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Novel vanadium(III) complexes with rigid phenylpolycarboxylate ligands: synthesis, structures and application in C-H bond activation

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Two novel vanadium(III) complexes: V(dipic)(Hbdc)(H₂O)₂ (1) and [V₂(dipic)₂(H₂btec)(H₂O)₄]·2H₂O (2) (H₂dipic=2,6-pyridinedicarboxylic acid, H₂bdc=1,3-benzene-dicarboxylic acid, H₄btec=1,2,4,5benzenetetracarboxylic acid) are synthesized by the reaction of V₂(SO₄)₃, 2,6-pyridinedicarboxylic acid and 1,3-benzene-dicarboxylic acid (for 1) or 1,2,4,5-benzenetetracarboxylic acid (for 2) under ¹⁰ hydrothermal condition with 120°C for 3 days. They were characterized by elemental analysis, IR, UV– Vis, single crystal X-ray diffraction analysis and thermo gravimetric analyses (TG). Structural analyses show that the vanadium atoms in the complexes 1 and 2 are both in a pentagonal-bipyramidal coordination environment with the NO6 donor set, and there are intermolecular hydrogen bonding in each

complex. Research results found that the complexes exhibited bromination catalytic activity in the single-¹⁵ pot reaction of the conversion of phenol red to bromophenol blue in the mixed solution of H₂O–DMF at the constant temperature of 30 ± 0.5 °C with pH=5.8, and catalytic C-H bond cleavage activity for the peroxidative oxidation (with hydrogen peroxide) of cyclohexane to cyclohexanol and cyclohexanone (the maximum total turnover number is 395) under the mild conditions.

Introduction

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- ²⁰ To be in the face of increasing global crisis of energy, diminishing petroleum reserves and rising emissions of CO₂, nonedible lignocellulose has received great interest recently as a renewable source of fuel and chemicals.¹ For the rich reserve and low-cost of lignocellulose (cellulose, hemicellulose and lignin),
- ²⁵ we will possess an exhaustless energy storehouse if they can be fully used. However, breaking down the highly functionalized polymers lignin and cellulose for using is a major challenge, and the main problem is how to active the inert C-C/C-O or C-H bond in lignocellulosic biomass.
- ³⁰ Functionlization reactions of saturated hydrocarbons of lignocellulosic biomass, in particular oxidation reactions, provide rather promising methods towards the reuse of unreactive compounds. A typical example is the oxidation of cyclohexane, with the main products as cyclohexanol and cyclohexanone that
- ³⁵ are important raw materials for the production of adipic acid and caprolactam used in the manufacture of nylon-6,6 and nylon-6, respectively.² To the best of our knowledge, precious metals zirconium, ruthenium, rhodium, and iridium complexes were usually used as catalysts for the activation of C-H.³⁻⁷ In addition,
- ⁴⁰ the transition metals such as nickel and iron complexes as catalysts have also received intensive attention with the development of technology.⁸⁻¹⁰ However, they were not applied widely in industrial production, this is because whatever precious metals or transitional metal complexes have a limitation of 45 themselves, such as stability of catalyst, catalyst life,
- environmental pollution, etc. which stimulates researchers to seek

green catalysts with more new environment friendly catalytic processes for industrial use. We explored a homogeneous catalytic reaction with various transition metal complexes as so catalyst and fortunately found that vanadium complexes as catalysts yielded excited results and displayed good catalytic properties in the oxidation reaction of the cyclohexane.

Besides the cyclohexane oxidation, the oxidation of bromide by H₂O₂ catalyzed by vanadate(V)-dependent bromoperoxidase 55 and functional enzyme mimics attracted considerable attention owing to the ability in predicting selectivity for biomimetic synthesis of organobromines. Although molecular bromine is a favorable agent for the synthesis of organobromines, it is corrosive and toxic. So, it is necessary that how to choose better 60 bromine source for the green bromiding reaction. We think that the common bromine source should be bromide, such as bromocarnallite (MgBr₂, KBr) and bromosylvinite [K(Cl, Br)]. In addition, the use of organobromines in life and society is attributed to the unique properties of the carbon-bromine bond. A 65 bromo-substituent is able to raise lipophilicity of an organic molecule, which improves a substance in physical and chemical properties to serve as emulsifier, insecticide, orbiologically active compound.^{11,12} Aryl-bound bromosubstituents lower the rate of oxidative arene metabolism, which is important to increase the 70 stability of pharmaceuticals in vivo. In the mean time, conjugation between an aromatic π -system and a pair of nonbonding electrons at bromine shifts electronic excitation energies of chromophors and thus induces auxochromic effects. In other arenes, the carbon bromine bond is a key structural 75 element to achieve flame retarding properties of material

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(videinfra).¹³⁻¹⁶ The aliphatic carbon-bromine bond, on the other hand, combines in a unique manner stability and chemical reactivity. This bond can be selectively broken in heterolytic or homolytic reactions, which to serve as progenitor of carbocations, 5 carbanions, or free carbon radicals.¹⁷ In recent decades, oxidovanadium(IV) and dioxovanadium(V) complexes have been studied for their synthesis, structures and properties. For example, D. Rehder et al. have reported the mechanism that vanadium haloperoxidase catalyzed the oxidation of halides;¹⁸ C. J. Carrano 10 et al. reported the reactions of vanadium on various oxidation states (III/IV/V) with hydridotris(pyrazoly1)borate ligands and discussed their spectroscopic properties in detail;¹⁹ A. J. L. Pombeiro, et. al. reported novel scorpionate and pyrazole dioxovanadium complexes, catalysts for carboxylation and 15 peroxidative oxidation of alkanes.²⁰ However, the studies of V(III) complexes were obviously less than that of V(IV) or V(V)complexes reported and metal centre of concerning V(III) complexes was six-coordinate mode, while studies on V(III) complexes with seven-coordinate were relatively rare.21-27 20 Although our group has a long-standing interest in the

