

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa



Synthesis, structures and properties of the catalytic bromination reaction of a series of novel scorperate oxidovanadium complexes with the potential detection of hydrogen peroxide in water



Rui Zhang^a, Jing Liu^b, Chen Chen^a, Yong-Heng Xing^{a,*}, Qing-Lin Guan^a, Ya-Nan Hou^a, Xuan Wang^a, Xiao-Xi Zhang^a, Feng-Ying Bai^{c,*}

^a College of Chemistry and Chemical Engineering, Liaoning Normal University, Huanghe Road 850#, Dalian 116029, PR China

^b Regenerative Medicine Centre, First Affiliated Hospital of Dalian Medical University, Dalian 116011, PR China

^c College of Life Science, Liaoning Normal University, Dalian 116029, PR China

HIGHLIGHTS

- Four novel oxidovanadium complexes.
- Poly(pyrazolyl)borate ligand modified by iodine.
- Crystal structure.
- Bromination reaction activity.
- Potential detection of hydrogen peroxide.

A R T I C L E I N F O

Article history: Received 28 March 2013 Received in revised form 13 June 2013 Accepted 19 June 2013 Available online 1 July 2013

Keywords: Oxidovanadium complex Poly(4-1-pyrazoly1)borate Bromination reaction activity Synthesis Crystal structure

GRAPHICAL ABSTRACT

Four scorpionate oxovanadium (IV) complexes: $[VO(Tp^{4l})(pz)(SCN)] \cdot 1/2CH_2Cl_2$ (1), $[VO(Tp)(pzTp)] \cdot 2H_2O$ (2), $[VO(Bp)(Tp^{4l})]$ (3) and $[VO(C_5H_7O_2)(Tp^{4l})] \cdot CH_3OH$ (4) (Bp: $[H_2B(pz)[2-]]$; Tp: $[HB(pz)^{3-}]$; Tp[4l]: $[HB(4I-pz)^{3-}]$; pzTp: $[B(pz)^{4-}]$) have been synthesized and characterized by elemental analysis, IR, UV-Vis spectroscopy, powder X-ray diffraction, single-crystal X-ray diffraction and thermal gravimetric analyses (TG).



ABSTRACT

A series of scorpionate oxovanadium (IV) complexes: $[VO(Tp^{4l})(pz)(SCN)] \cdot 1/2CH_2Cl_2$ (1), $[VO(Tp)(pzTp)] \cdot 2H_2O$ (2), $[VO(Bp)(Tp^{4l})]$ (3) and $[VO(C_5H_7O_2)(Tp^{4l})] \cdot CH_3OH$ (4) (Bp: $[H_2B(pz)^{2-}]$, Tp: $[HB(pz)^{3-}]$, Tp^{4l}: $[HB(4l-pz)^{3-}]$, pzTp: $[B(pz)^{4-}]$) have been synthesized and characterized by elemental analysis, IR spectra, UV–Vis spectroscopy, powder X-ray diffraction, single-crystal X-ray diffraction and thermal gravimetric analysis (TG). Structural analysis shows that the coordination environment of vanadium atom is N₅O, to form a distorted octahedron geometry. In addition, the catalytic activities of the bromination reactions for complexes 1 and 2 in phosphate buffer with phenol red as a trap were evaluated primary by UV/Vis spectroscopy, and a practical application of H_2O_2 detection was firstly observed in the catalytic reaction system.

© 2013 Elsevier B.V. All rights reserved.

* Corresponding authors. Tel.: +86 411 82156987.

E-mail addresses: yhxing2000@yahoo.com (Y.-H. Xing), baifengying2000@163.com (F.-Y. Bai).

Introduction

Vanadium complexes have been studied for a long time owning to the biological and catalytic properties of relevant systems, such as haloperoxidation, nitrogen fixation, metalloprotein, and insulin mimicking [1,2]. Among these systems, vanadium haloperoxidases (V-HPOs) have received continuing attention since their unique characteristics and potential catalyzing activities in oxidation reactions, which are able to oxidize the two-electron oxidation/oxygenation of halide to an {X⁺}, where {X⁺} is X₂, X₃⁻ and/or XOH, i.e. hypohalous acid in the presence of peroxides [3–6].

