hydroxy-3-methoxybenzylidene)-2-methoxybenzohydrazonato](methanol)(methoxy)oxovanadium(V)

Jun-Min Wang, Hui-Min Liu, Dong-Nuan Zhang, Peng-Lei Cui, and Jing-Jun Ma
Hebei Key Laboratory of Bioinorganic Chemistry, College of Sciences, Agricultural University of Hebei, Baoding, P. R. China

The aroylhydrazone Schiff base ligand *N'*-(2-hydroxy-3-methoxybenzylidene)-2-methoxybenzohydrazide (H_2L) reacts with $VO(acac)_2$ in methanol gave the complex [*N'*-(2-hydroxy-3-methoxybenzylidene)-2-methoxybenzohydrazonato] (methanol) (methoxy)oxovanadium(V), [$V^VOL(CH_3OH)(CH_3O)$]. The structure of the complex was characterized by elemental analysis and IR spectroscopic method in the solid state. Single-crystal X-ray analysis was also performed, which indicates that the V atom in the mononuclear complex is six-coordinated in an octahedral geometry. V^{IV} in $VO(acac)_2$ was oxidized to V^V by aerial oxygen in the synthesis and crystallization. Thermal stability of the complex was determined.

Keywords aroylhydrazone, crystal structure, thermal property, vanadium complex

INTRODUCTION

The presence of vanadium(IV) and vanadium(V) compounds in many vanadium-dependent enzymes,[1–3] as well as insulin mimicking,[4,5] have stimulated the search for structural and functional models based on vanadium complexes. In addition, oxovanadium complexes have been attracted much attention for their versatile catalytic properties in organic preparation.[6–8] In recent years, the remarkable biological activity of aroylhydrazones and the dependence of their mode of chelation with transition metal ions in living systems have been of significant interest.[9–14] In order to understand clearly the properties of such complexes, detailed structures should be characterized. Considering that single-crystal X-ray diffraction is the best choice for the characterization of metal complexes, recently, we have reported some aroylhydrazone compounds[15,16] and a 8-hydroxyquinoline coordinated vanadium complex with an aroylhydrazone ligand.[17] As a further study on the coordination of aroylhydrazone to vanadium ions, in this paper, a new vanadium complex, [$V^VOL(CH_3OH)(CH_3O)$], [*N*′-(2-hydroxy-3-methoxybenzylidene)-2-methoxybenzohydrazonato](methanol)(methoxy)oxovanadium(V), was synthesized and characterized.

EXPERIMENTAL

Materials and Methods

3-Methoxysalicylaldehyde, 2-methoxybenzohydrazide, and vanadium(IV) oxide acetylacetonate ([$VO(acac)_2$]) were purchased from Merck and Fluka and used as received. The aroylhydrazone Schiff base ligand *N*′-(2-hydroxy-3-methoxybenzylidene)-2-methoxybenzohydrazide (H_2L) was prepared in a 93% yield by condensation reaction of 3-methoxysalicylaldehyde with 2-methoxybenzohydrazide in methanolic media, according to the literature method.[15,16] All other chemicals and solvents used in this work were of analytical grade available commercially and were used without further purification. The elemental analyses (carbon, hydrogen, and nitrogen) of the compounds were obtained from a Carlo Erba Model EA 1108 analyzer. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. Solution electrical conductivity was measured with a DDS-11A conductivity meter. Thermal analysis of the complexes was carried out by heating at a rate of 10°C/min on a Perkin Elmer TGA-4000 thermo balance.