investigation of vanadium complexes with poly(pyrazolyl)borate ligands,²⁸ schiff-base ligands²⁹ and dicarboxylic acid ligands,³⁰ in order to further extend structural variety and investigate relationship between structure and function of the vanadium 25 complexes, here, we firstly designed and synthesized two novel seven-coordinate vanadium(III) complexes with rigid polycarboxylate as ligands, V(dipic)(Hbdc)(H₂O)₂ (1) and $[V_2(dipic)_2(H_2btec)(H_2O)_4]$ ·2H₂O (2), and studied the catalytic properties in the aspect of aryl-bound bromosubstituent and 30 oxidation of cyclohexane. It was rather surprising that high catalytic efficiency with total turnover number (TON) value of 395 was reached in the cyclohexane oxidation under mild conditions, which is much higher than 19, 167 or 308 that have been reported in previous reports.^{20b,31,32}

35 Results and Discussion

Synthesis

Two novel vanadium (III) coordination complexes $[V(dipic)(Hbdc)(H_2O)_2]$ (1) and $[V_2(dipic)_2(H_2btec)(H_2O)_4] \cdot 2H_2O$ (2) were successfully synthesized for the first time via the 40 reaction of V₂(SO₄)₃ with mixed ligands of dipic and bdc or btec, together with vitamin C as antioxidant at 120 °C for three days (Scheme 1). It was surprise to found that vitamin C affect the reaction results to some extent owing to the easily oxidization of $V_2(SO_4)_3$ in the reaction based on our previous experience.



Scheme 1 The reaction processes of the complexes.

IR spectra

The IR spectral data of the complexes 1 and 2 are listed in Table 55 S1 and the corresponding spectra are shown in Fig. S1 and S2. For the two complexes, the broad absorption bands in the region

of 3257-3467 cm⁻¹ were assigned to v(O-H) of the coordinated or uncoordinated water. The bands due to v(=C-H) of benzene ring or pyridine ring were appeared in the range of 3056-3075 $_{60}$ cm⁻¹. The bands attributed to asymmetric v_{as}(COO⁻) and symmetric $v_s(COO^-)$ vibrations of the carboxyl group are at 1652 and 1395 cm⁻¹ for 1, 1672 and 1379 cm⁻¹ for 2. Band of v(V- O_{water}) is at 512 cm⁻¹ for 1 and 539 cm⁻¹ for 2, while those at 475 cm⁻¹ for 1 and 491 cm⁻¹ for 2 are assigned to $v(V-O_{carboxyl})$ and $_{65}$ the bands due to v(V–N) are in the range of 449-455 cm⁻¹.

UV–Vis spectra

The UV-Vis absorption spectra of the complexes 1 and 2 (Fig. S3 and S4) are recorded in the form of solid sample and their characteristic UV-Vis bands are listed in Table S2. The high-70 frequency absorption bands at 262 nm for 1 and 268 nm for 2 are assigned to π - π^* transition of the aromatic-like chromophore from the bdc, btec or dipic ligands. The absorption bands at 420 nm for 1 and 456 nm for 2 are attributed to the LMCT (charge transfer from ligand to metal) transition. While the broad bands at 742, 75 1040 nm for 1 and 742, 1100 nm for 2 are assigned to d-d transition of vanadium atom.34, 24 The absorption bands of the complex 2 relative to 1 happened slightly red-shift, which may be attributed to different ligands and coordination environment.

Structural description of complexes 1 and 2

⁸⁰ The molecular structures of the complexes 1 and 2 are depicted in



Fig. 1 (a) The molecular structure of the complex 1 (All H atoms are omitted for clarity). (b) A view of 2D hydrogen bonding network on ab-105 face in the complex 1. (All H atoms except for the hydrogen bonds are omitted for clarity.)



Fig. 2 The molecular structure of the complex 2 (All H atoms are omitted for clarity)

