Accepted Manuscript

Novel vanadium complexes with rigid carboxylate ligands: Synthesis, structure and catalytic bromine dynamics of phenol red

Yang Wang, Xiao-Meng Lin, Feng-Ying Bai, Li-Xian Sun

PII: S0022-2860(17)30936-5

DOI: 10.1016/j.molstruc.2017.07.015

Reference: MOLSTR 24042

To appear in: Journal of Molecular Structure

Received Date: 13 April 2017

Revised Date: 8 July 2017

Accepted Date: 10 July 2017

Please cite this article as: Y. Wang, X.-M. Lin, F.-Y. Bai, L.-X. Sun, Novel vanadium complexes with rigid carboxylate ligands: Synthesis, structure and catalytic bromine dynamics of phenol red, *Journal of Molecular Structure* (2017), doi: 10.1016/j.molstruc.2017.07.015.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Graphical Abstract



ACCEPTED MANUSCRIPT



Journal of Molecular Structure

journal homepage: www.elsevier.com

Novel vanadium complexes with rigid carboxylate ligands: synthesis, structure and catalytic bromine dynamics of phenol red

Yang Wang^a, Xiao-Meng Lin^a, Feng-Ying Bai^a*, Li-Xian Sun^b*

^a College of Chemistry and Chemical Engineering, Liaoning Normal University, Huanghe Road 850#, Dalian 116029, P.R. China ^b Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, P.R. China.

ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

Keywords: Vanadium (IV) complexes Crystal structure Haloperoxidases Mimicing bromoperoxidase Hydrogen peroxide determination

ABSTRACT

In this work, by selecting appropriate ligands, novel vanadium complexes $[V^{IV}O(2,6-pdc)(Phen)]\cdot 3H_2O$ (1) and $[(V^{IV}O)(C_5H_5N_2O_2)_2H_2O]\cdot 2H_2O$ (2) (2,6-pdc = 2,6-pyridinedicarboxylic acid, Phen= 1,10-Phenanthroline monohydrate) were synthesized by the reaction of $V_2(SO_4)_3$, 2,6-pdc and Phen (for 1), $VO(acac)_2$ and $C_5H_6N_2O_2$ (for 2) via solution or hydrothermal methods. Two complexes were characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis (TG), UV-vis spectroscopy and the single crystal X-ray diffraction. Structural analyses reveal that the vanadium atom has distorted octahedral geometry in 1 and 2 with donor sets of N3O3 and N2O4, respectively. The complexes which catalyze the oxidation of the organic substrate phenol red in the presence of H_2O_2 and bromide exhibited catalytic bromination activity, and the reaction system is considered as an effective model for hydrogen peroxide determination. The reaction rate constant (*k*) for complexes 1 and 2 can be calculated as 2.13×10^2 and 2.64×10^2 (mol/L)⁻²s⁻¹, respectively.

2009 Elsevier Ltd. All rights reserved.

1. Introduction

The coordination chemistry of vanadium, in particular with multidentate ligands, is attracting much attention on account of its application in various filed such as catalysis, medicine, electrical conductivity, magnetism, etc.¹⁻⁷ The multifarious structures and compositions of inorganic-organic hybrid materials are derived from the enormous compositional of the inorganic and organic components.⁸⁻¹² A lot of inorganic-organic hybrid vanadium complexes with multidimensional structures are prepared on account of the particularly variable oxidation states and coordination geometries of the vanadium atom. Our group has been working on the synthesis and properties of the oxovanadium/vanadium complexes for many years.^{13,14} Up to now, our group has synthesized some vanadium complexes such $[V(2,6-pdc)_2(H_2O)_2] \cdot 2H_2O$, $[V(dipic)(Hbdc)(2H_2O)],$ as $[V_2((dipic)_2(H_2btec)(4H_2O)] \cdot 2H_2O,$ $(VO)_2(bpz*T-O),$ $[VO(SO_4)(bpz^*P)(H_2O)] \cdot H_2O,$ VO(bpz*eaT)(SCN)₂, $VO(SO_4)(bpz*P-Me)(H_2O)^{15-17}$ and so on, and has carried out mimicking catalytic bromine dynamics research, which exhibited the better catalytic bromine activity.

As is known to all, vanadium haloperoxidase (V-HPOs) which are found in marine algae can expedite the oxidative halogenation of the aromatic organic complexes in the presence of organic hydroperoxides, hydrogen peroxide or molecular oxygen.¹⁸⁻²⁰ Vanadium catalysis oxidation with hydrogen peroxide has attracted great attention because of the functional properties of this metal in terms of selectivity and reactivity.²¹ In addition, it brings anti-cancer and anti-bacterial properties when the aromatic complexes are introduced by halogen group. The traditional way for bromine oxidation of aromatic complexes is electrophilic substitution, but the method is low availability of bromide and produces a lot of industrial waste which pollutes environment seriously. Therefore, it will be one of the key topics to search and synthesize substantial catalyzers with high activity in safe and non-toxic process. Under the mild condition, natural vanadium haloperoxidases (V-HPOs) can be applied for realizing the aim. Regretfully, the natural enzymes as proteins have some serious disadvantages, for instance, digestion by proteases, easily denaturationed by environmental changes and expensive preparation, etc. Therefore, we are trying to find some stable artificial vanadium complexes to mimics natural vanadium haloperoxidases.²²⁻²⁴ To our best knowledge, many vanadium complexes have been synthesized for researching and understanding the relationship between their structures and catalytic activities.²⁵⁻²⁷ As a part of continuing to work on the structures and catalytic bromine activity, it is necessary to expand and study synthesis, structures and the properties of this family of the vanadium complexes. Based on these reasons, we

