



Original Research article

Vanadium(IV) Schiff base Complex: Synthesis, Characterization, Crystal Structure and Thermal Decomposition into V₂O₅ Particles



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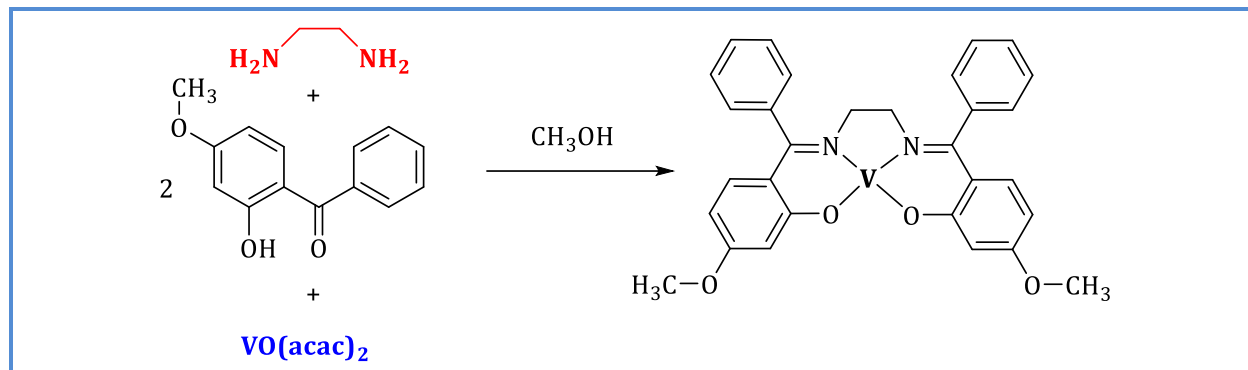
KEYWORDS

Vanadium(IV) complex
Distorted square pyramid
Spectroscopy
Thermogravimetric analysis

ABSTRACT

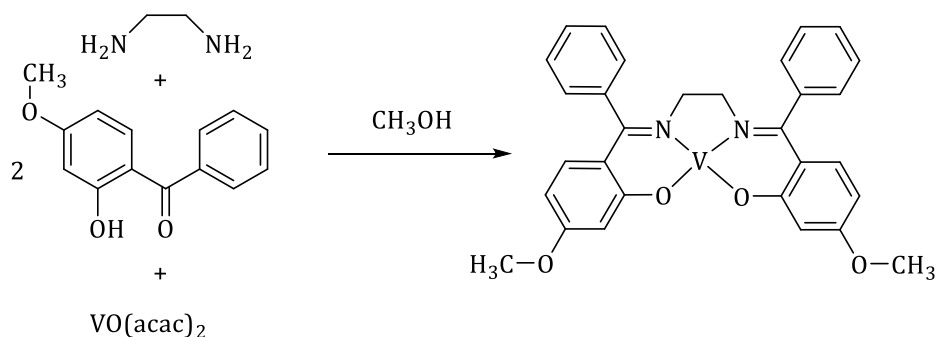
Vanadium(IV) complex [VO((MeO-bph)₂en)] (**1**), (MeO-bph)₂en=*N,N'*-bis(2-hydroxy-4-methoxybenzophenone)-1,2-ethanediamine, was synthesized and characterized by elemental analyses (CHN), FT-IR spectroscopy, thermogravimetry, SEM and single crystal X-ray diffraction. The title complex **1** was prepared by the reaction of VO(acac)₂, 1,2-ethanediamine and 2-hydroxy-4-methoxybenzophenone (molar ratio 1:1:2). The single-crystal X-ray analysis of **1** shows that the vanadium(IV) ion is located in a distorted square pyramid (N₂O₃) environment with the tetradentate Schiff base ligand coordinated in equatorial positions and one oxygen atom in the axial position. Thermogravimetric analysis shows that the complex **1** decomposes in two stages. Finally, the complex was calcinated at 500 °C for 3 h and the V₂O₅ products characterized by FT-IR and SEM.