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Table 1 Selected bond distances (Å) and angles (°) of the complexes 1 and 2						
Selected bond lengths (Å) and angles (°) of complex 1						
V1–O1 2.086(2)	V1-O2	2.057(2)	V1–O3	2.062(2)	V1-05	2.038(2)
V1–O7 2.142(2)	V1-O8	2.090(2)	V1–N	2.107(2)	C8–O7	1.270(3)
C8–O8 1.268(3)	C14-O10	1.212(3)	C14–O9	1.323(3)	O2-V1-O3	88.66(7)
O5–V1–O1 89.49(8)	O2-V1-O1	178.35(8)	O3-V1-O1	89.74(8)	O5-V1-O8	75.97(6)
O2–V1–O8 90.61(8)	O3-V1-O8	137.41(6)	O5-V1-O2	92.07(7)	O1-V1-O8	90.29(9)
O5–V1–N 73.43(6)	N-V1-07	149.34(7)	O2-V1-N	89.85(8)	O3-V1-N	73.20(7)
O1–V1–N 90.08(8)	O8-V1-N	149.39(7)	O5-V1-O7	137.21(7)	O2-V1-O7	90.01(7)
O3–V1–O7 76.14(6)	O5-V1-O3	146.62(6)	O1-V1-O7	89.21(7)	O8-V1-O7	61.27(6)
Selected bond lengths (Å) and an	gles (°) of complex 2					
V1-O1 2.062(1)	V1-O2	2.046(1)	V1–O3	2.041(1)	V1-05	2.049(1)
V1-07 2.117(1)	V1-O8	2.129(2)	V1–N	2.110(2)	C8–O7	1.267(2)
C8–O8 1.257(2)	C11–O17	1.207(2)	C11–O18	1.303(2)	O2-V1-O3	92.36(6)
O3–V1–O1 87.62(6)	O2-V1-O1	175.69(5)	O5-V1-O1	90.51(5)	O3-V1-O8	138.79(5)
O2–V1–O8 90.03(6)	O5–V1–O8	74.96(5)	O3-V1-O2	91.79(6)	O1-V1-O8	87.61(6)
O3–V1–N 73.40(6)	07–V1–N	150.42(5)	02–V1–N	88.60(6)	O5–V1–N	72.97(6)
O1–V1–N 95.32(5)	O8–V1–N	147.81(5)	O3–V1–O7	77.87(6)	O2–V1–O7	85.34(5)
05-V1-07 136.13(5)	O5-V1-O3	145.98(5)	01-V1-07	90.36(5)	08-V1-07	61.26(5)
5 Table 2 Hydrogen bonds (Å) ar	nd angles (°) of the comp	lexes 1 and 2.				
D–H···A	d(D–H)	d	(H…A)	d(D…A)	∠D–H·	···A□
Complex 1						
O1 ^{#1} –H1A…O7	0.7225	2	.1304	2.8523	177.32	
O1 ^{#1} -H1B…O9 ^{#2}	0.7871	2	.1715	2.9548	173.46	
O2 ^{#3} -H2A…O6 ^{#4}	0.8513	1	.8156	2.6587	170.34	
O2 ^{#3} -H2B…O10 ^{#2}	0.8422	1	.8903	2.7184	167.42	
O9–H9…O4 ^{#2}	0.9034	1	.6778	2.5587	164.12	
C3–H3…O6 ^{#4}	0.9144	2	.2650	3.1679	169.22	
C4–H4…O8 ^{#4}	0.9549	2	.4828	3.4229	168.12	
Complex 2						
O1W ^{#5} -H1WA…O7 ^{#6}	0.7407	2	.2357	2.8393	139.39	
O1–H1A…O6 ^{#7}	1.0160	1	.6580	2.6670	171.44	
O1–H1B…O3 ^{#8}	0.8726	1	.9675	2.8040	160.14	
O1W ^{#5} –H1WB…O5 ^{#6}	0.7067	2	.2892	2.9070	146.91	
O2-H2A…O4 ^{#9}	O2-H2A···O4 ^{#9} 0.8193 1.8186 2.6316 171.47					
O2-H2B····O9 ^{#10}	O2-H2B···O9 ^{#10} 0.8506 1.9140 2.7628 175.45		175.45			
O10–H20…O1W ^{#5}	0.7915	1	.8169	2.5947	167.21	

Symmetry transformation used to generate equivalent atoms: #1: -x, 1-y, -z; #2: -1-x, 1-y, -z; #3: -x, 0.5+y, 0.5-z; #4:1-x, 0.5+y, 0.5-z; #5: 2-x, 2-y, 1-z; #6 : x, 1+y, z; #7: 2-x, -y, -z; #8: 2-x, 1-y, -z; #9: 1-x, 1-y, -z; #10: 2-x, 1-y, 1-z.

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Fig. 1a and 2, and some selected bond distances and angles are summarized in Table 1. Single-crystal X-ray structure analyses revealed that each vanadium atom of the two complexes posses a distorted pentagonal-bipyramidal geometry defined by the NO6 5 donor set.

For the complex 1, the vanadium atom is coordinated by two oxygen atoms (O1, O2) from coordinated water, two oxygen atoms and one nitrogen atom (O3, O5, N) from a 2,6pyridinedicarboxylic acid (dipic) ligand and two oxygen atoms

10 (O7, O8) from the carboxyl group of a 1,3-benzene-dicarboxylic acid (bdc), forming a slightly distorted pentagonal-bipyramidal vanadium center, with O3, N, O5, O7 and O8 in the equatorial plane, O1 and O2 in the axial positions. Dipic ligand adopts a k^{3} -O, N, O coordination mode to coordinate with vanadium atom, 15 namely, O, N, O atoms of dipic ligand are coordinated only one metal atom; for bdc ligand, one carboxyl group is coordinated to vanadium with $\mu_1 - \eta^1 - \eta^1$ -bidentate chelated mode, while another is uncoordinated and protonated. It is found that V-Owwater distances are 2.086(2) Å and 2.057(2) Å, V-Ocarboxyl distances are ²⁰ in the range of 2.038(2)-2.142(2) Å, V-N_{dipic} distance is 2.107(2) Å.

It is worthy to note that there is obvious difference on the bond length of C-O between coordinated and uncoordinated carboxyl groups of bdc ligand, C14-O9 and C14-O10 distances 25 of uncoordinated carboxyl are 1.323(3) Å and 1.212(3) Å, respectively, which indicates that C14-O9 is a single bond and C14-O10 is a double bond. However, C8-O7 and C8-O8 distances of coordinated carboxyl are 1.270(3) Å and 1.268(3) Å, respectively. Their bond length are between the single bond and 30 double bond, indicating that the presence of the coordinated carboxyl group make electron cloud distribution uniformly, which led to the closer of the two C–O bond lengths.

As illustrated in Fig. 1b, there are two kinds of hydrogen bonds O-H…O and C-H…O in the complex 1. The relevant H-35 bond parameters are listed in Table 2. Thereinto, hydrogen bond of O-H…O comes from among coordinated water molecules. coordinated carboxyl groups and uncoordinated carboxyl groups: O1^{#1}-H1A···O7 (2.8523 Å, #1: -x, 1-y, -z), O1^{#1}-H1B···O9^{#2} (2.9548 Å, #2: -1-x, 1-y, -z), O2^{#3}-H2A···O6^{#4} (2.6587 Å, #3:-x, 40 0.5+y, 0.5-z; #4: 1-x, 0.5+y, 0.5-z) and O2#3-H2B-O10#2 (2.7184 Å), and between carboxyl of bdc ligand and carboxyl of dipic ligand: O9-H9···O4^{#2} (2.5587 Å); hydrogen bonds of C-H…O are from among carbon atom of dipic ring, coordinated carboxyl groups and uncoordinated carboxyl groups: C3-45 H3…O6^{#4} (3.1679 Å) and C4–H4…O8^{#4} (3.4229 Å). Through the hydrogen bonding interaction of O9-H9-O4#2, C3-H3-O6#4 and C4-H4...O8#4, a two-dimensional hydrogen bonding network on the ab-plane is formed, the 2D network is further connected via hydrogen bonding interaction of O1#1-H1A…O7, O1#1-

a 3D supramolecular structure.