synthesized two new vanadium complexes $C[V^{IV}O(2,6-M)]$ pdc)(Phen)]·3H₂O (1), $[(V^{IV}O)(C_5H_5N_2O_2)_2H_2O]·2H_2O$ (2). These complexes were characterized by elemental analysis, IR spectra, UV–Vis spectroscopy, single-crystal X-ray diffraction and thermogravimetric analysis (TG). In addition, mimic catalytic bromination dynamics of the vanadium complexes and the potential detection of hydrogen peroxide in water were also studied in this work.

2. Experimental

2.1. Materials and methods

Elemental analyses for C, H, and N were carried out on a Perkin Elmer 240C automatic analyzer. The infrared spectra wasrecorded on a Bruker AXS TENSOR–27 FT–IR spectrometer with KBr pellets in the range of 4000–400 cm⁻¹. UV-vis spectra was recorded on JASCO V-570 spectrometer (200-2000 nm, in form of solid sample). The X–ray powder diffraction data was collected on a Bruker AXS D8 Advance diffractometer using Cu–K α radiation ($\lambda = 1.5418$ Å) in the 2 θ range of 5–60° with a step size of 0.02° and a scanning rate of 3°/min. Thermogravimetric analysis (TG) was performed under atmosphere with a heating rate of 10 °C min⁻¹ on a Perkin Elmer Diamond TG/DTA.

2.2. Synthesis

[V^{IV}O(2,6-pdc)(Phen)]·3H₂O (1) A mixture of V₂(SO₄)₃ (0.039 g, 0.10 mmol), 2,6-pdc (0.02 g, 0.12 mmol), Phen (0.02 g, 0.11 mmol), ascorbic acid (V_C) (0.02 g, 0.10 mmol) and deionized water (10 mL) was loaded into a Pyrex flask. After the solution was stirred at room temperature for 3 h, the Pyrex flask was sealed and heated at 100 °C for two days, and then cooled to room temperature. Finally, brown black crystals of the complex were obtained in ca. 66% yield (0.0301g) based on V. Elemental Analysis (%) Calcd. For $C_{19}H_{17}N_3O_8V$: C, 48.93; H, 3.65; N, 9.01%. Found: C, 49.76; H, 2.62; N, 9.07%.

 $[(V^{IV}O)(C_5H_5N_2O_2)_2H_2O] \cdot 2H_2O$ (2) VO(acac)₂ (0.0265 g, 0.1 mmol) and 5-pyrazol-1H-pyrazol-3-carboxylic acid (0.025 g, 0.2 mmol) were mixed and stirred for 3 h in a solution of 95% methanol (8 mL) at room temperature. After two days, purple crystals of complex were obtained. Yield (based on V): 0.036g, 48.78%. Anal. Calc. For $C_{10}H_{16}N_4O_8V$: C, 32.35; H, 4.3; N, 15.09. Found: C, 32.35; H, 4.28; N, 15.05.

2.3. X-ray crystallographic determination

Suitable single crystals of the three complexes were mounted on glass fibers for X-ray measurement, respectively. Reflection data was obtained at room temperature with a Bruker AXS SMART APEX II CCD diffractometer (Bruker AXS, Karlsruhe, Germany) with graphite-monochromated Mo-K alpha radiation (l = 0.7107 Å) and a ω scan mode. All measured independent reflections (I > 2 sigma (I)) were used in the structural analysis and semi-empirical absorption corrections were applied using the SADABS program.²⁸ The structures were solved by the direct method using SHELXL-97.²⁹ All non-hydrogen atoms were refined anisotropically and by temperature factor with the fullmatrix least squares method. Hydrogen atoms of the organic frameworks were fixed at calculated positions with isotropic thermal parameters and refined using a riding model. Hydrogen atom of free water molecules were found in difference Fourier map. For complex 1, it should be noted that one of the O3W from free water was full occupancy and the other two O1W and O2W were disordered and split into two position with occupancy 0.7:0.3. Crystal data and structure refinements were shown in Table 1. The selected bond lengths and bond angles were giving in TableS1-S2. Hydrogen bonds of the complexes 1 and 2 were given in TableS3-S4.

2.4. Measurement of mimic catalytic bromination dynamics in solution

A We have studied catalytic bromination dynamics according to the method in the literature: ¹³⁻¹⁷ the reactions were initiated with the presence of phenol red solution, buffer solution of NaH₂PO₄– Na₂HPO₄ (pH=5.8), KBr, vanadium complex and H₂O₂. The UV spectral changes were recorded using a UV-1000 spectrophotometer at 5 min intervals. We collected the spectra data during the reaction. Finally, we calculated the bromine reaction rate constant of vanadium complexes through the experimental data.³⁰