The structure of V-HPOs active centers reveals that the central vanadium is in a trigonal-bipyramidal environment by four oxygen atoms and the axially binding N^{ε} of a histidine residue, which is embedded in the protein through an extensive hydrogen-bonding network. The active site is considered to consist of oxidovanadium with V=O moiety containing O, N donor ligands [7-11]. In particular, the interaction of simple vanadium species (VO^{2+} and VO^{3+}) with various ON or NN donor atoms having bioactive ligands is of growing interest recently. Based on the points above, we are trying to find some stable artificial enzyme mimics, such as VO-Tp (Tp: poly(pyrazolyl)borate ligands) complexes [12-15]. To our best knowledge, a number of vanadium complexes have been synthesized for studying and understanding the relationship between their structures and catalytic activities [16-20]. However, It is worth to mention that chelate scorpionate ligands used in the complexes are almost the common and simple poly(pyrazolyl)borate ligands, such as: $[H_2B(pz)^{2-}]$ (Bp), $[HB(pz)^{3-}]$ (Tp), $[HB(3,5-Me_2pz)^{3-}]$ (Tp^{*}), $[HB(4l-pz)^{3-}]$ (Tp^{4l}), and $[B(pz)^{4-}]$ (pzTp), and the poly(pyrazolyl)borate ligands were divided into three kinds, such as: (i) the scorpionate peroxidevanadium complexes: $VO(O_2)(pzH)(Tp)$ and $VO(O_2)(pz)$ (pzTp), etc. [21]; (ii) the scorpionate oxovanadium complexes: TpVO(acac) [22] and Tp*VO(Me-acac), etc. [23]; (iii) the scorpionate oxovanadium complexes with carboxylic acids: Tp*VO(pzH*)(HOO-CCH₂CH₂COO) [24] and Tp*VO(pz*)(C₆H₅COO), etc. [25]. Although a number of oxovanadium complexes containing scorpionate ligands have been reported, vanadium complexes with substituted scorpionate ligands, namely, pyrazole ring of which is modified by other functional groups (ph, NO₂, I, etc.) are relatively rare. Therefore, we are interested in studying on modified Tp ligands by iodine and their oxidovanadium complexes. As we all know that iodine is a functional group with special property (e.g. donor electron ability, large ion radius, inducing action and so on). In this work, it is found that the H atom of the pz ring from Tp is replaced by iodine, leading to the change of some chemical characterization of ligand Tp⁴¹ (e.g. the coordination ability and solubility, etc.) comparable to Tp, thus, in order to study the influence of the structure and the function of the oxovanadium complexes on this diversification, we designed and synthesized four new complexes, [VO(Tp⁴¹)(pz)(SCN)]·1/2CH₂₋ Cl₂ (**1**), [VO(Tp)(pzTp)]·2H₂O (**2**), [VO(Bp)(Tp^{4I})] (**3**) and [VO(C₅H₇₋ O_2)(Tp⁴¹)]-CH₃OH (**4**) by the reaction of oxovanadium starting material (VOSO₄ or VO(acac)₂), Tp ligand (Bp, Tp, Tp^{4l} or pzTp) with two common auxiliary ligands (pyrazolyl and KSCN) in the mixture solution of methanol and water at room temperature. These complexes were characterized by elemental analysis, IR spectra, UV-Vis spectroscopy, single-crystal X-ray diffraction and thermo gravimetric analyses (TG).

Experimental section

Materials and methods

All the chemicals used were analytical grade and without further purification. The scorpionate ligands were synthesized according to the literature method [26]. Elemental analyses for C, H, and N were carried out on a Perkin Elmer 240C automatic analyzer. The infrared spectra were recorded on a JASCO FT/IR-480 spectrometer with pressed KBr pellets in the range 200–4000 cm⁻¹. UV–Vis spectra were recorded on JASCO V-570 spectrometer (200–1100 nm, in form of solid sample).

Synthesis of the complexes

$[VO(Tp^{4I})(pz)(SCN)] \cdot 1/2CH_2Cl_2$ (1)

VOSO₄ (0.0163 g, 0.1 mmol), Tp⁴¹ (0.063 g, 0.1 mmol), pz (0.0068 g, 0.1 mmol) and KSCN (0.0097 g, 0.1 mmol) were dissolved in methanol (10 mL), stirred at room temperature for 4 h, and then produced a large amount of violet precipitate. The product was separated by filtration, and the purple crystals were recrystallized from CH₂Cl₂ solution. Yield (based on V): 0.052 g, 63.4%. Anal. Calc. For $C_{13.5}H_{12}ON_9BCISVI_3$: C, 19.62; H, 1.47; N, 15.26. Found: C, 19.64; H, 1.48; N, 15.28.

$[VO(Tp)(pzTp)] \cdot 2H_2O(2)$

A methanol solution of Tp (0.025 g, 0.1 mmol) and pzTp (0.0318 g, 0.1 mmol) was added dropwise to an aqueous solution (10 mL) of VOSO₄ (0.0163 g, 0.1 mmol) with continuous stirring for 3 h to get a blue mixture. The precipitate was filtered out, and the light blue filtrate was placed at room temperature for several days. Blue crystals suitable for X-ray diffraction were obtained. Yield (based on V): 0.029 g, 48.57%. Anal. Calc. For C₂₁H₂₈O₃N₁₄B₂-V: C, 42.24; H, 4.73; N 32.84. Found: C, 42.25; H, 4.72; N, 32.86.

$[VO(Bp)(Tp^{4l})]$ (3)

The synthesized method of complex **3** was similar to that of complex **2**, however, ligands Tp and pzTp were replaced by Tp⁴¹ (0.063 g, 0.1 mmol) and Bp (0.0147 g, 0.1 mmol). The bluish violet crystals were obtained. Yield (based on V): 0.032 g, 39.77%. Anal. Calc. For $C_{15}H_{15}O$ N₁₀B₂VI₃: C, 22.39; H, 1.88; N, 17.41. Found: C, 22.41; H, 1.87; N, 17.44.