For the complex 2, the molecule contains two vanadium atoms, two 2,6-pyridine-dicarboxylic ligands, four coordinated water molecules and one 1,2,4,5-benzene-tetracarboxylic acid 55 (btec). Each vanadium atom is coordinated by two oxygen atoms (O1, O2) from two coordinated water, two oxygen atoms and one nitrogen atom (O3, O5, N) from a 2,6-pyridinedicarboxylic acid (dipic) ligand and two oxygen atoms (O7, O8) from the carboxyl group of the btec ligand. The coordination mode of dipic ligand is 60 the same as complex 1, and the btec ligand shows a μ_2 -bridging linkage with 1- and 4-positions coordinated to carboxylate group, respectively in $\mu_1 - \eta^1 - \eta^1$ -bidentate mode, and another two carboxylate groups are uncoordinated and protonated. Adjacent two vanadium atoms are connected via the btec ligand. V-Owater 65 distances are 2.062(2) Å and 2.046(2) Å, V–O_{carboxvl} distances are in the range of 2.041(2)–2.129(2) Å, V–N_{dipic} distance is 2.110(2) Å.



Fig. 3 (a) An infinite 1D chain of the complex 2. (b) A view of 3D hydrogen bond network in the complex 2. (All H atoms except for the hydrogen bonds are omitted for clarity.)

Similarly, there are abundant hydrogen bonds of O-H…O in the complex 2 (listed in Table 2). As illustrated in Fig. 3, according to oxygen atoms from different groups, which can be divided into two types: (1) lattice water molecule and coordinated 85 carboxyl groups or uncoordinated carboxyl groups: O1W^{#5}-H1WA···O7^{#6} (2.8393 Å, #5: 2-x, 2-y,1-z; #6: x, 1+y, z), O1W^{#5}-H1WB····O5^{#6} (2.9070 Å) and O10-H20···O1W^{#5} (2.5947 Å); (2) coordinated water molecules and coordinated or uncoordinated carboxyl groups: O1-H1A···O6^{#7} (2.6670 Å, #7:2-x, -y, -z), O1-90 H1B···O3^{#8} (2.8040 Å, #8: 2-x, 1-y, -z), O2–H2A···O4^{#9} (2.6316 Å, #9: 1-x, 1-y, -z) and O2-H2B···O9^{#10} (2.7628 Å, #10: 2-x, 1-y, 1-z). Each independent molecule form a 1D chain by the hydrogen bonding interaction of O10-H20...O1W^{#5}, O1W^{#5}-H1WA···O7^{#6} and O1W^{#5}-H1WB···O5^{#6}. The chains are further 95 linked through the hydrogen bonds O1-H1A···O6^{#7}, O1-H1B···O3^{#8}, O2-H2A···O4^{#9} and O2-H2B···O9^{#10} to generate a 3D hydrogen bond network (shown in Fig. 3b).

Table 3 A	appropriate a flow hand	longths (Å) for the	a complexes report	tod proviously

50 H1B···O9^{#2}, O2^{#3}-H2A···O6^{#4} and O2^{#3}-H2B···O10^{#2}, to generate

Table 5 A comparison of Key bond lengths (A) for the complexes reported previously.				
Number	Complexes	V-N _{dipic}	V-O _{dipic}	References
	V(III)			
1	V(dipic)(Hbdc)(H ₂ O) ₂	2.107(2)	2.062(2), 2.038(2)	This work
2	[V ₂ (dipic) ₂ (H ₂ btec)(H ₂ O) ₄]·2H ₂ O	2.110(2)	2.041(1), 2.049(1)	This work
	V(IV)			
3	[(CH ₃ CH ₂) ₄ N][VO(dipic)(HMDCl)]	2.031(1)	2.014(1), 2.027(1)	35

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4	VO(dipic-Cl)(Me ₂ NO)(H ₂ O)	2.077(3)	2.027(2), 2.027(2)	36
5	VO(dipic)(Me ₂ NO)(H ₂ O)	2.067(3)	2.026(3), 2.008(3)	37
6	VO(dipic)(H ₂ NO)(H ₂ O)	2.064(3)	2.031(3), 2.039(3)	38
	V(V)			
7	K[VO ₂ (dipic-OH)]·H ₂ O	2.089(6)	2.033(5), 1.990(5)	39
8	C(NH ₂) ₃ [VO ₂ (dipic)]·2H ₂ O	2.086(2)	1.983(2),1.988(2)	38
9	NH ₄ [VO ₂ (dipic)]	2.091(2)	1.974(2), 1.988(2)	40

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It is found that average bond length of V-O_{water} of the complex 1 is slightly longer than that of the complex 2. The average bond length of V-Odipic of the complex 1 is close to that s of the complex 2 as well as the distance of V-N_{dipic}. While average bond length of V-O_{bdc} of the complex 1 is slightly shorter than that of V-O_{btec} in the complex 2. Furthermore, for the dipic ligand coordinated to vanadium, a comparison of key bond lenghs(Å) reported previously are listed in Table 3. The average 10 distance of V(III)-N_{dipic}, V(IV)-N_{dipic} and V(V)-N_{dipic} are 2.109(2), 2.060(3) and 2.089(3) Å, respectively. The bond lengths of V(III)-O_{dipic}, V(IV)-O_{dipic} and V(V)-O_{dipic} are in the range of 2.038(2) -2.062(2) Å, 2.014(1) -2.039(3) Å and 1.974(2) -2.033(5) Å, respectively. It indicates that different oxidation states of 15 center vanadium atom indeed influence the bonding characteristic of the complexes.