Table 1.	Summary	of crystal	data and	refinement	results for
complex	es 1 and 2	*			

Complexes	1	2
Formula	$C_{19}H_{17}N_3O_8V$	$C_{10}H_{16}N_4O_8V$
M (g mol ⁻¹)	466. 3	371.21
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_{1}/c$	Pbca
a (Å)	14.0293(12)	17.7913(10)
b (Å)	13.5844(12)	16.9218(2)
c (Å)	10.5485(9)	20.4769(11)
α (°)	90	90
β (°)	101.2370(10)	90
γ (°)	90	90
V (Å ³)	1971.8(3)	6164.8(6)
Z	4	16
D _{calc} (Mg m ⁻³)	1.544	1.600
Crystal size (mm)	0.54×0.44×0.03	0.34×0.3×0.23
F(000)	924	3056
$\mu \ (Mo\text{-}K\alpha) \ / \ mm^{\text{-}1}$	0.556	0.691
θ (°)	1.48 to 25.00	1.94 to 28.32
Reflections collected	9785	38066
Independent reflections	3471	7662
Parameters	277	409
$\Delta(\rho)$ (e Å ⁻³)	1.827 and -0.833	0.780 and -0.771
Goodness-of-fit	1.093	1.063
R_1^a	0.0660(0.0749) ^b	$0.0514(0.0780)^{b}$
$\mathrm{wR}_2^{\mathrm{a}}$	0.2025(0.2116) ^b	0.1470(0.1650) ^b

* ^a $R = \Sigma ||F_o| - ||F_o|| / \Sigma ||F_o||$, w $R_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; $F_o| > 4\sigma(||F_o||)$.^b Based on all data.

3. Results and discussion

3.1. Synthesis

We have successfully synthesized complexes 1 and 2 with a hydrothermal reaction for 1 and the solution reaction for 2, as shown in Scheme 1. Starting material $V_2(SO_4)_3$ was used to synthesize complex 1, while VO(acac)₂ was used for 2. The complex 1 with 2,6-pdc as ligand has been synthesized by hydrothermal methods at 100 °C, it was interesting to note that the chemical valence of the central metal vanadium has been changed. A possible reason was that the higher temperature could lead to V(III) atom being oxidized into a V(IV) atom by the oxygen from air. All of the complexes were synthesized for



Scheme 1: The reaction route of the complexes 1 and 2.

3.2. IR spectra

The IR spectras of the complexes **1** and **2** were listed in (Fig.S1-S2). The broad absorption bands centered in region of 3426 and 3437 cm⁻¹ were assigned to the stretching vibrations of the unassociated O–H in the water molecules. The peaks at 3088 and 3083 cm⁻¹ were attributed to the C–H stretching vibrations of the benzene rings, pyridine rings or pyrazole rings. The bands belonged to asymmetric $v_{as}(COO⁻)$ and symmetric $v_{s}(COO⁻)$ vibrations of the carboxyl group were in 1653 and 1349 cm⁻¹ for complex **1** and in 1647 and 1324 cm⁻¹ for complex **2**. The stretching vibration of V=O was varied at approximately 982 cm⁻¹ for **1** and 964 cm⁻¹ for **2**, as expected. The band at 577 cm⁻¹ for **2** was characteristic of the stretching vibrations of V–O_{water}. The bands at 543 cm⁻¹ for **1** and 540 cm⁻¹ for **2** were attributed to the stretching vibration of V–O_{carboxyl}. Absorptions at 440 and 470 cm⁻¹ were characteristic of the stretching vibration of V–N.

3.3. Thermal analysis

In order to examine the thermal stability of the complex 1-2, thermogravimetric analysis (TG) was carried out at a heating rate of 10 °C /min under nitrogen in the temperature range of 30-1000 ^oC (Fig.S3-S4). For 1, the initial loss of 34.5 % before 515 °C was assigned to the departure of three free water molecules and partial framework collapse of Phen, the second weight loss in the range of 515-1000 °C was due to the release of remainder framework of Phen and a coordinated 2, 6-pdc ligand. The final residue of the complex corresponded to the oxide of vanadium. (24.45%) For 2, the initial weight loss of 13.68% before 292 °C was assigned to the departure of two free water molecules and a coordinated water (calc: 14.55%). The second step up to 909 °C (obs: 68.3%) was attributed to the removal of two coordinated 5pyrazol-1H-pyrazol-3-carboxylic acid. (calc: 67.4%) The final residue of the complex corresponded to the oxide of vanadium. (18.02%)

3.4. PXRD analysis

In order to confirm whether the crystal structures were truly representative of the bulk materials, the PXRD patterns of the complexes 1-2 were recorded, as shown in the Fig.S5-S6. The phase of the corresponding complex was considered as purities owning to the agreement of the peak positions. The different intensity may be due to the preferred orientation of the powder samples.

3.5. UV-Vis spectra

The UV–vis absorption spectras of the complexes 1-2 (Fig.S7-S8) were recorded in the form of solid sample and their characteristic of the UV-vis bands were listed in Table 2. They have similar absorption patterns. Bands at 216 and 266 nm for 1, and 219 and 262 nm for 2 were attributed to the π - π * transition of the ligands. The bands at 376 and 452 nm for 1, 294 nm for 2 were assigned to the LMCT (ligand to metal charge transfer) transition. The broad peaks at 742 nm for 1 and 549 and 786 nm