$[VO(C_5H_7O_2)(Tp^{4l})] \cdot CH_3OH(4)$

VO(acac)₂ (0.027 g, 0.1 mmol) and Tp⁴¹ (0.063 g, 0.1 mmol) were dissolved in methanol (15 mL), and stirred for 4 h at room temperature and gave a violet solution. The mixed solution was placed at room temperature for a few days, and then the purple crystals were obtained. Yield (based on V): 0.11 g, 71.15%. Anal. Calc. For $C_{29}H_{32}O_7N_{12}B_2V_2I_6$: C, 22.54; H, 2.09; N, 10.87. Found: C, 22.55; H, 2.12; N, 10.86.

X-ray single crystal structural determination

The crystals of **1–4** were mounted on glass fibers for X-ray measurement, respectively. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffratometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) and a ω scan mode. All the measured independent reflections ($I > 2\sigma$ (I)) were used in the structural analyses, and semi-empirical absorption corrections were applied using SADABS program [27]. The structures were solved by the direct method using SHELXL-97 [28]. All hydrogen atoms of the organic ligands were fixed at calculated positions geometrically and refined by using a riding model. The hydrogen atoms of the lattice water or free CH₃O group were found in difference Fourier map. The non-hydrogen atoms were refined with anisotropic thermal parameters.

Measurement of bromination activity in solution

The bromination reaction activity tests were carried out at the constant temperature of 30 °C \pm 0.5 °C. Oxidovanadium complexes were dissolved in a mixed solution of 25 mL H₂O–DMF (DMF:

2 mL; H₂O: 23 mL). The solutions used for kinetic measurements were maintained at a constant concentration of H^+ (pH 5.8) by the addition of NaH₂PO₄—Na₂HPO₄ buffer solution [29]. Reactions were initiated with the presence of phenol red solution. The oxidovanadium complexes with five different concentrations were confected in five cuvettes which were put into the constant temperature of warming water and spectral changes were recorded using a 721 UV-Vis spectrophotometer every interval 5 min. Finally, we collected the resulting data during the reaction. It is assumed that the rate of this reaction is described by the rate equation: dc/ $dt = kc_1^x c_2^y c_3^z$, then the equation of " $\log(dc/dt) = \log k + x \log c_1 +$ $y \log c_2 + z \log c_3$ " was obtained, it is corresponding to " $-\log(dc/$ dt) = $-x\log c_1 - b$ ($b = \log k + y\log c_2 + z\log c_3$)" where k is the reaction rate constant; c_1 , c_2 and c_3 are the concentrations of the complex, KBr and phenol red, respectively; while x, y, z are the corresponding reaction orders. According to Lambert-Beer's law. $A = \varepsilon \cdot d \cdot c$, which is differential. $dA/dt = \varepsilon \cdot d \cdot (dc/dt)$, where A is the measurable absorbance of the resultant; ε is molar absorption coefficient, which of bromophenol blue is measured as 14,500 M⁻¹ cm^{-1} at 592 nm; *d* is light path length of sample cell (*d* = 1). When the measurable absorbance data were plotted versus reaction time, a line was obtained and the reaction rate of the complexes (dA/dt)was given by the slope of the line. By changing the concentration of oxovanadium complexes in the reaction system, a series of dA/ dt data could be obtained. The reaction rate constant (k) could be obtained according to a plot of $-\log(dc/dt)$ versus $-\log c_1$ and were fitted using the curve-fitting software in the program Microsoft Excel by generating a least squares fit to a general equation of the form "y = mx - b", in which "m" is the reaction order of the oxovanadium complexes in this reaction and "b" is the intercept of the line. In the experiment, considering that the reaction orders of KBr and phenol red (y and z) are 1 according to the literature [7,30]; c_2 and c_3 are known as 0.4 mol/L and 10^{-4} mol/L , respectively. Based on the equation of " $b = \log k + y \log c_2 + z \log c_3$ ", and then the reaction rate constant (k) can be obtained. The bromination of phenol red was monitored by the measurement of the absorbance at 592 nm for the reaction solution which were taken at specific time points and diluted into the phosphate buffer solution (pH = 5.8).

Results and discussion

Synthesis

By analyzing the preparation process of the complexes 1-4, it is found that starting materials are different. VOSO₄ was used for 1-3, while VO(acac)₂ was used for **4**. The complexes **1** and **4** were synthesized in the methanol solutions, while the complexes **2** and **3** were in the mixed solution of methanol–water. All the synthesis were accomplished at room temperature. It is worth to mention that, we only obtained the powder of complex **1** in the reaction solution, then we dissolved it in CH₂Cl₂, and successfully got the single crystals. As we all known that it is difficult to get directly the single crystals of VO-Tp complexes from the reaction solution, so the complexes must be recrystallized in the other solvents, e.g. CH₂Cl₂. In addition, the complexes **1–4** are all stable at room temperature, and can be easily soluble in DMF. Detail IR and UV–Vis spectra data are provided in supplement material.