Graphical Abstract



Introduction

Schiff bases have played an important role in the development of the V(IV) complexes, because they are capable of giving the complexes interesting structural features, suitable properties and applications [1-3]. The interest in the vanadium Schiff base complexes has grown due to their catalytic applications and biological activity [4-6]. The vanadium(IV) Schiff base complexes are colored either green with a monomeric structure [7] or orange with a polymeric linear chain structure [8]. Recently, *Grivani* et al., have focused on the coordination chemistry of vanadium Schiff base complexes because of their structural features and catalytic application [7-10]. In this paper, mononuclear vanadium(IV) Schiff base complex [VO((MeO-bph)₂en)] (**1**) (Scheme 1) was prepared and characterized.



Scheme 1. The preparation procedure of tetradentate Schiff base ligand (MeO-bph)₂en and its vanadium(IV) complex

Experimental

General

All reagents and solvents were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and

results agreed with calculated values. FT-IR spectra were recorded as a KBr disk on a FT-IR PerkinElmer spectrophotometer. The TG/DTA were performed on a PerkinElmer TG/DTA lab system 1 (technology by SII) in argon atmosphere with a heating rate of 20 °C/min in the temperature span of 50–800 °C. The scanning electron microscopy (SEM) images were obtained from a Philips XL-30ESEM.

Preparation of **1**

A solution of 1,2-ethanediamine (0.1 mmol) in 15 mL methanol is added drop-wise to a methanolic solution of 2-hydroxy-4-methoxybenzophenone (0.2 mmol) under stirring condition. The reaction mixture is then refluxed for 1 h during which the solution color turns yellow. Then, a solution of VO(acac)₂ (0.1 mmol in 15 mL methanol) was added drop-wise. After the addition was completed, the stirring was continued at reflux for 3 h. After several days by slow evaporation of solvent, dark green crystals of the complex were filtered and washed with cold methanol and dried at room temperature. Anal. Calcd. for C₃₀H₂₆N₂O₅V: C, 65.99.; H, 4.77.; N, 5.13%. Found; C, 66.04.; H, 4.82.; N, 5.08%. FT-IR (KBr, cm⁻¹): 2925-3033 (CH aromatic and aliphatic), 2844 (CH=N), 1587 (C=N), 1465-1542 (C=C aromatic).

Preparation of V₂O₅ particles

About 0.5 g of the title compound was loaded into a platinum crucible and placed in an oven and heated at a rate of 10 °C min⁻¹ in air. The black product was obtained at 500 after 3 h, washed with ethanol to remove impurities, dried at room temperature and characterized by FT-IR and SEM.

X-ray structure determination

Suitable single crystal of the dimensions 0.23 mm×0.22 mm×0.16 mm for **1** was chosen for X-ray diffraction study. Crystallographic measurements were done at 120 K with a four circle CCD diffractometer Supernova of Rigaku oxford diffraction, using Cu-K α radiation from a micro-focus sealed tube collimated by mirrors. As a detector, we used the CCD detector Atlas S2. Crystal structures were solved by charge flipping with program SUPERFLIP [11] and refined with the Jana 2006 program package [12] by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by diamond 4.0 [13]. All hydrogen atoms were discernible in different Fourier maps and could be refined to reasonable geometry. According to a common practice, H atoms bonded to C were kept in ideal positions with C–H=0.96 Å and with U_{iso} (H) set to 1.2 U_{eq} (C). Position of hydrogen atoms on nitrogen was refined with bond restraint, using also the above mentioned constraint for U_{iso} (H). All non-hydrogen atoms were refined using harmonic refinement.

Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

Results and discussion

Syntheses and characterization

From the one-pot reaction of VO(acac)₂, 1,2-ethanediamine and 2-hydroxy-4-methoxybenzophenone in methanol, vanadium(IV) Schiff base complex [VO((MeO-bph)₂en)] (**1**) was prepared and characterized. In the FT-IR spectra of **1**, the band at 1580 cm⁻¹ was assigned to C=N-group. Also, another band at 945 cm⁻¹ was assigned to V=O group (Grivani et al., 2015). The vibrational frequency of the OH group is absent in the complexes (Grivani et al., 2015).

The complex **1** was thermally decomposed in an electric furnace. The FT-IR spectra of the final residue (Figure 1) confirmed the formation of V₂O₅ [14, 15], by showing peaks at about at 1076, 990, 758 and 434 cm⁻¹ assigned to V=O stretching mode [14]. The peaks at 1609 and 3461 cm⁻¹ in the FT-IR spectra assigned to H₂O molecules were adsorbed on the surface of particles [16].

Table 1. Crystallographic data and structural refinement details of **1**

Formula weight	C ₃₀ H ₂₆ N ₂ O ₅ V ₁	μ , mm ⁻¹	3.67
Formula weight	545.5	R_{int}	0.019
Crystal system	Triclinic	S	1.52
Space group	$P1$	Measured reflections	8024
a (Å)	10.2604(3)	Independent reflections	4344
b (Å)	10.6916(4)	Parameters	343
c (Å)	12.1174(6)	Reflections with $I > 3\sigma(I)$	4059
α (°)	80.469(4)	$R(F^2 > 2\sigma(F^2))$	0.031
β (°)	74.310(3)	$wR(F^2)$	0.090
γ (°)	82.953(3)	T_{min}	0.532
V (Å ³)	1257.83(9)	T_{max}	0.646
Z	2		

The TG curve of **1** (Figure 2) shows that there is no detectable change up to 130 °C, and then during further heating the complex undergoes decomposition in three stages (130–285 (11.5%), 285–400 °C (14.5%) and 400–620 °C (57.5%)). These mass losses correspond to C₆H₆ (12.09%), C₇H₇ (14.11%) and C₁₉H₁₇N₂O₃ (58.84%), respectively. The reminder part at the end of decomposition is VO₂ (exp=16.5%, theor=15.21%).