Table 2 Characteristic UV-Vis bands (nm) for complexes 1-2

Complexes	1	2
π-π*	216, 266	219, 262
LMCT	376, 452	294
d-d*	742	549, 786

3.6. Structural description of complexes **1-2**

 $[V^{IV}O(2,6-pdc)(Phen)]$ ·3H₂O (1) Structural analyses reveal that the complex crystallize in the monoclinic, space group $P2_1/c$. The molecular structure of the complex **1** is shown in Figure 1a. It consists of one V^{IV} atom, a terminal oxygen atom, one 2,6-pdc ligand, one Phen ligand, three free water molecules. V^{IV} is sixcoordinate with one nitrogen atom (N3) from the 2,6-pdc ligand, two oxygen atoms (O1, O4) from the 2,6-pdc ligand, two nitrogen atom (N1, N2) from Phen ligand and a terminal oxygen atom (O5) to form a distorted octahedral geometry. 2,6-pdc ligands adopt tridentate chelating coordination and Phen ligand adopt bidentate chelating coordination mode. V-O bond lengths ranged from 2.035(3) to 2.137(8) Å. V-N bond lengths ranged from 2.029(4) to 2.320(3) Å. The bond length of V=O (O5) was 1.592(3) Å, which was shorter than the single bond of V-O. Because of the inverse trans effect of the V=O (O5), the bond length of V-N2 (2.320(3) Å) was slightly longer than that of V-N1 (2.142(3) Å).

In the packing structure, there are two kinds of hydrogen bonding: (i) hydrogen bonding of C-H⁻⁻O: between the carbon atom from 2,6-pdc ligands (C15, C17) and the oxygen atoms from 2,6-pdc ligands (O2) and terminal oxygen (O5): C15-H15⁻⁻O5^{#2}, C17-H17⁻⁻O2^{#3}(#2 -x+1,-y,-z+1; #3 -x+1,y+1/2,z+3/2). (ii) hydrogen bonding of O-H⁻⁻O: between the O (donor) and the O (donor): O(1W) -H(1D)...O(2W), O(1B)-H(1F)...O(3W)^{#8}, O(2W)-H(2C)...O(3)^{#7}, O(2B)-H(2F)...O(3)^{#7}, O(3W)-H(3C)...O(1)^{#2}, O(3W)-H(3D)...O(1W)^{#5}(#2 -x+1,-y,z+1; #5 x,y,z+1; #7 -x+1,y-1/2,-z+1/2; #8 x,-y+1/2,z-1/2). By the hydrogen bonding of C15-H15⁻⁻O5^{#2}, two adjacent molecules [V^{IV}O(2,6-pdc)(Phen)] were connected to form a dimer with a closed twelve number ring structure. (Figure 1b) Then, through the hydrogen bonding of C17-H17⁻⁻O2^{#3}, the dimer was further connected to form a 2D sheet structure which was parallel with cb. The formation of the dimer was more stable through the connection of the above hydrogen bonds. (Figure 1c).



Figure 1: a: The molecular structure of the complex **1**; b: The biopolymers structure of **1**; c: A view of a 2D supramolecular network structure formed by the hydrogen bonds.

 $[(V^{IV}O)(C_5H_5N_2O_2)_2H_2O]\cdot 2H_2O$ (2) The complex crystallize in the orthorhombic, space group Pbca. The molecular structure of the complex 2 was shown in Figure 2a. It comprised two

identical crystallographically [(VO)(C₅H₅N₂O₂)₂H₂O] and four free water molecules. Each molecule was composed of one vanadium atom, two 5-pyrazol-1H-pyrazol-3-carboxylic acid molecules, one coordinated water, a terminal oxygen atom and two free water molecules, in which V^{IV} was six-coordinate with two oxygen atoms (O9, O11) and two nitrogen atoms (N1, N3) from the 5-pyrazol-1H-pyrazol-3carboxylic acid molecules, one oxygen atom (O8) from the coordinated water, and a terminal oxygen atom (O7) to form a distorted octahedral geometry. 5-pyrazol-1H-pyrazol-3carboxylic acid molecules adopt bidentate chelating coordination mode, the dihedral angle of two five number rings between (V1 O11 C1 C2 N1) and (V1 O9 C6 C7 N3) is 81.34 (8)°. V-O bond lengths ranged from 1.599(2) to 2.192(2) Å. The bond length of V=O was shorter than V-O obviously. V-N bond lengths ranged from 2.192(2) to 2.066(3) Å. O-V-O bond angles ranged from 83.27(9) to $168.83(10)^{\circ}$, O-V-N bond angles ranged from 73.34(9)to 161.99(10)°, N-V-N bond angles ranged from 91.89(10) to $94.96(10)^{\circ}$. It should be pointed out that distortion of two ligands in a molecular is different which maybe bacause free water is asymmetric distribution and build the different H-bonding.