Spectra properties

IR spectra

The IR spectra of the complexes **1–4** are shown in Figs. S1–S4 and the selected data are listed in Table 1. The weak peaks observed at $3100-3200 \text{ cm}^{-1}$ are attributed to the =C–H stretching vibration. Bands at 2900–3000 cm⁻¹ are attributed to the vibration of –C–H, while it is not observed for the complexes **2** and **3**, which

indicate the absence of the $-CH_3/-CH_2$. The characteristic bands around 2500 cm⁻¹ are assigned to B–H stretching vibration from the Bp, Tp, Tp^{4I} or pzTp moiety: 2524 cm^{-1} for **1**, 2493 cm^{-1} for **2**, 2507 cm⁻¹ for **3** and 2489 cm⁻¹ for **4**, respectively. The strong bands at 1507 cm^{-1} for **1**, 1507 cm^{-1} for **2**, 1504 cm^{-1} for **3** and 1519 cm^{-1} for **4** are attributed to the stretching vibration of C=N from the pz or 4I-pz of the scorpionate ligands. Two wide and strong bands at 1580 cm^{-1} and 1370 cm^{-1} for the complex **4** are attributed to the absorption of the asymmetric and symmetric stretching vibration of the C=O group. Band of SCN group is at 2087 cm^{-1} for **1**. The strong and sharp stretching vibration bands of the V=O are observed in the region of 970-977 cm⁻¹, which is similar to those in related complexes [31]. The strong absorption bands at 610 cm⁻¹ for **1**, 611 cm⁻¹ for **3** and 610 cm⁻¹ for **4** are assigned to the C–I vibration of Tp^{4I} ligands. Band of 463 cm⁻¹ is due to the V–O stretching vibration, while bands at 356-481 cm⁻¹ are assigned to stretching vibration of V-N bonds [31-33]. The infrared spectra of the complexes (1-4) are consistent with the structural characterization of the complexes 1-4.

UV-Vis absorption spectra

The UV–Vis absorption spectra of the complexes **1**, **2** and **4** are recorded in form of the solid sample (Fig. 1). They have similar absorption patterns. In the high-frequency region, the absorption peaks at 266 nm for the complex **2** is assigned to π – π * transition of the pyrazoly ring from the Tp ligands and pzTp ligands, and absorption peaks at 340 nm for **1** and 330 nm for **4** are assigned to n– π * transitions of the scorpionate ligands. In the visible range, the complexes **1**, **2** and **4** exhibit two set of absorption peaks at 504–544 nm and 658–762 nm, peaks at 714 nm for **1**, 658 nm for **2** and 762 nm for **4** are traditionally assigned to d–d transitions of the central metal vanadium, peaks at 538 nm for **1**, 504 nm for **2** and 544 nm for **4** are attributed to d–d transitions produced from ligands to metal [34,35].

Structural description of complexes 1-4

The molecular structures of complexes **1–4** are depicted in Fig. 2. Some selected bond distances, bond angles and hydrogen bonds are summarized in Tables S1 and S2.

Structural analysis shows that the complex **1** is crystallized in the monoclinic system with P2(1)/n space group. The asymmetric unit of **1** is completed by one vanadium atom, one terminal oxygen atom, one coordinated Tp⁴¹ ligand, one pz and one -SCN group, and 0.5 free dichloromethane molecule. This vanadium atom is coordinated by one terminal oxygen atom (0), three nitrogen atoms (N2, N4 and N6) from Tp⁴¹ ligand, one nitrogen atom (N7) from pz and one nitrogen atom (N9) from -SCN atom, to form a distorted octahedron geometry (Fig. 2a). The bond lengths of V-N are in the range of 2.025 (9)-2.301(8) Å. The distance of V-O is 1.586(7) Å. The angles of the O-V-N and N-V-N are in the range of 95.8(4)–175.2(4)° and 79.4(3)–164.5(4)°, respectively. In addition, there are two kinds of hydrogen bonds in the complex 1: (i) hydrogen bond between the terminal oxygen atoms and C-H of Tp⁴¹ ligand; (ii) hydrogen bond of nitrogen from Tp^{4I} and sulfur from SCN group. The molecules are connected to a 2D superamolecular sheet by the hydrogen interactions of C4–H3 \cdots O^{#1} (3.4261(0) Å, 168.07(0)°, #1: -0.5 + x, 1.5 - y, -0.5 + z) and N8-H7····S^{#2} $(3.3612(0) \text{ Å}, 164.03(0)^\circ, \#2: 0.5 - x, -0.5 + y, 1.5 - z)$ (Fig. S5).

