Synthesis, Characterization and Crystal Structures of Oxovanadium(V) Complexes with Benzohydrazone and 8-Hydroxyquinoline

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Two new oxovanadium(V) complexes, [VOL¹(HQ)] (**1**) and [VOL²(HQ)] (**2**), were prepared by the reaction of [VO(acac)₂] (where acac = acetylacetonate), 8-hydroxyquinoline (HHQ) with *N'*-(5-fluoro-2-hydroxybenzylidene)-4-fluorobenzohydrazide (H₂L¹) and *N'*-(5-fluoro-2-hydroxybenzylidene)-4-methoxybenzohydrazide (H₂L²), respectively, in methanol. Crystal and molecular structures of the complexes were determined by elemental analysis, infrared and UV-visible spectra and single crystal X-ray diffraction. Complex **1** crystallizes in the orthorhombic space group Pbcn, with unit cell dimensions *a* = 32.327(2) Å, *b* = 8.189(2) Å, *c* = 16.817(1) Å, *V* = 4451.9(9) Å³, *Z* = 8, GOOF = 1.060, *R*₁ = 0.0587 and *wR*₂ = 0.0921. Complex **2** crystallizes in the monoclinic space group P2₁/n, with unit cell dimensions *a* = 12.4965(8) Å, *b* = 13.3795(9) Å, *c* = 13.8324(9) Å, β = 115.555(2)°, *V* = 2086.5(2) Å³, *Z* = 4, GOOF = 1.047, *R*₁ = 0.0378 and *wR*₂ = 0.0919. The V atoms in the complexes are in octahedral coordination, with the phenolate oxygen, imino nitrogen and enolate oxygen of the benzohydrazone ligand and the hydroxy oxygen of 8-hydroxyquinoline in the equatorial plane and with the pyridine nitrogen of 8-hydroxyquinoline and one oxo group in the two axial positions. Thermal stability of the complexes was also studied.

Keywords: Benzohydrazone ligand, 8-Hydroxyquinoline, Oxovanadium complex, Crystal structure, Thermal property.

INTRODUCTION

Metal complexes with hydrazones have been received particular attention in biological and medicinal chemistry¹⁻⁴. In recent years, vanadium complexes have been reported to have interesting biological activities such as normalizing the high blood glucose levels and acting as models of haloperoxidases⁵⁻⁹. Recently, our research group has reported a few vanadium complexes with biological activities¹⁰⁻¹². 8-Hydroxyquinoline (HHQ) is a widely known bidentate ligand in coordination chemistry¹³⁻¹⁶, however, only two HQ coordinated oxovanadium complexes with hydrazone ligands have been reported so far^{17,18}. In the present paper, two new oxovanadium(V) complexes with hydrazone and HQ ligands, [VOL¹(HQ)] (**1**) and [VOL²(HQ)] (**2**) (H₂L¹ = *N'*-(5-fluoro-2-hydroxybenzylidene)-4-fluorobenzohydrazide, H₂L² = *N'*-(5-fluoro-2-hydroxybenzylidene)-4-methoxybenzohydrazide; **Scheme-I**), have been presented.

Scheme-I: Benzohydrazone ligands. H₂L¹: X = F; H₂L²: X = OMe

EXPERIMENTAL

Commercially available 5-fluorosalicylaldehyde, 4-fluorobenzohydrazide and 4-methoxybenzohydrazide were purchased from Sigma-Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. H₂L¹ and H₂L² were prepared according to the literature method^{19,20}. C, H and N elemental analyses were performed with a Perkin-Elmer elemental analyser. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the (4000-400) cm⁻¹ region. UV-visible spectra were recorded on a Lambda 900 spectrometer with acetonitrile as the solvent. Thermal stability analysis was performed on a Perkin-Elmer Pyris Diamond TGA-DTA thermal analyses system.

Synthesis of [VOL¹(HQ)] (1**):** A methanolic solution (10 mL) of [VO(acac)₂] (0.1 mmol, 26.5 mg) was added to a methanolic solution (10 mL) of H₂L¹ (0.1 mmol, 27.6 mg) and 8-hydroxyquinoline (0.1 mmol, 14.5 mg) with stirring. The mixture was stirred for 0.5 h at room temperature 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 diffraction were formed at the bottom of

the vessel. The isolated products were washed three times with cold methanol and dried in air. Yield: 55 %; Anal. Calcd. for $C_{24}H_{17}FN_3O_5V$: C, 58.0; H, 3.4; N, 8.4. Found: C, 57.7; H, 3.5; N, 8.6 %.