In the packing structure, there are three kinds of hydrogen bonding: (i) hydrogen bonding of C-H^{...}O: between the C atom from 5-pyrazol-1H-pyrazol-3-carboxylic acid molecules (C16), and the O atom from free water molecule (O4W): C16- $H16E^{--}O4W^{\#6}$ (#6: -0.5+x, y, 0.5-z). (ii) hydrogen bonding of O-H^{...}O: between the O atom from free water molecule (O1W, O2W), 5-pyrazol-1H-pyrazol-3-carboxylic acid molecules (O4, O6, O10, O12), coordinated water (O2, O8) and terminal oxygen atoms (O1, O7): O1W-H1WA^{...}O10, O1W-H1WB^{...}O12^{#7} (#7: 1x, y+0.5, 0.5-z), O2W-H2WA⁻⁻⁻O4^{#1} (#1: 1-x, 1-y, 1-z), O2W--H2WB^{...}O6^{#8} (#8: 1.5-x, y+0.5, z), O8–H8D^{...}O1, O8– H2(H2) = 0.00 $H8C\cdots O1W^{#2}$ (#2: 1.5-x, -0.5+y, z), O2-H2A···O2W, O2- $H2C\cdots O7^{\#5}$ (,#5: 1.5-x, 1-y, 0.5+z). (iii) hydrogen bonding of N-H^{...}O: between the N from 5-pyrazol-1H-pyrazol-3-carboxylic acid molecules (N2, N4, N6, N8) and the O from 5-pyrazol-1Hpyrazol-3-carboxylic acid molecules (O3, O6, O9, O11): N2-H2…O6^{#3}, N4–H4…O3^{#3} (#3: 1.5-x, 1-y, z-0.5), N6–H6…O11, N8-H8...O9. By the hydrogen bonding of N6-H6"O11 and O2-H2C^{-07^{#5}, the adjacent molecules [(V^{IV}O)(C₅H₅N₂O₂)₂H₂O]} were connected to form an infinite 1D chain structure.(Figure 2b) Moreover, by the hydrogen bonding of O1W-H1WB^{...}O12^{#7} and O8-H8C^{...}O1W^{#2} the 1D chain structures are further connected to form a 2D sheet structure.(Figure 2c)



Figure 2 a: The molecular structure of the complex **2**; b: An infinite chain structure of **2**; c: A view of a 2D network structure formed by the hydrogen bonds.

Compared with other similar complexes, from the Table S3, it is found that V(IV) complexes were usually six-coordinate, there were N3O3 or N2O4 coordinate mode. The bond length of the V=O was about 1.592-1.603 Å, the bond lengths of the V-O were

independent C molecules M in the range of 1.966- 2.228 Å, ones of the

Complex 1

V-N were about 2.029- 2.320 Å.

Table 3 Hydrogen bonds (Å) for complex 1

complex 1				
D–H···A	d(D–H)/Å	d(H···A)/Å	$d(D\cdots A)/Å$	$\angle D - H \cdots A / ^{\circ}$
$C(15)-H(15)\cdots O(5)^{\#2}$	0.93	2.57	3.264(2)	131.9
$C(17)-H(17)\cdots O(2)^{\#3}$	0.93	2.55	3.380(3)	148.00
O(1W)-H(1D)···O(2W) ³	0.827(19)	1.97(2)	2.778(4)	166(5)
O(1B)-H(1F)···O(3W) ^{#8}	0.82(2)	2.56(4)	3.157(10)	166(5)
O(2W)-H(2C)···O(3) ^{#7}	0.848(19)	1.97(2)	2.806(3)	131(5)
O(2B)-H(2F)····O(3) ^{#7}	0.83(2)	2.24(9)	2.931(8)	171(5)
O(3W)-H(3C)···O(1) ^{#2}	0.822(18)	2.38(3)	3.076(3)	141(12)
O(3W)-H(3D)···O(1W) ^{#5}	0.838(18)	2.00(2)	2.826(4)	143(4)

* Symmetry code:#2 -x+1,-y,-z+1; #3 -x+1,y+1/2,-z+3/2; #5 x,y,z+1; #7 - x+1,y-1/2,-z+1/2; #8 x,-y+1/2,z-1/2

Table 4 Hydrogen	bonds (Å) :	for complex 2
------------------	-------------	---------------

D–H····A	d(D–H)/Å	d(H···A)/Å	$d(D\cdots A)/Å$	∠D–H····A/°
O8−H8C…O1W ^{#2}	0.819(9)	1.762 (11)	2.581(3)	173(3)
08–H8D···O1	0.819(9)	1.927(13)	2.730(2)	166(3)
N2-H2···O6 ^{#3}	0.86(3)	1.98(3)	2.829(3)	167(3)
N4–H4····O3 ^{#3}	0.86(3)	1.94(3)	2.792(3)	173(3)
O2−H2A····O2W	0.824(10)	1.690(10)	2.513(3)	177(3)
O2−H2C····O7 ^{#5}	0.827(9)	1.873(11)	2.697(2)	174(3)
N6–H6····O11	0.878(10)	2.190(19)	2.941(3)	143(2)
N8–H8····O9	0.83(3)	1.99(3)	2.781(3)	158(3)
O1W–H1WA···O10	0.809(10)	1.98(2)	2.742(3)	157(4)
O1W–H1WB····O12 ^{#7}	0.815(10)	2.005(15)	2.800(3)	165(4)
O2W−H2WA····O4 ^{#1}	0.816(10)	1.852(13)	2.663(3)	172(6)
O2W−H2WB・・・O6 ^{#8}	0.817(10)	1.927(12)	2.739(3)	173(6)
C16–H16E····O4W ^{#1}	0.960	2.4778	3.349(10)	150.87

Symmetry code: #1: 1-x, 1-y, 1-z; #2: 1.5-x, -0.5+y, z; #3:1.5-x, 1-y, z-0.5; #5: 1.5-x, 1-y, 0.5+z; #6: -0.5+x, y, 0.5-z; #7: 1-x, y+0.5, 0.5-z; #8: 1.5-x, y+0.5, z

3.7. Mimic catalytic bromination dynamics studies of the vanadium complexes

As mentioned above, in the presence of bromide and H_2O_2 , vanadium complexes can mimic a haloperoxidases reaction in which vanadium complex catalyze the bromination of organic substrates.³¹⁻³⁵ Herein, we have also researched the bromination reaction activities of complexes **1-2** using phenol red as organic substrate, which was converted to bromophenol blue during the reaction. The reactive process is shown in Scheme 2. The solution of complex **1** was added to the standard reaction of bromide in phosphate buffer with phenol red as a trap for oxidized bromine resulted in the visible color changing of the solution from yellow to blue. The UV absorption spectra



Scheme 2: Reactive process of the bromination reaction for the complexes.