Thermal properties

To examine the thermal stability of the complexes, thermo gravimetric analyses (TG) were carried out in the range of 30-20 1000 °C. For the complex 1, the TG curve indicated three steps (Fig. S5): the first step in the temperature range of 230–330 °C with mass loss of 19.06% accords with a loss of two coordinated water molecules and a uncoordinated carboxyl of bdc (calcd: 19.17%). The second step of decomposition occurred within the

- ²⁵ range of 330–565 °C with a percentage weight loss of 31.62%. which was due to the loss of three coordinated carboxyl (calcd: 31.65%). The last step of decomposition occurred within the range of 565-1000 °C, which is considered the loss of framework of the ligands. The TG curve of 2 (Fig. S6) is different from 1, 30 which shows four stages: the first stage occurs in the temperature
- region of 115-150 °C with a mass loss of 4.63% corresponding to the loss of two lattice water (calcd: 4.54%). The second stage in the temperature region of 150-230 °C with mass loss of 9.22% accords with a loss of four coordinated water molecules (calcd:
- 35 9.09%). For the third stage in the temperature region of 230–400 °C, 11.31% weight loss is observed, which due to the release of two uncoordinated carboxyl of btec (calcd: 11.36%). And the last step is observed in 400–1000 °C, which is similar to the complex 1 that considered the gradual decomposition of framework of the 40 ligands.

Mimicking bromination reaction of the complexes

To our knowledge, oxidovanadium complexes are able to mimic the reaction in which vanadium haloperoxidases catalyze the bromination of organic substrates in the presence of H₂O₂ and ⁴⁵ bromide. For example, the bromination of trimethoxybenzene,⁴¹ benzene, salicylaldehyde and phenol catalyzed by the VO₂⁺

- moiety.42,43 Herein, we investigated the bromination reaction activities of the complexes 1 and 2 using phenol red as an organic substrate which is shown by the conversion of phenol red to
- 50 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 as follows (Scheme 2).



60 Scheme 2 The reactive process of the bromination reaction for the complexes



Fig. 4 Oxidative bromination of phenol red catalyzed by the complex 2. Spectral changes at 10 min intervals, c(phosphate buffer) = 50 mmol/L, $_{75}$ pH = 5.8, c(KBr) = 0.4 mol/L, c(phenol red) = 10^{-4} mol/L

Addition of the solution of the complex 2 to the standard reaction of bromide in phosphate buffer with phenol red as a trap for oxidized bromine resulted in the visible color change of the 80 solution from yellow to blue. As is shown in Fig. 4, the electronic absorption spectra are collected during such a color change catalyzed by 2. It shows that a decrease in absorbance of the peak at 443 nm due to the loss of phenol red and a increase in the absorbance of the peak at 592 nm characteristic of the 85 bromophenol blue product, showing that the complex 2 performs significant catalytic activity. The result of the mimic catalytic activities for 1 (Fig. S7) is similar to that of 2.

Kinetic studies of mimicking bromination reaction

As vanadate-dependent haloperoxidases catalyze the visible 90 conversion of phenol red to bromophenol blue under peroxide conditions, the role of the oxidovanadium complexes in the bromide oxidation reaction was investigated in the mixed solution of H₂O–DMF under the constant temperature of 30 ± 0.5 °C. Solutions used for kinetic measurements were maintained at a 95 constant concentration of H⁺ by the addition of the buffer solution with NaH₂PO₄-Na₂HPO₄. Reactions were initiated in the presence of H₂O₂ and KBr.



Fig. 5 The measurable absorbance(592 nm) dependence of time for the 10 complex 2. Conditions used: pH = 5.8, c(KBr) = 0.4 mol/L, c(H₂O₂) = 1 mmol/L, c(phenol red) = 10^{-4} mol/L. c(complex 2/mmol/L) = a: 1.1359×10^{-5} ; b: 3.4077×10^{-5} ; c: 4.5436×10^{-5} ; d: 5.6795×10^{-5} ; e: 6.8154×10^{-5}

Taking the complex **2** as an example, a series of dA/dt data were obtained (Fig. 5) by changing the concentration of the oxidovanadium complex (the measurable absorbance dependence of time for complex **1** is shown in Fig. S8).



Fig. 6 $-\log(dC/dt)$ dependence of $-\log c$ for the complex **2** in DMF-H₂O ³⁰ at 30 ± 0.5 °C (c is the concentration of the complex **2**; Conditions used: c(phosphate buffer) = 50 mmol/L, pH 5.8, c(KBr) = 0.4 mol/L, c(phenol red) = 10^{-4} mol/L.

And then as is shown in Fig. 6, the plot of -log(dc/dt) versus ³⁵ (-log c) for complex **2** gives a straight line with a slope of 1.0381 and b=-1.0857, the former confirms the first-order dependence on vanadium. Basing on the equation of " $b=log k + ylog c_2 + zlog c_3$ ", the reaction rate constant, k, is determined by the concentrations of KBr and phenol red (c_2 and c_3), the reaction ⁴⁰ orders of KBr and phenol red (y and z), as well as b. While in the experiment, considering that the reaction orders of KBr and phenol red (y and z) are **1** according to the literature;⁴⁴ c_2 and c_3 are known as 0.4 mol/L and 10⁻⁴ mol/L, respectively, so the reaction rate constant (k) for complex **2** can be calculated as ⁴⁵ 2.054×10³ (mol/L)⁻² s⁻¹.