Synthesis of [$V^VOL(CH_3OH)(CH_3O)$]

[$VO(acac)_2$] (0.01 mmol, 2.65 g) dissolved in methanol (30 mL) was added dropwise to a stirred methanolic solution (30 mL) of H_2L (0.01 mol, 3.00 g). The mixture was gently refluxed for 2 h, then most of the solvent was evaporated by distillation. After cooling, the resulting brown solid was filtered off, washed with cold absolute methanol, and dried in a vacuum containing anhydrous $CaCl_2$. Yield: 3.27 g (76%). IR data (cm^{-1}, KBr): 3443 (w), 3208 (m), 1607 (s), 1558 (m), 1523 (m), 1488 (m), 1471 (m), 1451 (w), 1436 (w), 1352 (w), 1340 (m),

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Address correspondence to Jing-Jun Ma, Hebei Key Laboratory of Bioinorganic Chemistry, College of Sciences, Agricultural University of Hebei, Baoding 071001, P. R. China. E-mail: majingjun71@aliyun.com

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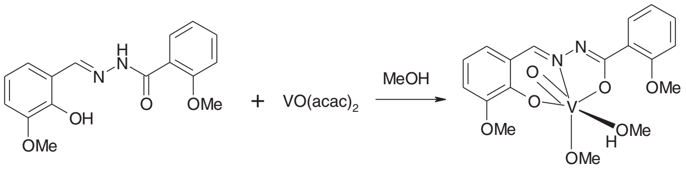
TABLE 1
Crystallographic data for the complex

Chemical formula	$C_{18}H_{21}N_2O_7V$	ρ (g cm^{-3})	1.416
Formula weight	428.31	μ (mm^{-1})	0.535
Crystal system	Monoclinic	$T_{\min}$, $T_{\max}$	0.8868, 0.9005
Space group	$P2_1/c$	Reflections collected	11527
Unit cell dimensions		Reflections unique	4361
a (Å)	9.9882(5)	Reflections observed [$I > 2\sigma(I)$]	3904
b (Å)	19.4232(10)	Parameters	260
c (Å)	10.8912(6)	Restraints	1
α (°)	90	R_1, wR_2 [$I > 2\sigma(I)$]	0.0349, 0.0913
β (°)	108.060(1)	R_1, wR_2 (all data)	0.0395, 0.0947
γ (°)	90	Goodness-of-fit on F^2	1.085
V (Å^3)	2008.8(2)	Largest difference in peak and hole (e Å^{-3})	0.203, –0.453
Z	4		

1291 (m), 1256 (s), 1222 (w), 1106 (w), 973 (s), 917 (w), 870 (w), 752 (m), 700 (w), 682 (w), 601 (m), 435 (w). Dark brown block-like single crystals of the complex, suitable for single crystal X-ray diffraction, were obtained by slow evaporation of a methanol solution containing the complex. Anal. Calcd. for $C_{18}H_{21}N_2O_7V$ (%): C, 50.48; H, 4.94; N, 6.54. Found: C, 50.30; H, 5.05; N, 6.36.

X-Ray Crystallography

A suitable X-ray quality crystal of the complex was placed under a microscope and investigated in a diffraction experiment at 298(2) K on a Bruker Apex II diffractometer with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) obtained from a graded multilayer X-ray optics. The structure was solved by direct methods with SHELXS-97,[18] and refined with full-matrix least-squares techniques on F^2 with SHELXL-97.[18] The C-bonded hydrogen atoms were calculated in an idealized geometry, riding on their parent atoms, with distances restrained to 0.93–0.96 Å. H5A atom attached to O5 in the complex was located from a difference Fourier map and refined isotropically, with O–H distance restrained to 0.85(1) Å. The crystal data and refinement parameters are listed in Table 1.



SCH. 1. The synthesis of the complex.

RESULTS AND DISCUSSION

Synthesis and Characterization

The reaction of $VO(acac)_2$ with the tridentate aroylhydrazone Schiff base ligand *N*′-(2-hydroxy-3-methoxybenzylidene)-2-methoxybenzohydrazide in methanol under aerobic conditions afforded the neutral oxovanadium(V) complex (Scheme 1). Most likely during the synthesis and crystallization of the complex from oxovanadium(IV) starting material, the aerial oxygen acts as the oxidizing agent. Elemental analyses of the complex are consistent with the general molecular formula proposed by single-crystal X-ray determination. The complex is soluble in common organic solvents such as dimethylsulfoxide, dimethylformamide, methanol, and ethanol. In absolute methanolic solution, it is electrically nonconducting.