Figure 3: oxidative bromination of phenol red catalyzed by **1**. Spectral changed at 10 min intervals. The reaction mixture contained phosphate buffer (pH=5.8), KBr (0.4 mol·L⁻¹), H₂O₂ (1 mol·L⁻¹), phenol red (10⁻⁴ mol·L⁻¹) and complex **1** (2×10⁻⁴ mmol·L⁻¹).

In order to study the catalytic reaction process, taking complex 1 as an example to execute kinetic studies of the mimicking bromination reaction. Changing the reaction time and concentration of the complex 1, a series of linear calibration plots of the absorbance at 592 nm were obtained, according to relationship of the UV absorbance data with the different reaction time.(Figure 4) Then, the catalytic reaction kinetic equation about $dc/dt = k \cdot cx \cdot c_2 y \cdot c_3 z$ was dealt with log into lg(dc/dt) = lgk $+xlgc+ylgc_2+zlgc_3$. We used dA/dt data (where A = absorbance at 592 nm) corresponding to the concentration change of the oxidovanadium complexes, as the function of $-\log (dc/dt)$ vs. variable of $-\log c$ (where c = concentration of complex) to obtain a straight line (Figure 5)³⁶⁻³⁸ We can know the slope (1.091) and intercept (2.260) through the straight line. The slope confirmed that the reaction order was first-order reaction dependence on vanadium. On the basis of the intercept, we can calculate the reaction rate constant (k) of complex 1 was $2.13 \times 10^2 \text{ (mol/L)}^{-2} \text{ s}^{-1}$. Similar plots for 2 was generated in the same way (Figure 6-7), and values of the slope and the intercept was 1.089 and 1.974, respectively. According to similar calculating method, The reaction rate constant (k) for complex 2 was $2.64 \times 10^2 \text{ (mol/L)}^{-2} \text{ s}^{-1}$.



Figure 4: A series of linear calibration plots of the absorbance at 592 nm dependence of time for different concentration of the complex **1**. Condition used: pH=5.8, c(KBr)=0.4 mol·L⁻¹, c(H₂O₂)=1 mol·L⁻¹, c(phenol red)=10⁻⁴ mol·L⁻¹. c(complex 2×10^{-4} mol·L⁻¹)= a: 10^{-5} ; b: 2×10^{-5} ; c: 3×10^{-5} ; d: 4×10^{-5} ; e: 5×10^{-5} .



Figure 5: –log (dc/dt) dependence of –logc for 1 in DMF-H_2O at $30{\pm}0.5^{o}C$



Figure 6: A series of linear calibration plots of the absorbance at 592 nm dependence of time for different concentration of the complex **2**. Condition used: pH= 5.8, c(KBr)= 0.4 mol·L⁻¹, c(H₂O₂)= 1 mol·L⁻¹, c(phenol red)= 10^{-4} mol·L⁻¹. c(complex 4×10^{-4} mol·L⁻¹)= a: 2×10^{-5} ; b: 4×10^{-5} ; c: 6×10^{-5} ; d: 8×10^{-5} , e: 10^{-4}



Figure 7: -log (dc/dt) dependence of -logc for 2 in DMF-H₂O at 30±0.5°C

Vanadium complexes played an important role in the catalytic reaction. For further research, we proposed a cyclic catalytic brominated reaction mechanism based on a large number of experimental results. (Figure 8) The tetravalent vanadium complex was easily oxidized to form an oxidovanadium intermediate by H2O2 as an oxidation regent. Br was oxidized rapidly by the oxidovanadium intermediate, while at the same time X^+ (X^+ =HOBr/Br₂/Br₃⁻ mixture) was formed with the losing of OH^{-} , in which (X^{+}) further brominated oxidized phenol red into bromophenol blue. Although the details of the mechanism still need more experimental proof, the study on application of the vanadium complex has a great prospect.

Figure 8: The catalytic brominated reaction mechanism for $V^{\left(IV\right) }$ complex.



 X^+ = HOBr / Br₂ / Br₃ mixture = Br⁻

Table 4 Kinetic data for the complexes in DMF-H₂O at 30±0.5°C

Complex	m	b	$k(mol L^{-1})^{-2}s^{-1}$
1	1.091	2.260	2.13×10 ²
2	1.089	1.974	2.64×10^2

Conditions used: c(phosphate buffer) =50 mmol·L⁻¹, pH =5.8, c(KBr) =0.4 mol·L⁻¹, c(phenol red) = 10^{-4} mol·L⁻¹. "x" is the reaction order of the vanadium complex; "b" is the intercept of the line; "k" is the reaction rate constant for the vanadium complex

Above the experimental results showed that (i) the reaction orders of the vanadium complexes in the bromination reaction are all close to 1, confirming appreciatively the first-order dependence on vanadium; (ii) the reaction rate constants of the two complexes is 2>1 (Table 4). Different ligand lead to different catalytic reaction activity of the vanadium complexes. In complex 1 and 2, the complex with coordinated water has higher catalytic activity, such as 2, attributed to low bond energy of the V-O_{H2O} and easy dissociation of water, resulting in easier formation of the intermediate. These results show that the catalytic activity of the complexes may have great connection with their structural characterization.