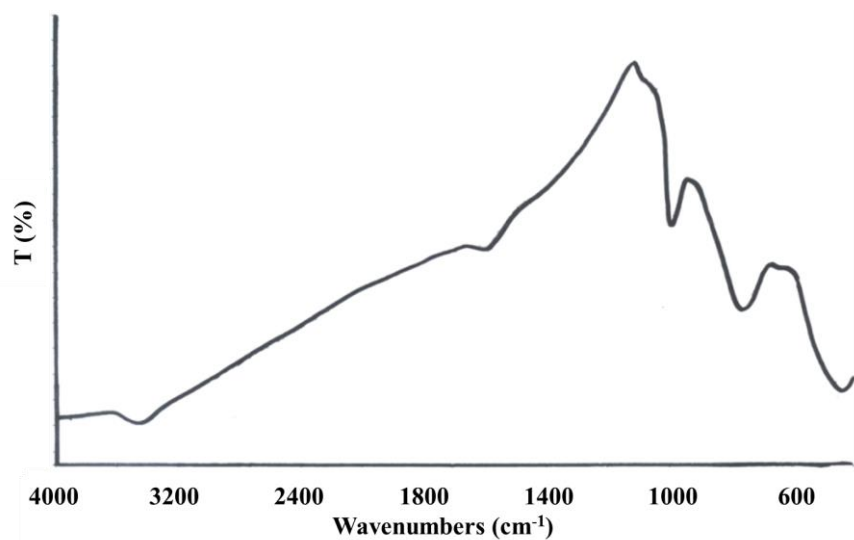


Figure 1. FT-IR spectrum of the V_2O_5 particles obtained from **1**

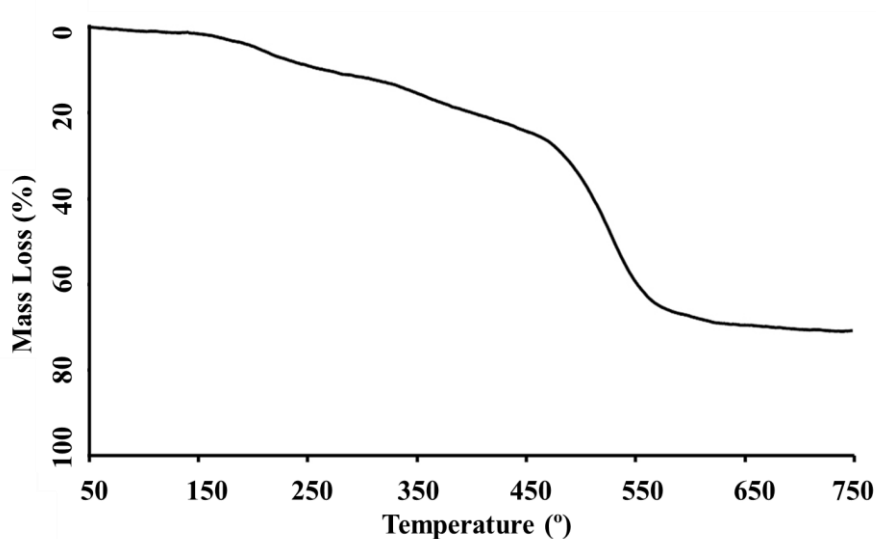


Figure 2. TG curve of **1**

The morphology of the vanadium(IV) Schiff base complex $[VO((MeO-bph)_2en)]$ (**1**) and the obtained V_2O_5 particles were further investigated by SEM. Figure 3 shows the SEM images of **1** and the obtained particles.

Description of the structure of **1**

Selected bond distances and angles of **1** are summarized in Table 2. A molecule of **1** is shown in Figure 4. The vanadium(IV) ion is five coordinated in a form of strongly distorted square-pyramid geometry [7, 8].

The coordination sphere of vanadium is completed by two iminic nitrogen atoms N1, N2, two phenoxy oxygen atoms O1, O3 of the Schiff base ligand, and a non-bridging oxo atom O1 v. The V1-N1, V1-N2, V-O1, V1-O3 single bond lengths and the V1=O1 v double bond length are respectively 2.0604 (15), 2.0535 (14), 1.9118 (12), 1.9155 (11) and 1.6015 (14) Å, and they are similar like in other mononuclear square-pyramid vanadium(IV) complexes [7, 8]. The chelating angles N1-V1-N2, N1-V1-O1 and N1-V1-O3 of 80.85 (6), 87.23 (5) and 87.45 (5)°, respectively, and also other angles around the vanadium center (see Table 2) indicate the distortion of the square-pyramidal geometry around the vanadium atom [7, 8].