IR Spectroscopic Characteristics

The infrared spectra of the free aroylhydrazone Schiff base ligand and the complex gave information about the coordination. The free ligand displays a broad band centered at 3415 cm^{-1} and a weak and sharp band at 3223 cm^{-1}. These bands are possibly due to the O–H and N–H stretches. However, the sharp band is absence in the spectrum of the complex. The absence of the ν(C=O) band, presents in H_2L at 1651 cm^{-1}, indicates the enolization of the amide functionality upon coordination to the V atom. Strong band observed at 1607 cm^{-1} for the complex can be attributed to the stretching vibrations of the azomethine group, $\nu_{C=N}$.[19] The spectrum of the complex displays typical and intense band at 973 cm^{-1}, which can be assigned to the stretch of the V=O bonds.[20]

Description of the Crystal Structure of the Complex

The molecular structure and the atom numbering scheme for the complex is depicted in Figure 1. Selected bond lengths and angles are given in Table 2. The complex is a neutral mononuclear oxovanadium compound. The coordination geometry around the vanadium atom can be described as a distorted octahedral with the tridentate aroylhydrazone ligand coordinated in a meridional fashion, forming five- and six-membered chelate rings with bite angles of 74.49(5)° (N1–V1–O2) and 83.48(5)° (N1–V1–O1), typical for this type of ligand system.[17,21,22] The aroylhydrazone Schiff base ligand coordinates in its dianionic enolate form, which is consistent with the observed C8–O2 and C8–N2 bond lengths of 1.298(2) and 1.300(2) Å. The three donor atoms of the aroylhydrazone ligands and O6 atom of the deprotonated methanol ligand define the equatorial

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TABLE 2
Selected bond lengths (Å) and angles (°) for the complex

Bond lengths (Å)			
V1–O1	1.8475(12)	V1–O2	1.9596(12)
V1–O5	2.3071(13)	V1–O6	1.7778(12)
V1–O7	1.5857(14)	V1–N1	2.1309(14)
Bond angles (°)			
O7–V1–O6	102.09(7)	O7–V1–O1	100.37(7)
O6–V1–O1	101.91(6)	O7–V1–O2	97.29(7)
O6–V1–O2	94.50(5)	O1–V1–O2	152.69(6)
O7–V1–N1	94.45(7)	O6–V1–N1	161.26(6)
O1–V1–N1	83.48(5)	O2–V1–N1	74.49(5)
O7–V1–O5	174.99(6)	O6–V1–O5	82.75(6)
O1–V1–O5	79.73(5)	O2–V1–O5	80.88(5)
N1–V1–O5	80.57(5)		

plane of the octahedral coordination. The two axial positions of the octahedral coordination are occupied by the O5 atom of the methanol ligand, and one oxo group. The O5 atom coordinates to the V atoms at rather elongated distance of 2.307(1) Å, due to the *trans* influence of the oxo groups. This is accompanied by a significant displacement of the V atom from the equatorial plane towards the oxo group by 0.296(2) Å.

In the crystal structure of the complex, molecules are linked through intermolecular O5–H5A···N2 hydrogen bonds [O5–H5A = 0.85(1) Å, H5A···N2^{i} = 1.955(11) Å, O5···N2^{i} = 2.791(2) Å, O5–H5A···N2^{i} = 172(3)°; symmetry code for i: x, $1/2 - y$, $-1/2 + z$], forming 1D chains along the c axis (Figure 2).

Thermal Property

Thermogravimetric analysis of the complex was carried out in the temperature range 50–1000°C at a heating rate of 10°C min^{-1}. The TG and DTA curves of the complex are given following degradation schemes (Figure 3). The complex is stable up to 87°C. Above this temperature, the TG curve show four steps of weigh losses. The first step of decomposition in the temperature range 87–132°C involved the removal of methanol ligand. The second step of decomposition in the temperature range 132–190°C involved the removal of the deprotonated methanol ligand. The third step of decomposition in the temperature range 190–400°C involved the removal of two methoxy groups of the aroylhydrazone Schiff base ligand. With further elevation in temperature, a rapid weigh loss in the temperature range 400–520°C was observed. The decomposition of the final stage weight loss may be ascribed to the dissociation of the remaining part of the aroylhydrazone Schiff base ligand, and the formation of the final product V_2O_5.