3.8. The effect of the concentration of H_2O_2 on bromination

A series of lines dependent on $c(H_2O_2)$ at 5 min intervals (among 20-45 min) were plotted for **1** (Figure 9). In the detection of hydrogen peroxide, we need to ensure accuracy of the detection and the time as short as possible. The R^2 of the lines with different reaction time was calculated, R_{20min}^2 =0.987, $\begin{array}{c} {R_{25}} \\ {R_{25}} \\ {min}^2 = 0.9415 \end{array} , \quad {R_{30}} \\ {R_{30min}}^2 = 0.9531 \end{array} , \quad {R_{35min}}^2 = 0.9576 \hspace{0.5cm}, \\ {R_{40min}}^2 = 0.965 \hspace{0.5cm}, \\ {R_{45min}}^2 = 0.9709 \end{array} . \quad To get best linear relationship$ and shortest time, we chosen 20 min as the reaction time for the detection of H₂O₂.



Figure 9: The relationship between the amount of hydrogen peroxide and the absorbance of the reaction with different time. Condition used: pH=5.8, c(KBr)=0.4 mol·L⁻¹, c(complex)= 4×10^{-5} mol·L⁻¹, c(phenol red)= 10^{-4} mol·L⁻¹, V(H₂O₂)= 1.3, 1.5, 1.7, 1.9, 2.1, 2.3 mL, $c(H_2O_2) = 1.273, 1.47, 1.665, 1.86, 2.057, 2.253 \text{ mol} \cdot L^{-1}$.



Figure 10: The linear relationship between the amount of hydrogen peroxide and the absorbance of the reaction of complex 1. Condition used: pH= 5.8, c(KBr)= 0.4 mol·L⁻¹, c(complex)= 4×10^{-5} mol·L⁻¹, c(phenol red)= 10^{-4} mol·L⁻¹, V(H₂O₂)= 1.3, 1.5, 1.7, 1.9, 2.1, 2.3 mL, $c(H_2O_2)=1.273, 1.47, 1.665, 1.86, 2.057, 2.253 \text{ mol} \cdot L^{-1}.$

From Figure 10, every line denotes a linear relationship between the amount of hydrogen peroxide and the absorbance of the reaction system at given time with complex 1 as catalyzer.

According to the same method, and the linear data of absorbance M_1 dependence of $c(H_2O_2)$ from other complex is also obtained (Figure S9). The detection limit value of the concentration H_2O_2 is estimated to be 1.019 mol/L for **1** and 1.098 mol/L for **2** by extension of the line. All these observations further confirm that the catalytic reaction system can be used as a potential method for the detection of H_2O_2 .

4. Conclusion

In this work, by selecting appropriate ligands, two new vanadium complexes have been successfully synthesized for the first time. In order to investigate their applicability, we tested the bromination reaction activities with phenol red as organic substrate in the presence of H_2O_2 , KBr, and a phosphate buffer solution to explore the model oxovanadium complexes mimicking the active center of VHPO and the further study the H_2O_2 detection system which is simple and sensitive. We will investigate deeply the application of the vanadium complexes as catalysts in the future.

Acknowledgements

This work was supported by the grants of the National Natural Science Foundation of China (Nos. 21571091, 21371086) and Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, P.R. China (Project No. 151002-K) for financial assistance for financial assistance.

References and notes

- 1 J. C. Pessoa. Inorg. Biochem., 2015, 147, 4.
- 2 V. Conte, B. Floris, Inorg. Chim. Acta, 2010, 1935,1946.
- 3 V. Conte, B. Floris, Dalton Trans, 2011, 40, 1419.

4 N. Taniyama, Y. Ohki and K. Tatsumi, Inorg Chem., 2014, 53, 5438-5446.

5 J. Kauppila, L. Lund, T. Laiho, M. Salomäki, J. Kankare and J. Lukkari, J. Mater. Chem. C, 2014,2, 3602-3609.

6 F. Marchetti, C. Pettinari, C. D. Nicola, R. Pettinari, A. Crispini, M. Crucianelli and A. D. Giuseppe, Appl. Catal., A 2010, 378, 211-220.

7 W. Plass, Coord. Chem. Rev., 2011, 255, 2378-2387.

8 S. H. Feng and R. R. Xu, Acc. Chem. Res., 2001, 34 (3), 239–247.

9 Z. Shi, S. Feng, S. Gao, L. R. Zhang, G. Y. Yang, J. Hua, Angew. Chem., Int. Ed. 2000, 39(13), 2325-2327.

10 Z. Shi, S. Feng, L. Zhang, G. Yang, J. Hua, Chem. Mater. 2000, 12(10), 2930-2935.

11 M. Schindler, F. C. Hawthorne, W. H. Baur, Chem. Mater. 2000, 12(5), 1248-1259.

12 Z. M. Dai, Z. Shi, G H. Li, D. Zhang, W. S. Fu, H. Y. Jin, W. Xu, S. H. Feng, Inorg. Chem., 2003, 42, 7396-7402.

13 R. Zhang, J. Liu, C. Chen, Y. H. Xing, Q. L. Guan, Y. N. Hou, X. Wang, X. X. Zhang and F. Y. Bai, Spectrochim. Acta, Part A, 2013, 115, 476-482.

