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

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Two new oxovanadium(V) complexes, [VOL^1(HQ)] (**1**) and [VOL^2(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 (H$_2$L^1) and N'-(5-fluoro-2-hydroxybenzylidene)-4-methoxybenzohydrazide (H$_2$L^2), 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) Å^3, Z = 8, GOOF = 1.060, R$_1$ = 0.0587 and wR$_2$ = 0.0921. Complex **2** crystallizes in the monoclinic space group P2$_1$/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) Å^3, 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 chemistry[1-4]. 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 haloperoxidases[5-9]. Recently, our research group has reported a few vanadium complexes with biological activities[10-12]. 8-Hydroxyquinoline (HHQ) is a widely known bidentate ligand in coordination chemistry[13-16], 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, [VOL^1(HQ)] (**1**) and [VOL^2(HQ)] (**2**) (H$_2$L^1 = N'-(5-fluoro-2-hydroxybenzylidene)-4-fluorobenzohydrazide, H$_2$L^2 = N'-(5-fluoro-2-hydroxybenzylidene)-4-methoxybenzohydrazide; **Scheme-I**), have been presented.
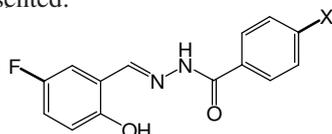
Scheme-I: Benzohydrazone ligands. H$_2$L^1: X = F; H$_2$L^2: X = OMe

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. H$_2$L^1 and H$_2$L^2 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 [VOL^1(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 H$_2$L^1 (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 [VOL$_2$(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$_\alpha$ radiation (λ = 0.71073 Å). The collected data were reduced using the SAINT program[21], and multi-scan absorption corrections were performed using the SADABS program[22]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL[23]. 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 × 0.30 × 0.27	0.29 × 0.26 × 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$_\alpha$) (mm^{-1})	0.496	0.530
F(000)	2032	984
Measured reflections	39935	20074
Independent reflections	3956	3886
Observed reflections (I ≥ 2σ(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 ≥ 2σ (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} $R_1 = F_o-F_c/F_o$, $wR_2 = [\sum w(F_o^2-F_c^2)/\sum w(F_o^2)^2]^{1/2}$

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.

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} cm^2 mol^{-1}, indicating they are non-electrolytes[24].

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

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**.
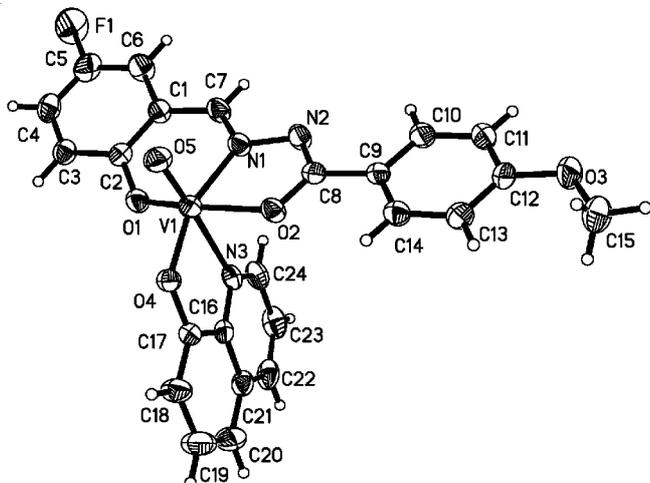

Fig. 1. ORTEP plot of the molecular structure of **1**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30 % probability level
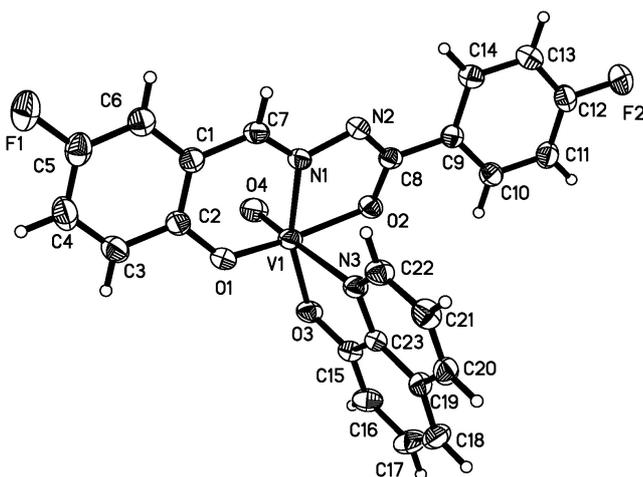