Synthesis of [VOL₂(HQ)] (2): This complex was prepared according to the same method as that described for **1**, with H_2L^1 replaced by H_2L^2 (0.1 mmol, 28.8 mg). Yield: 45 %; Anal. Calcd. for $C_{23}H_{14}F_2N_3O_4V$: C, 56.9; H, 2.9; N, 8.7. Found: C, 56.8; H, 2.9; N, 8.5 %.

X-ray crystallography: Diffraction intensities for the complexes were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with MoK_{α} radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program²¹, and multi-scan absorption corrections were performed using the SADABS program²². The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL²³. All of the non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data are listed in Table-1. Selected bond lengths and angles are given in Table-2.

TABLE-1
CRYSTALLOGRAPHIC AND EXPERIMENTAL
DATA FOR **1** AND **2**

Complex	1	2
m.f.	$C_{24}H_{17}FN_3O_5V$	$C_{23}H_{14}F_2N_3O_4V$
m.w.	497.35	485.31
T (K)	298(2)	298(2)
Crystal shape/color	Block/deep brown	Block/deep brown
Crystal size (mm ³)	$0.30 \times 0.30 \times 0.27$	$0.29 \times 0.26 \times 0.22$
Crystal system	Orthorhombic	Monoclinic
Space group	Pbcn	$P2_1/n$
a (Å)	32.327(2)	12.4965(8)
b (Å)	8.189(2)	13.3795(9)
c (Å)	16.817(1)	13.8324(9)
α (°)	90	90
β (°)	90	115.555(2)
γ (°)	90	90
V (Å ³)	4451.9(9)	2086.5(2)
Z	8	4
D_c (g cm ⁻³)	1.484	1.545
μ (MoK α) (mm ⁻¹)	0.496	0.530
F(000)	2032	984
Measured reflections	39935	20074
Independent reflections	3956	3886
Observed reflections ($I \geq 2\sigma(I)$)	2075	2919
Min. and max. transmission	0.8655 and 0.8778	0.8614 and 0.8923
Parameters	308	298
Restraints	0	0
Goodness-of-fit on F^2	1.060	1.047
R_1, wR_2 [$I \geq 2\sigma(I)$] ^a	0.0587, 0.0921	0.0378, 0.0919
R_1, wR_2 (all data) ^a	0.1460, 0.1168	0.0592, 0.1039
Largest peak and deepest hole (e Å ⁻³)	0.212, -0.223	0.247, -0.260

$$^a R_1 = F_o - F_c / F_o, wR_2 = [\sum w(F_o^2 - F_c^2) / \sum w(F_o^2)]^{1/2}$$

TABLE-2
SELECTED BOND DISTANCES (Å)
AND ANGLES (°) FOR THE COMPLEXES

Complex 1			
Bond lengths, Å			
V1-O1	1.856(2)	V1-O2	1.930(2)
V1-O4	1.839(2)	V1-O5	1.582(3)
V1-N1	2.077(3)	V1-N3	2.346(3)
Bond angles, °			
O5-V1-O4	99.82(12)	O5-V1-O1	99.32(12)
O4-V1-O1	103.34(11)	O5-V1-O2	100.27(12)
O4-V1-O2	91.60(10)	O1-V1-O2	152.88(11)
O5-V1-N1	97.00(13)	O4-V1-N1	159.98(12)
O1-V1-N1	84.46(11)	O2-V1-N1	74.71(11)
O5-V1-N3	175.98(12)	O4-V1-N3	76.20(11)
O1-V1-N3	81.22(11)	O2-V1-N3	80.55(10)
N1-V1-N3	87.01(11)	—	—
Complex 2			
Bond lengths, Å			
V1-O1	1.8497(18)	V1-O2	1.9427(16)
V1-O3	1.8304(15)	V1-O4	1.5879(16)
V1-N1	2.0860(18)	V1-N3	2.3577(18)
Bond angles, °			
O4-V1-O3	101.21(8)	O4-V1-O1	100.12(9)
O3-V1-O1	102.23(7)	O4-V1-O2	97.90(8)
O3-V1-O2	92.03(7)	O1-V1-O2	154.29(7)
O4-V1-N1	98.03(8)	O3-V1-N1	158.13(7)
O1-V1-N1	84.39(7)	O2-V1-N1	75.02(7)
O4-V1-N3	175.40(9)	O3-V1-N3	76.31(6)
O1-V1-N3	84.25(7)	O2-V1-N3	78.43(6)
N1-V1-N3	83.75(6)	—	—

The complexes are soluble in DMF, DMSO, methanol, ethanol and acetonitrile. Molar conductance of the complexes at the concentrations of 10^{-4} mol L⁻¹ are in the range 20-35 Ω^{-1} cm² mol⁻¹, indicating they are non-electrolytes²⁴.