14 R. Zhang, X. X. Zhang, F. Y. Bai, C. Chen, Q. L. Guan, Y. N. Hou, X. Wang and Y. H. Xing, J. Coord. Chem., 2014, 67, 1613-1628.

15 X. D. Feng, X. X. Zhang, Z. N. Wang, J. Song, Y. H. Xing and F. Y. Bai, New J. Chem., 2016, 40, 1222-1229.

16 C. Chen, Q. Sun, D. Ren, R. Zhang, F. Y. Bai and Z. Shi, Cryst. Eng. Commun., 2013, 15, 5561-5573.

18 M. Isupov, A. Dalby, A. Brindley, T. Izumi, T. Tanabe and J. Littlechild, J. Mol. Biol., 2000, 299, 1035-1049.

19 J. Littlechild and E. Garcia-Rodriguez, Coord. Chem. Rev., 2003, 237, 65-76.

20 M. Almeida, S. Filipe, M. Humanes, M. F. Maia, R. Melo, N. Severino, J. A. L. da. Silva, J. J. R. Frau´sto da Silva and R. Wever, Phytochemistry, 2001, 57, 633-642

21 A. Colettia, P. Gallonia, A. Sartorelb, V. Contea and B. Florisa, Catalysis Today, 2012, 192, 44-55.

22 N. Teshima, M. Kuno, M. Ueda, H. Ueda, S. Ohno and T. Sakai, Talanta, 2009, 79, 517-522.

23 F. Natalio, R. Andre', A. F. Hartog, B. Stoll, K. P. Jochun, R. Wever and W. Tremel, Nat. Nanotechnol., 2012, 7, 530-535.

24 M. Sandy, J. N. Carter-Franklin, J. D. Martin and A. Butler, Chem. Commun., 2011, 47, 12086-12088.

25 M. Kosugi, S. Hikichi, M. Akita and Y. Moro-oka, Inorg. Chem., 1999, 38, 2567-2578.

26 M. Etiennc, Coord. Chem. Rev., 1996, 156, 201-236.

27 M. Herberhod, G. Frohmader, T. Hofmann and W. Milius, J. Darkwa, Inorg. Chim. Acta, 1998, 267, 19-25.

28 G. M. Sheldrick. SADABS, Program for Empirical Absorption Correction for Area Detector Data, University of Götingen, Götingen, Germany, 1996.

29 G. M. Sheldrick. SHELX-97, Program for Crystal Structure Analysis, University of Gottingen: Gottingen, Germany, 1997.

30 E. Verhaeghe, D. Buisson, E. Zekri, C. Leblanc, P. Potin and Y. Ambroise, Anal. Biochem., 2008, 379, 60-65.

31 M. R. Maurya, Coord. Chem. Rev., 2003, 237,163-181.

32 A. Messerschmidt and R. Wever, Proc. Natl. Acad. Sci. U S A, 1996, 93, 392-396.

33 S. Patra, S. Chatterjee, T. Kr. Si and K. K. Mukherjea, Dalton Trans., 2013, 42, 13425-13435.

34 V. Conte and B. Floris, Inorg. Chim. Acta, 2010, 363, 1935-1946.35 G J. Colpas, B. J. Hamstra, J. W. Kampf and V. L. Pecoraro, J. Am. Chem. Soc., 1996, 118, 3469-3478.

36 G Zampella, J. Y. Kravitz, C. E. Webster, P. Fantucci, M. B. Hall, H. A. Carlson, V. L. Pecoraro and L. D. Gioia, Inorg. Chem., 2004, 43, 4127-4136.

37 T. N. Mandal, S. Roy, A. K. Barik, S. Gupta, R. J. Butcher and S. K. Kar, Polyhedron, 2008, 27, 3267-3274.

38 A. Pohlmann, S. Nica, T. K. K. Luong and W. Plass, Inorg.Chem. Commun., 2005, 8, 289-292.

39 O. Bortolini, V. Conte, C. Chiappe, G. Fantin, M. Fogagnolo and S. Maietti, Green Chem., 2002, 4, 94-96.

40 Z. Li, X. H. Zheng, Q. L. Sheng, Z. Y. Yang and J. B. Zheng, RSC Adv., 2016, 6, 11218-11225.

41 H. H. Deng, G. W. Wu, D. He, H. P. Peng, A. L. Lin, X.H. Xia and W. Chen, Analyst, 2015, 140, 7650-7656.

42 C. Perez, J. P. Monserrat, Y. Chen and S. M. Cohen, Chem. Commun., 2015, 51, 7116-7119.

Supplementary data

Figures of Infrared spectra, TG analysis, PXRD, UV-Vis spectrum, hydrogen bonds of complexes, Coordination modes and bond lengths (Å) range compare with other complexes, the bond lengths (Å) and angles (°) are presented in the supplementary material. CCDC: 1496249 and 1496250.

ACCEPTED MANUSCRIPT

- Syntheses and crystal structures of two novel vanadium complexes
- catalyze the bromination reaction of the organic substrate phenol red in the presence of $\ensuremath{H_2O_2}$
- detection of H₂O₂