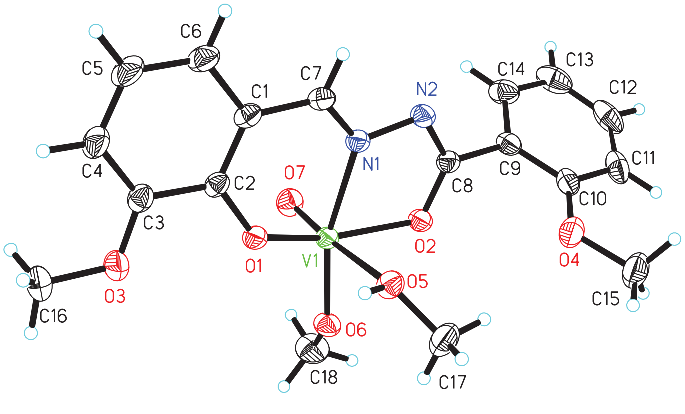

FIG. 1. Structure of the complex with atom labeling scheme. All non-hydrogen atoms are represented at 30% probability thermal ellipsoids.

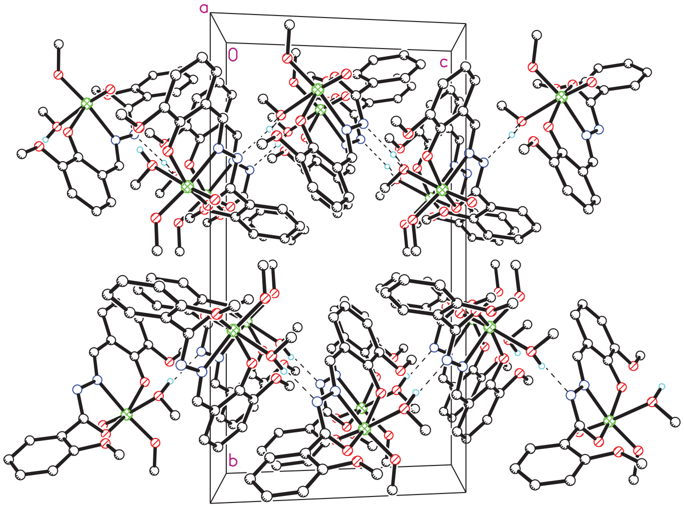

FIG. 2. Molecular packing diagram of the complex, viewed down the *a* axis. Hydrogen bonds are drawn as dashed lines.

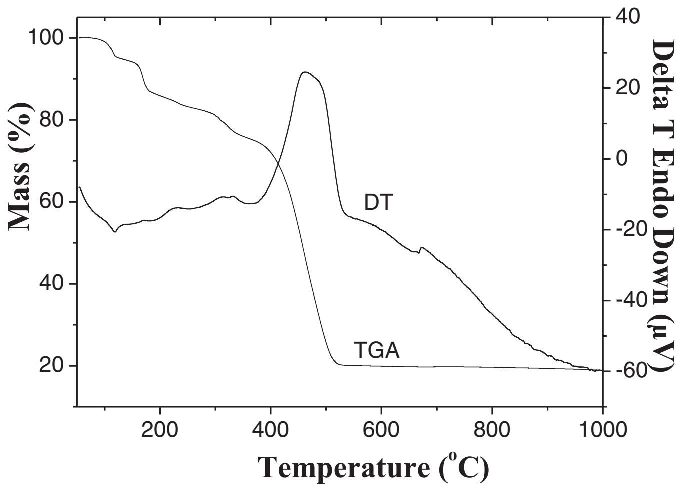

FIG. 3. DT-TGA curves of the complex.

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SUPPLEMENTAL MATERIAL

CCDC 906159 contains the supplementary crystallographic data for the complex. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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