X-ray single crystal analysis indicates that the complex **2** is crystallized in the monoclinic system with P2(1)/n space group. The crystal structure comprises a monomeric TpVO(pzTp) neutral complex molecule and two lattice water molecules. In the asymmetric unit, vanadium atom is coordinated by one terminal oxygen (O) atom, three nitrogen atoms (N1, N3 and N5) from three pyrazolyl moieties of Tp and two nitrogen atoms (N7 and N9) from

Table 1IR data (cm⁻¹) for complexes 1–4.

Complex	=C—H	CH ₃ / CH ₂	В—Н	SCN	C=N	V=0	C—I	V—N
1	3186, 3115	2994, 2923	2524	2087	1507	970	610	481, 457, 438, 400,
2	3141	-	2493	-	1507	977	-	401
3	3122	-	2507	-	1504	976	611	456, 393, 369
4	3119	2967, 2920	2489	-	1519	972	610	413, 356



Fig. 1. The UV-Vis spectra for the complexes 1, 2 and 4.

four pyrazolyl moieties of pzTp (Fig. 2b), to form a distorted octahedron geometry. The V–O bond distance is 1.616(6) Å. The bond lengths of V–N are in the range of 2.110(12)–2.290(12) Å. The angles of the O–V–N and N–V–N are in the range of 95.6(5)–177.0(5)° and 80.3(5)–164.0(7)°, respectively. In addition, there are two kinds of hydrogen bonds in the complex **2**: (i) hydrogen bond between the lattice water molecule and the C–H of Tp ligand; (ii) hydrogen bond between lattice water molecule and the N–H of the pzTp ligand. And the molecules of the complex **2** are linked to form a 1D chain superamolecular structure by the hydrogen interactions of N14–H14B…O2W^{#3} (2.9511 Å, 125.23°, #3: 0.5 + *x*, *y*, *z*) and C4–H4A…O2W^{#4} (3.3424 Å, 148.4°, #4: 0.5 + *x*, 0.5 – *y*, -0.5 + z) (Fig. S6).

Structural crystal analysis shows that the complex **3** is crystallized in the orthorhombic system with *Pnma* space group. The molecular structure contains one vanadium atom, one terminal oxygen atom, one Bp ligand and one Tp^{41} ligand. The vanadium atom is coordinated by one terminal oxygen (O) atom, three nitrogen atoms (N1, N3 and N1A) from Tp^{41} ligand and two nitrogen atoms (N5 and N5A) from Bp ligand to form a distorted octahedron geometry (Fig. 2c). The V—O bond distance is 1.575(7) Å. The bond lengths of V—N are in the range of 2.071(7)–2.239(9) Å. The angles of the O–V–N and N–V–N are in the range of 94.7(3)–172.0(4)° and 79.5(2)–166.8(3)°, respectively.

The crystal structure of **4** comprises two monomeric $[Tp^{4l}]$ -VO(acac) neutral molecules and one free methanol molecule (Fig. 2d). The framework structure of the complex is the same as



Fig. 2. (a) The molecular structure of the complex **1**; (b) the molecular structure of the complex **2**; (c) the molecular structure of the complex **3**; (d) the molecular structure of the complex **4** (the hydrogen atoms and the free dichloromethane molecule are omitted for clarity).

that of the complex reported previously by our group [36]. However, due to the presence of the lattice methanol molecule, it is found that the connection fashion of the hydrogen bonds is different. As is shown in Fig. S7, hydrogen bonds come from the terminal oxygen atom and C—H of the Tp⁴¹ ligand, furthermore, the molecule of the complex **4** is linked to form a 1D chain superamolecular structure by the hydrogen bonding interactions of O7—H7A…O1^{#5} (2.8797 Å, 154.15°, #5: 0.5 + x, 0.5 - y, 0.5 + z), C28—H28A…O7 (3.3506 Å, 159.49°) and C20—H20A…O4^{#6} (3.4163 Å, 156.10°, #6: 1 - x, 1 - y, 1 - z).

By comparison, it is found that there is an obvious difference among the coordination abilities of three nitrogen atoms of Tp or Tp^{4I}, the V—N bond distances trans to the V=O bonds for the four complexes are considerably longer than the other V—N bonds and this is mainly because of the consequence of the strong trans influence of the terminal oxo group. Furthermore, the angles of $O_{(terminal)}$ —V— $N_{(trans)}$ of the four complexes are all closed to 180°, which are 175.2(4)°, 177.0(5)°, 172.0(4)° and 173.29(14)°, respectively. It is similar to those reported in the literature [25]. While the order of the angles of O_t —V— $N_{(trans)}$ is 2 > 1 > 4 > 3, it should be attributed to the different substituted scorpionate ligands. While for the complexes with Tp^{4I}, the differences of the corresponding angles were influenced by the steric hindrance of the second ligands.