Crystal structure description of the complexes: The molecular structures and atom numbering schemes of complexes **1** and **2** are shown in Figs. 1 and 2, respectively. Vanadium atoms in the complexes are in octahedral coordination, with the three donor atoms of the benzohydrazone ligands and the hydroxy O atom of the HQ ligand defining the equatorial plane and with one oxo O atom and the pyridine N atom of the 8-hydroxyquinoline ligand occupying the axial positions. The distances between atoms V1 and O5 in **1** and V1 and O4 in **2** are 1.58(2) Å, indicating they are typical V=O double bonds. The V-N_{pyridine} bonds in the complexes are significantly longer than the other coordinate bonds, yet, it is not uncommon for such complexes^{17,18}. The bond lengths in both complexes are comparable to each other and also similar to those observed in the mononuclear oxovanadium(V) complexes with octahedral coordination^{17,18}. The angular distortion in the octahedral environment around vanadium comes from the five- and six-membered chelate rings taken by the benzohydrazone ligands. For the same reason, the *trans* angles significantly deviate from the ideal values of 180°. Distortion of the octahedral coordination can be observed from the coordinate bond angles, ranging from 74.71(11)° to 103.34(11)° for the perpendicular angles and from 152.88(12)° to 175.98(12)° for the diagonal angles for **1** and from 75.02(7)° to 102.23(7)° for the perpendicular angles and from 154.29(7)° to 175.40(9)° for the diagonal angles for **2**. The displacement of the vanadium atoms from

RESULTS AND DISCUSSION

Replacement of two acetylacetonate ligands of [VO(acac)₂] by benzohydrazone and 8-hydroxyquinoline ligands in methanol resulted in the formation of two structurally similar complexes.

the equatorial plane are 0.305(1) Å for **1** and 0.315(1) Å for **2**. The dihedral angles between the two benzene rings of the benzohydrazone ligands are 16.7(3)° in **1** and 5.5(3)° in **2**.

Fig. 1. ORTEP plot of the molecular structure of **1**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30 % probability level

Fig. 2. ORTEP plot of the molecular structure of **2**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30 % probability level

IR and UV-visible spectra: Complexes **1** and **2** exhibit typical bands at 970 and 973 cm^{-1} , respectively, assigned to the $\text{V}=\text{O}$ vibration^{9b}. The bands due to $\text{V}=\text{O}$ were absent in the complexes, but new $\text{C}=\text{O}$ stretches appeared at 1257 cm^{-1} for **1** and **2**. This suggests occurrence of *keto-imine* tautomerization of the ligands during complexation. The intense $\text{V}=\text{N}$ absorptions are observed at 1605 cm^{-1} for **1** and 1610 cm^{-1} for **2**. The weak peaks in the low wave numbers in the region (650–450) cm^{-1} may be attributed to $\text{V}-\text{O}$ and $\text{V}-\text{N}$ bonds in the complexes.

The acetonitrile solutions of the complexes with concentration of $10^{-5} \text{ mol L}^{-1}$ have been used to record the electronic spectra. The main features of all the spectra are quite similar (Fig. 3). There are two major absorptions within the ranges 650–450 and 360–320 nm in the visible region. These are attributed to the ligand-to-metal charge transfer transitions (LMCT). The high energy absorptions (300–220 nm) are most likely due to the transition involving ligand orbitals only.

Fig. 3. UV-visible spectra of the VO(II) complexes

Thermal property: Differential thermal and thermal gravimetric analyses were conducted to examine the stability of the complexes under air atmosphere and with standard corundum crucible sample holder (Fig. 4 for **1** and Fig. 5 for **2**). The rate of the gas flow is $20 \text{ cm}^3 \text{ min}^{-1}$. The heating rate is $10^\circ\text{C min}^{-1}$. For **1**, the complex decomposed from 240 to 520 $^\circ\text{C}$, corresponding to the loss of the benzohydrazone and HQ ligands and the formation of V_2O_5 . The total observed weight

Fig. 4. DTA-TGA curve of complex **1**

Fig. 5. DTA-TGA curve of complex **2**

loss of 83 % is close to the calculated value of 81.7 %. For complex **2**, the complex decomposed from 200 to 520 °C, corresponding to the loss of the benzohydrazone and HQ ligands and the formation of V₂O₅. The total observed weight loss of 83.5 % is close to the calculated value of 81.3 %.

Supporting information: CCDC 991929 for **1** and CCDC 991930 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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