Fig. 2. ORTEP plot of the molecular structure of **2**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30 % probability level

IR and UV-visible spectra: Complexes **1** and **2** exhibit typical bands at 970 and 973 cm⁻¹, respectively, assigned to the V=O vibration[9b]. The bands due to $\nu_{C=O}$ were absent in the complexes, but new C-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 νC=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 V-O and V-N bonds in the complexes.

The acetonitrile solutions of the complexes with concentration of 10^{-5} 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.
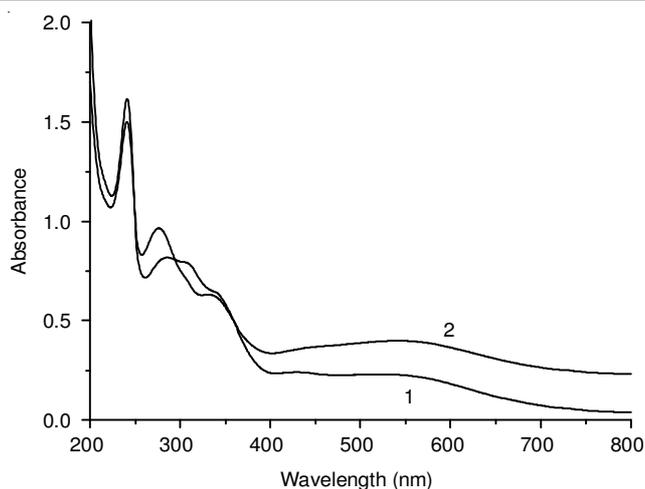

Fig. 3. UV-visible spectra of the VO(II) complexes

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 cm³ min⁻¹. The heating rate is 10 °C min⁻¹. For **1**, the complex decomposed from 240 to 520 °C, corresponding to the loss of the benzohydrazone and HQ ligands and the formation of V_2O_5. The total observed weight
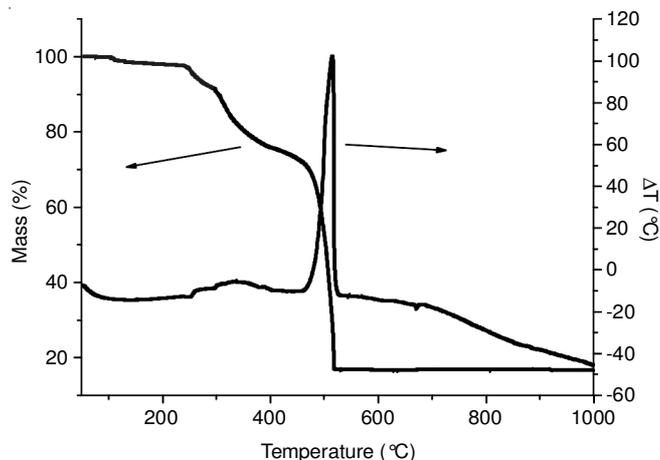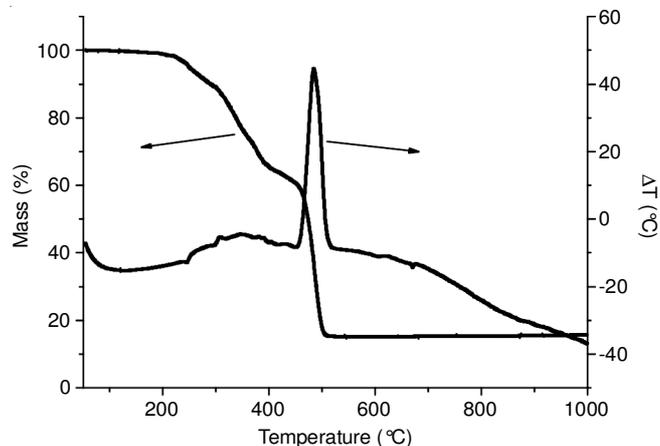

Fig. 4. DTA-TGA curve of complex **1**

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 V_2O_5. 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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