Thermal properties

To examine the thermal stability of the complexes 1-4, thermal gravimetric analysis (TG) was carried out at a heating rate of 10 $^{\circ}C/min$ under the condition of N₂ atomosphere with the temperature range of 30-1000 °C (Fig. 3). In 1, the result shows the initial weight loss of 60.14% before 545 °C is due to the release of the half free dichloromethane molecule, one -SCN, one -pz and parts of Tp⁴¹ ligand (they could be including BH, one pz and two I atoms) (calc 60.14%). The second weight loss occurs in the range of 545–1000 °C, which is ascribed to the release of the remaining part of TP⁴¹ ligand, and the final residue is corresponded to vanadium oxide and nitride. The TG behaviours of these four complexes are slightly different due to the differences of their structures. The TG curve of 2 is divided into three steps. The first weight loss of 28.84% in the range of 30-352 °C was attributed to two lattice water molecules and two uncoordinated pyrazolyl moiety of the pzTp ligand. The second weight loss occurs in the range of 352-434 °C, with a percentage weight loss of 24.27%, which is ascribed to the release of BH moiety and two coordinated pyrazolyl moiety of the pzTp ligand. The last step of decomposition occurred within the range of 434-1000 °C, which is considered the loss of framework of Tp ligand, and the final residue is corresponding to vanadium oxide and nitride. The TG curve of **3** shows three stages: The initial weight loss of 3.06% in the range of 30-271 °C is attributed to the release of two B-H moieties. The second weight loss of 16.76% in the range of 271-337 °C is due to the release of two pyrazolyl moieties of the Bp ligand. The last step is observed in 337-1000 °C, which is considered the loss of framework of the Tp ligand. The TG curve of **4** can be divided into two stages. The initial weight loss of 11.8% in the range of 21-184 °C is due to the release of one free methyl alcohol molecule, two B-H moieties and one I group. The second weight loss of 73.14% in the range of 184–1000 °C is according to the release of five I groups, six pyrazolyl groups and one acac group. The final residue is corresponded to two V=O moieties and one acac group.

XRD analysis

The powder X-ray diffraction data of the complexes **1**, **2** and **4** were obtained and compared with the corresponding simulated



Fig. 3. The TG curves for the complexes 1-4.

single-crystal diffraction data (Figs. S8–S10). The phase of the corresponding complex is 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.

Functional mimics of the vanadium haloperoxidases

Mimicking bromination reaction of the complexes

It is well known that oxidovanadium complexes are able to mimic a reaction in which vanadium haloperoxidases could catalyze the bromination of organic substrates in the presence of H_2O_2 and bromide. For example, the bromination of trimethoxybenzene [6], benzene, salicylaldehyde and phenol by the VO_2^+ ion [37], and the bromination of phenol red by $[VO(O_2)H_2O]^+$ and related species [38]. Herein, we have investigated the bromination reaction activity of the complexes **1** and **2** using phenol red as an organic substrate, which is shown by the conversion of phenol red to bromophenol blue. The reaction is rapid and stoichiometric, producing the halogenated product by the reaction of oxidized halogen species with the organic substrate, and the reactive process is shown in Scheme S1.

The electronic abosorption recorded a decrease in absorbance of the peak at 443 nm with the loss of phenol red and an increase of



Fig. 4. Oxidative bromination of phenol red catalyzed by **1**. Spectral changes at 10 min intervals. The reaction mixture contained phosphate buffer (pH 5.8), KBr (0.4 mol L^{-1}), phenol red (10^{-4} mol L^{-1}) and complex **1** (0.1 μ mol L^{-1}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. (I) The cycle catalytic brominated reaction mechanism. (II) 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, c(H₂O₂) = 1 mol/L, c(phenol red) = 10^{-4} mol/L. c(complex **1**/mmol/L) = (a) 1.94×10^{-2} ; (b): 3.87×10^{-2} ; (c): 5.81×10^{-2} ; (d): 7.75×10^{-2} ; (e): 9.68×10^{-2} . (III) $-\log(dc/dt)$ dependence of $-\log c$ for **1** in DMF-H₂O at 30 ± 0.5 °C (*c* is the concentration of the complex **1**).

the peak at 592 nm with production of the bromophenol blue (shown in Fig. 4), investigating that the complex **1** possess better catalytic activity. The results of the mimic catalytic activities for **2** and **4** are similar to that of **1**.

Kinetic studies of mimicking bromination reaction

Take the complex **1** for an example to carry out kinetic studies of mimicking bromination reaction. A series of dA/dt data (Fig. 5-II) were obtained by changing the concentration of the oxovanadium complex, then the plot of $-\log(dc/dt)$ versus $-\log c$ for the complex **1** was depicted according to the data of Fig. 5-II, obtaining a straight line (Fig. 5-III) with a slope of 1.0314 and an intercept of -2.0537. Similar plots for **2** were generated in the same way (Figs. S11 and S12), and values of the slope and the intercept are 1.0458 and -2.1349, respectively. The experiment results showed that: (i) the reaction orders of the oxidovanadium complexes in bromination reactions are all close to **1**, confirming the first-order dependence on vanadium; (ii) the order of the reaction rate constants for them is 1 > 2, which is probably due to the influence of the iodine ion.