Table 4. Kinetic data for the complexes in DMF–H ₂ O at 30 ± 0.5 °C. ³				
Complexes	m	b	k(mol/L) ² s ¹	
1	1.0495	-1.3284	1.174×10^{3}	
2	1.0381	-1.0857	2.054×10^{3}	

Similar plot for the complex 1 (Fig. S9) was generated in the same way. Kinetic data for the complexes 1 and 2 in DMF-H₂O at 30 ± 0.5 °C are shown in Table 4. It is found that: (i) the reaction orders of the oxidovanadium complex in bromination reaction are all close to 1, confirming the first-order dependence on vanadium; (ii) the order of the reaction rate constant is 1<2, which is probably due to the two "core" active site of the s5 complex 2, while mono "core" active site of the complex 1, in

which the two "cores" active site is in favor of forming a intermediate species of the peroxidovanadium($VO(O_2)^+$) and accelerating of the catalytic reaction. This shows that the intermediate species could be influenced by different molecular 60 structures of the complexes.^{45a} The catalytic bromination activities of the complexes (III) are similar to those of the oxovandium complexes (IV)45b,c, furthermore, it is found that related vanadium complexes also present different catalytic activity, which may be due to the diffence of the nature, the 65 electronic and steric effects of N-, and O- donor chelating aromatic ligands. In addition, for comparison, we are carried out some reactions with other transition metal complexes as catalyst (e.g. Cu, Ni, Co, Zn compounds, etc.), the results found that the compounds not exhibited obviously the catalytic bromination 70 activities in our experiment system except the copper compound, catalytic activity of which is close to those of the vanadium complexes.

To our knowledge, their detailed catalytic reaction mechanism is not clear up to now. Further catalytic reaction 75 mechanistic studies are underway. In general, the two complexes exhibit different catalytic activity and they can be considered as potential functional model vanadium-dependent haloperoxidases.

Catalytic activity studies

To screen and evaluate the catalytic oxidative activity of the so synthesized complexes, all of them were applied in the oxidation of cyclohexane with H₂O₂ as primary oxidant. The formation of the main products is outlined in Scheme 3. In search of suitable reaction conditions to achieve the best results in terms of maximum products formation, the effect of oxidant concentration (moles of H₂O₂ per mole of catalyst), acid concentration (moles of HNO₃ per mole of catalyst), nature of solvent and temperature were studied in detail.



Scheme 3 Main products observed during the catalytic oxidation of 95 cyclohexane



Fig. 7 Effect of H_2O_2 concentration on the cyclohexane oxidation with catalyst **2**. Reaction conditions: cyclohexane (0.34 g, 4 mmol), H_2O_2 ¹¹⁰ ($H_2O_2 \times 10^{-5}$ /catalyst molar ratio = 1, 2, 4 and 6), HNO₃ (0.1 g, 1.5 mmol), catalyst (0.0004 g, 0.0005 mmol), acetonitrile (3 mL), 40 °C

As shown in Fig. 7, the amount of hydrogen peroxide has an

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interesting effect on the catalytic activity. All the TON values displayed volcano shape curves, which may be caused by the further oxidation of cyclohexanol and cyclohexanone to cyclhexylhydroperoxide by H_2O_2 ,⁴⁶ which led to the decrease of ⁵ main products conversion. The maximum TON value was 20 or 44 upon 4 h when the $H_2O_2 \times 10^{-5}$ /catalyst molar ratio was 1:1 or 2:1. And it was 59 upon 3 h with the ratio of 4:1. When the $H_2O_2 \times 10^{-5}$ /catalyst molar ratio was higher to 6:1, the maximum TON reached to 177 and the time was shorted to 2 h. It means

¹⁰ that more H_2O_2 led to higher TON value and shorter time to get it, i.e. the participation of H_2O_2 can not only increase the conversion of the aimed products (cyclohexanol and cyclohexanone), but also increase the reaction rate. So, 2.59 g H_2O_2 was chosen to make the $H_2O_2 \times 10^{-5}$ /catalyst molar ratio equals to 6:1 in the ¹⁵ following experiments.



Fig. 8 Effect of HNO₃ concentration on the cyclohexane oxidation with catalyst 2. Reaction conditions: cyclohexane (0.34 g, 4 mmol), H_2O_2 (2.59 g, 0.08 mol), HNO₃ (HNO₃/catalyst molar ratio = 0, 1000, 2000 and 4000), catalyst (0.0004 g, 0.0005 mmol), CH₃CN (3 mL), 40 °C, 4 h

Similarly, four different molar ratios of HNO₃/catalyst i.e. 0, 1000:1, 2000:1 and 4000:1 were considered to evaluate the effect of nitric acid concentration on the oxidation of cyclohexane catalyzed by the complex **2**, while keeping fixed the amount of ³⁵ cyclohexane (0.34 g, 4 mmol), H₂O₂ (2.59 g, 0.08 mol), catalyst (0.0004 g, 0.0005 mmol) and CH₃CN (3 mL) at 40 °C, running for 4 h. As shown in Fig. 8, the complex displayed no catalytic activities in the absence of nitric acid. It indicates that H⁺ displays a significant role in the reaction of cyclohexane oxidation. The ⁴⁰ complex shows its catalytic activity with TON value of 21 when the HNO₃/catalyst molar ratio was 1000:1. And the overall TON increased sharply to 214 with a higher HNO₃/catalyst molar ratio of 2000:1 (HNO₃, 0.188 g, 3 mmol). However, it decreased unexpectively to 17 with the ratio further increasing to 4000:1.