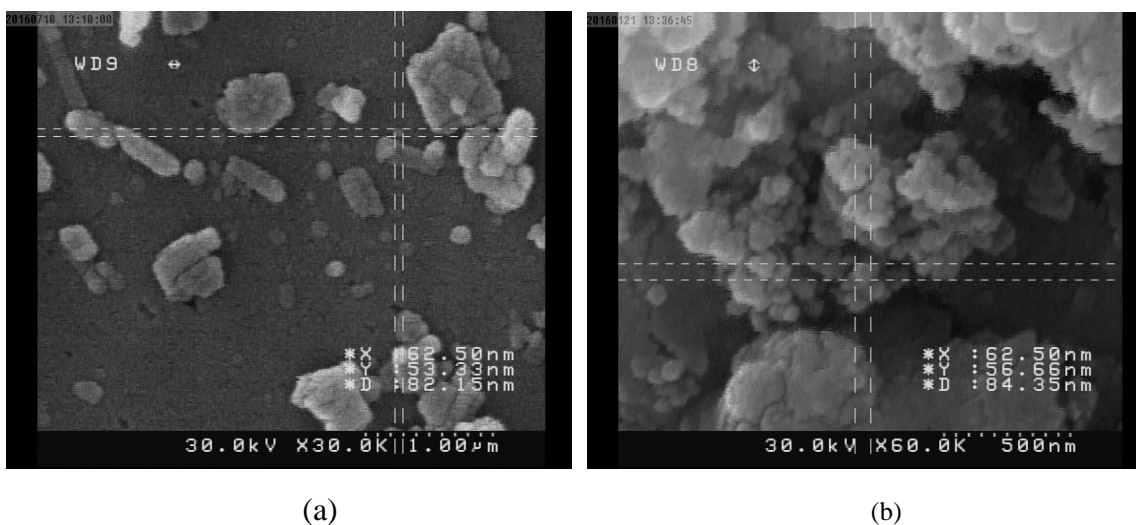


Figure 3. SEM images of 1 (a) and the V₂O₅ particles obtained from 1 (b)

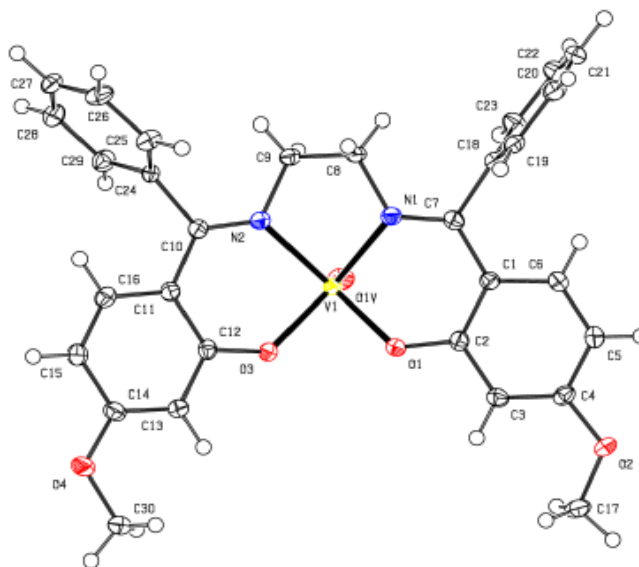


Figure 4. ORTEP view of 1

Table 2. Selected bond distances (Å) and angles (°) of **1**

V1-O1v	1.6015(14)	V1-N1	2.0604(15)
V1-O1	1.9118(12)	V1-N2	2.0535(14)
N2-C9	1.472(2)	N1-C8	1.483(2)
N1-C7	1.310(2)	V1-O3	1.9155(11)
N2-C10	1.3080(19)		
O1v-V1-O1	108.98(6)	O1v-V1-O3	111.06(6)
O1v-V1-N1	104.71(6)	O1v-V1-N2	103.01(6)
O1-V1-O3	84.85(5)	O1-V1-N1	87.23(5)
O1-V1-N2	147.76(6)	O3-V1-N1	144.03(6)
O3-V1-N2	87.45(5)	N1-V1-N2	80.85(6)
V1-N1-C8	112.77(10)	V1-N2-C10	129.91(12)
V1-O1-C2	130.53(10)	C7-N1-C8	119.52(15)
V1-N1-C7	127.66(12)	V1-O3-C12	132.68(11)
V1-N2-C9	106.69(9)	C9-N2-C10	123.18(14)

Conclusions

In conclusion, we synthesized the mononuclear complex [VO((MeO-bph)₂en)] (**1**) in simple procedure. X-ray result showed that the vanadium center had a distorted square pyramid geometry. In addition, thermal decomposition of the complex was investigated at the temperature about 600 °C. Finally, the analysis (FT-IR and SEM) of the obtained solid showed the formation of the V₂O₅ particles.

Acknowledgments

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Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 1543319 (**1**). Copies of the data can be obtained free of charge on deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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