In the meantime, we carried out some reactions with other transition metal complexes as catalysts (e.g. Cu, Co, Ni compounds, etc.) for comparison, the results indicated that the compounds almost exhibit the catalytic bromination activity in our experiment system except the copper compounds, catalytic activity of which is close to that of the vanadium complexes. Based on the upwards views, the halide oxidation catalytic cycle mechanism for vanadium peroxidase in this work is proposed in Fig. 5-I. The peroxidovanadium inermediate species of $[VO(O_2)Tp]$ was formed by the action of oxidovanadium complexes with H_2O_2 (step a). Then Br^- is oxidized rapidly by $[VO(O_2)Tp]$, with the creation of Br^+ and $[VO_2Tp]$ at the same time (step b). The oxidize bromides can be used to perform a halogenation reaction when an organic substrate is present (step c). While, the hydrogen peroxide was



Fig. 6. (1) The linear calibration plot of the absorbance at 592 nm on the concentration of H_2O_2 from 0.48 mol/L used the complex 1 as catalyzer in DMF-H₂O at 30 ± 0.5 °C. (II) The linear calibration plot of the absorbance at 592 nm on the concentration of H_2O_2 from 1.1 mol/L used the complex 2 as catalyzer in DMF-H₂O at 30 ± 0.5 °C.

erature [40].

Conclusions

Acknowledgement

decomposed into water and dioxygen in the absence of a substrate (step d) [39].

It is known that, the determination of H₂O₂ is of great practical

importance in many fields, such as food, clinical physic, pharma-

ceutical production and environment protection. While the perox-

idase is of great importance in practical application and it can be

used as a diagnostic kit for H₂O₂. Based on the view, we studied

the effect of the concentration of H₂O₂ upon our catalytic reaction

to furthermore extend a new H₂O₂ detection method. Through the

experiment results, it is found that the oxidation reaction catalyzed

by the oxovanadium complexes is H₂O₂ concentration-dependent,

and the absorbance at 592 nm presents a line relativity with diver-

sification of the concentration of H₂O₂ along with the formation of

bromophenol blue. The linear data of absorbance dependence of

 $c(H_2O_2)$ was obtained (Fig. 6). And the detection limit value of

the concentration H₂O₂ was estimated to be 0.48 mol/L for 1 and

1.1 mol/L for 2 by stretching of the line. All these observations fur-

of the reactions indicates that the catalyze activity of **1** is better

than that of 2. This experiment results are similar to that of the lit-

Four new complexes with scorpionate or substituted scorpio-

nate ligands were successfully synthesized firstly. Structure analy-

sis shows that, in all of these complexes, the vanadium atoms are

six-coordinated with a N₅O donor set in a distorted-octahedral

geometry. We tested the bromination reaction activities and finally

found the reaction rate constants (k) of complexes 1 and 2, which

indicated that they can be considered as potential functional

models of VHPO. In addition, a new method based on the catalytic

bromination reaction for the detection of H₂O₂ has been discovered

for the first time, this detection system is simple and sensitive.

Although the detailed catalytic reaction mechanism is not clear

up until now, our group will investigate deeply the application of

This work was supported by the grants of the National Natural

the vanadium complexes for catalysts in the future.

Science Foundation of China (No. 21071071).