⁴⁵ This indicates that excess acid is not good at the formation of the aimed products, which may be due to the large amount of water in the acid solution (68% HNO₃), which has a block effect on the catalytic activity.



Fig. 9 Effect of solvent on the cyclohexane oxidation with catalyst 2.
⁶⁰ Reaction conditions: cyclohexane (0.34 g, 4 mmol), HNO₃ (0.188 g, 3 mmol), H₂O₂ (2.59 g, 0.8 mol), catalyst (0.0004 g, 0.005 mmol), solvent (3 mL), 40 °C

A deep evaluation devoted to select the best solvent for our 65 catalytic reactions, has been carried out by comparing the results obtained in 3 mL of five different solvents as acetonitrile (CH₃CN), methanol (MeOH), ethanol (EtOH), chloroform (CHCl₃) and petroleum ether (PE), while keeping fixed the amount of cyclohexane (0.34 g, 4 mmol), HNO₃ (0.188 g, 3 70 mmol), H₂O₂ (2.59 g, 0.08 mol) and catalyst (0.0004 g, 0.0005 mmol), at 40 °C, running for 5 h. (shown in Fig. 9). All the curves display a volcano shape, which is in good accordance with the influence of H₂O₂ existing in the reaction solution on the TON value (Fig. 8). The complex almost has no catalytic activity in 75 chloroform, little in methanol and ethanol (maximum TON of 15 and 34, respectively), good in acetonitrile (maximum TON of 213) and best in petroleum ether (maximum TON of 297). This may be the first finding that in petroleum ether with low solvent polarity, a catalyst shows such high catalytic activity in cyclohexane 80 oxidation.

To our the best knowledge, acetonitrile usually be used as solvent in the catalytic oxidation of cyclohexane, 20b cyclohexene,⁴⁷ methyl phenyl sulfide,⁴⁸ diphenyl sulfide,⁴⁸ styrene⁴⁷ and its derivatives,⁴⁹ and epoxidation of cyclooctene³² 85 catalyzed by vanadium(IV) or vanadium(V) complex due to its high solvent polarity. In our previous study, we also found that, vanadium(IV) complex shown the best catalytic activity in acetonitrile and almost had no activity in petroleum ether for the oxidation of cyclohexane.⁵⁰ However, herein, acetonitrile is no 90 longer the best solvent for the oxidation catalyzed by vanadium(III) complex, but petroleum ether. We could not been clear that why vanadium complex(III) is higher catalytic activity in petroleum up to now. In order to further confirm higher catalytic activity of vanadium complex(III). So, we have designed $_{95}$ a catalytic reaction experiment with starting materal V₂(SO₄)₃(III) as a catalytst under the same conditions. The result shown that the TON value of 75 was obtained in the solvent of petroleum ether, which was also higher than those found by the oxidovanadium complexes with +4 or +5 oxidation state as a catalytst in the same 100 non-polar solvent.^{32,50a}

Under the optimal conditions: 2.59 g H₂O₂ (molar ratio of H₂O₂×10⁻⁵/catalyst=6:1); 0.188 g HNO₃ (molar ratio of HNO₃/catalyst=2000:1); 3 mL petroleum ether; 40 °C; 3 h, the catalytic activity of the complex **1** in the oxidation of ¹⁰⁵ cyclohexane was also studied. TON value of 395 was achieved, which is higher than that of the complex **2**.

The experimental results show that the catalytic oxidative activities of the vanadium (III or IV) complexes are higher than those of other metal complexes, such as Zn complexes (TON =1.07-9.31) and Mo complexes (TON=36 and 18), etc. in the oxidation of cyclohexane^{50b,c}. This is probably because that metal vanadium present variable oxidation states, form different activity intermediate oxide species. In addition, the related vanadium complexes also present different catalytic activity, samely, this is 115 also due to the infulence of the different N-, and O- donor chelating aromatic ligands.^{50a-e}

Experimental Section

Materials and methods

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All the chemicals used were of analytical grade and without further purification. $V_2(SO_4)_3$ was synthesized according to the s literature method.⁵¹ A 30% aqueous solution of hydrogen peroxide was used as primary oxidant in the cyclohexane oxidation reaction. The synthetic manipulations were carried out by hydrothermal reaction. The elemental analyses for C, H, and N were carried out on a Perkin Elmer 240C automatic analyzer. IR 10 spectra was recorded on a JASCO FT/IR-480 PLUS Fourier Transform spectrometer with pressed KBr pellets in the range 200-4000 cm⁻¹. UV-Vis absorption spectra diffuse reflection was recorded with a JASCO V-570 UV/VIS/NIR spectrophotometer in the 200-2500 nm. The cyclohexane oxidation products were 15 determined and analyzed by Shimadzu GC-16A series gas chromatograph equipped with a FID detector and a capillary column (PG20000, column length: 30 m; internal diameter: 0.25 mm).

Synthesis of V(dipic)(Hbdc)(H₂O)₂ (1). V₂(SO₄)₃ (0.09 g, 0.25 ²⁰ mmol), 2,6-pyridinedicarboxylic acid (H₂dipic, 0.08 g, 0.5 mmol), 1, 3-benzene-dicarboxylic acid (H₂bdc, 0.08 g, 0.5 mmol), vitamin C (0.02 g, 0.1 mmol) and H₂O (10 mL) were mixed in a 25 mL glass beaker. After stirring for 3 h, the mixture was sealed in a Teflon-lined autoclave and heated at 120 °C for three days, ²⁵ followed by slowly cooling to room temperature. Yellow-green crystals suitable for X-ray diffraction were obtained. Yield (based on V): 0.12 g, 57.53%. Anal. Calc. for C₁₅H₁₂NO₁₀V: C, 43.22; H, 2.81; N, 3.42. Found: C, 43.14; H, 2.88; N, 3.36%. IR (KBr, v, cm⁻¹): 3467, 3292, 3075, 3056, 1652, 1395, 512, 475, 449. UV– ³⁰ Vis (λ_{max} , nm): 262, 420, 742, 1040.