Appendix A. Supplementary material

The effect of the concentration of H₂O₂ on bromination reaction

References

- [1] D. Rehder, Coord. Chem. Rev. 182 (1999) 297-322.
- [2] A. Butler, Coord. Chem. Rev. 187 (1999) 17-35.
- [3] M.C. Feiters, C. Leblanc, F.C. Küpper, W. Meyer-Klaucke, G. Michel, P. Potin, J. Am. Chem. Soc. 127 (2005) 15340-15341.
- [4] R. Renirie, W. Hemrika, S.R. Piersma, R. Wever, Biochemistry 39 (2000) 1133-1141.
- [5] G.J. Colpas, B.J. Hamstra, J.W. Kampf, V.L. Pecoraro, J. Am. Chem. Soc. 116 (1994) 3627-3628.
- [6] R.I. de la Rosa, M.I. Clague, A. Butler, I. Am. Chem. Soc. 114 (1992) 760-761.
- [7] G.J. Colpas, B.J. Hamstra, J.W. Kampf, V.L. Pecoraro, J. Am. Chem. Soc. 118 (1996) 3469 - 3478.
- [8] M.V. Kirillova, M.L. Kuznetsov, P.M. Reis, J.A.L. Silva, J.J.R.F. Silva, A.J.L. Pombeiro, J. Am. Chem. Soc. 129 (2007) 10531-10545.
- [9] J.N. Carter-Franklin, A. Butler, J. Am. Chem. Soc. 126 (2004) 15060-15066.
- [10] G. Zampella, P. Fantucci, V.L. Pecoraro, L.D. Gioia, J. Am. Chem. Soc. 127 (2005) 953-960.
- [11] E. Kime-Hunt, K. Spartalian, M. DeRusha, C.M. Nunn, C.J. Carrano, Inorg. Chem. 28 (1989) 4392-4399.
- [12] M. Mohan, S.M. Holmes, R.J. Butcher, J.P. Jasinski, C.J. Carrano, Inorg. Chem. 31 (1992) 2029-2034.
- [13] C.J. Carrano, M. Mohan, S.M. Holmes, R. Rosa, A. Butler, J.M. Charnock, C.D. Garner, Inorg. Chem. 33 (1994) 646-655.
- [14] C.C. McLauchlan, K.J. McDonald, Acta Cryst. 61 (2005) 2379-2381.
- [15] C.C. McLauchlan, K.J. McDonald, Acta Cryst. 62 (2006) 588-590.
- 1369-1371
- Acta 267 (1998) 19-25.
- 2578
- Biochem, 101 (2007) 36-43.
- [22] Y.H. Xing, Z. Sun, W. Zou, J. Song, K. Aoki, M.F. Ge, J. Struct. Chem. 47 (2006) 924-932
- [23] Y.H. Xing, K. Aoki, Z. Sun, M.F. Ge, S.Y. Niu, J. Chem. Res. (2007) 108-114.
- (2011) 1025-1032.
- 25 (2009) 741-746.
- Detector Data, University of Göttingen, Göttingen, Germany, 1996.
- [28] G.M. Sheldrick, SHELXS 97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [29] E. Verhaeghe, D. Buisson, E. Zekri, C. Leblanc, P. Potin, Y. Ambroise, Anal. Biochem. 379 (2008) 60-65.
- [30] G. Zampella, J.Y. Kravitz, C.E. Webster, P. Fantucci, M.B. Hall, H.A. Carlson, V.L.
- [31] J. Tatiersky, S. Pacigová, M. Sivák, P. Schwendt, J. Argent. Chem. Soc. 97 (2009)
- [32] D.X. Ren, N. Xing, H. Shan, C. Chen, Y. Zhu Cao, Y.H. Xing, Dalton Trans. 42
- [33] C. Chen, F.Y. Bai, R. Zhang, G. Song, H. Shan, N. Xing, Y.H. Xing, J. Coord. Chem.
- [34] C. Chen, Q. Sun, D.X. Ren, R. Zhang, F.Y. Bai, Y.H. Xing, Z. Shid, Cryst. Eng.
- [35] R. Grybos, P. Paciorek, J.T. Szklarzewicz, D. Matoga, P. Zabierowski, G. Kazek, Polyhedron 49 (2013) 100-104.
- [36] N. Xing, H. Shan, H.Y. Zhao, Y.H. Xing, J. Coord. Chem. 65 (2012) 898-910.
- [37] M.R. Maurya, S. Agarwal, C. Bader, M. Ebel, D. Rehder, J. Chem. Soc., Dalton
- [38] M.R. Maurya, A. Kumar, M. Ebel, D. Rehder, Inorg. Chem. 45 (2006) 5924-5937. [39] M.J. Clague, A. Butler, J. Am. Chem. Soc. 117 (1995). 3404-3415.
- [40] S. Liu, J.Q. Tian, L. Wang, Y.W. Zhang, Y.L. Luo, H.Y. Li, A.M. Asiri, A.O. Al-Youbi,
- Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.06.081.

- ther confirmed that the catalytic reaction system can be used as a [16] P. Dapporto, F. Mani, C. Mealli, Inorg. Chem. 17 (1978). 1323. potential method for H₂O₂ detection. In the mean time, 30 min is [17] M. Kosugi, S. Hikichi, M. Akita, Y. Moro-oka, J. Chem. Soc. Dalton Trans. (1999) needed for **1** to complete the reaction and 40 min for **2**, the time
 - [18] M. Herberhod, G. Frohmader, T. Hofmann, W. Milius, J. Darkwa, Inorg. Chim.
 - [19] M. Kosugi, S. Hikichi, M. Akita, Y. Moro-oka, Inorg. Chem. 38 (1999) 2567-
 - [20] M. Etiennc, Coord. Chem. Rev. 156 (1996) 201-236.
 - [21] Y.H. Xing, Y.H. Zhang, Z. Sun, L. Ye, Y.T. Xu, M.F. Ge, B.L. Zhang, S.Y. Niu, J. Inorg.

 - [24] Y.Z. Cao, Z.P. Li, H. Xing, D.M. Wei, Z.F. Pu, M.F. Ge, Z. Shi, Chem. J. Chin. U 32
 - [25] Z.P. Li, Y.H. Xing, Y.H. Zhang, F.Y. Bai, X.Q. Zeng, M.F. Ge, Acta Phys. Chim. Sin.
 - [26] S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 6288-6294.
 - [27] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction for Area

 - Pecoraro, L.D. Gioia, Inorg. Chem. 43 (2004) 4127-4136.
 - 181-198.
 - (2013) 5379-5389
 - 66 (2013) 671-688.
 - Commun. (2013), http://dx.doi.org/10.1039/c3ce40410b.

 - Trans. 3 (2005) 537-544.

 - X.P. Sun, ChemPlusChem. 77 (2012) 541-544.