Synthesis of $[V_2(dipic)_2(H_2btec)(H_2O)_4]\cdot 2H_2O$ (2). Complex 2 was synthesized by a similar method of 1 except that 1,3benzene-dicarboxylic acid was replaced by 1,2,4,5benzenetetracarboxylic acid (H₄btec, 0.06 g, 0.25 mmol). Yield ³⁵ (based on V): 0.13 g, 65.63%. Anal. Calc. for C₂₄H₂₂N₂O₂₂V₂: C, 36.45; H, 2.68; N, 3.63. Found: C, 36.35; H, 2.78; N, 3.53%. IR (KBr, v, cm⁻¹): 3439, 3257, 3060, 1672, 1379, 539, 491, 455. UV-Vis (λ_{max}, nm): 268, 456, 742, 1100.

X-ray crystallographic determination

- ⁴⁰ Suitable single crystals of the two complexes 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 diffractometer with graphite monochromatized Mo K α radiation (λ =0.71073 Å) and a ω scan mode. All the
- ⁴⁵ measured independent reflections (I > 2σ (I)) were used in the structural analyses, and semi-empirical absorption corrections were applied using SADABS program.⁵² Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms on organic ⁵⁰ frameworks were fixed at calculated positions with isotropic
- thermal parameters. while the oxygen atoms of coordinated water molecules or lattice water molecules were located by different

 Table 5
 Crystallographic data and structure refinement for complexes 1

 ss and 2*

Complexes	1	2	

Formula	$C_{15}H_{12}NO_{10}V$	$C_{24}H_{22}N_2O_{22}V_2$
M (g mol ⁻¹)	417.20	792.32
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	<i>P1</i>
a (Å)	7.1920(6)	8.1031(2)
b (Å)	15.4368(12)	9.7398(2)
c (Å)	14.2060(12)	10.142(2)
α(°)	90	103.42(3)
$\beta(\circ)$	91.894(5)	109.89(3)
γ(°)	90	90.08(3)
V(Å ³)	1576.3(2)	729.3(2)
Ζ	4	1
D_{calc} (Mg m ⁻³)	1.758	1.804
Crystal size (mm ³)	$0.07 \times 0.141 \times 0.121$	$0.188 \times 0.209 \times 0.226$
F(000)	848	402
μ (Mo-K α) (cm ⁻¹)	6.91	7.47
Reflections collected	11312	7242
Independent	3916 (2512)	5476 (4732)
reflections		
$(I > 2\sigma(I))$		
Parameters	292	535
$\Delta(\rho) (e \text{ Å}^{-3})$	0.453 and -0.292	0.256 and -0.324
Goodness-of-fit	0.937	1.105
R ^a	0 0413 (0 0766) ^b	0.0266 (0.0330) ^b
wR_2^a	0.0904 (0.1033) ^b	$0.0685 (0.0772)^{b}$
··· ·		2.2.1/2

*^a R = $\Sigma ||$ Fo |-| Fc $||/\Sigma ||$ Fo $|, wR_2 = {\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]}^{1/2};$ [F_o> 4 σ (F_o)].

^b Based on all data

Fourier map. All calculations were performed using the ⁶⁰ SHELXS-97 program.⁵³ Crystal data, details of the data collection and the structure refinement were given in Table 5.

Thermal analysis

Thermogravimetric analyses (TG) experiments were carried out on a Perkin Elmer Diamond TG/DTA instrument. The samples ⁶⁵ are initially heated for 1 h at 50 °C to remove the rudimental air. During the simple ramping experiment, weight changes were recorded as a function of temperature for a 10 °C min⁻¹ temperature gradient between 30 and 1000 °C in nitrogen environments.

70 Experimental set up for bromination reaction

Bromination reaction activity tests were carried out in the mixed solution of H₂O–DMF at the constant temperature of $30 \pm 0.5^{\circ}$ C. Vanadium complexes were dissolved in a 25 mL H₂O–DMF mixed solution with the volume ratio of 4:1. Solutions used for ⁷⁵ kinetic measurements were maintained at a constant concentration of H⁺ (pH 5.8) by the addition of KBr, H₂O₂ and NaH₂PO₄–Na₂HPO₄ buffer solution.⁵⁴ Reactions were initiated by the addition of the phenol red solution. The oxidovanadium complexes in five different concentrations were confected in five ⁸⁰ cuvettes, respectively. Then the cuvettes were put in the constant temperature of water to heat 10 min and spectral changes were recorded using a 721 UV–Vis spectrophotometer every interval 5 min. Finally, the resulting data were collected of the reaction and fitted using the curve-fitting software in the program of Microsoft ⁸⁵ Excel.

It is assumed that the rate of this reaction is described by the

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rate equation: $dc/dt = kc_1^x c_2^y c_3^z$, then the equation of " $log(dc/dt) = logk + xlogc_1 + ylogc_2 + zlogc_3$ " was obtained, it is corresponding to " $-log(dc/dt) = -xlogc_1 - b$ ($b = logk + ylogc_2 + zlogc_3$)" where k is the reaction rate constant; c_1 , c_2 , c_3 are the s concentrations of oxidovanadium complexes, 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, namely, $dA/dt = \varepsilon \cdot d \cdot (dc/dt)$, where A is the measurable absorbance

of the resultant; ε is molar absorption coefficient, which of ¹⁰ bromophenol blue is measured as 14500 M⁻¹cm⁻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 oxidovanadium complexes (*dA/dt*) was given by the slope of this line. By changing the

¹⁵ concentration of oxidovanadium complexes, a series of dA/dt data can be obtained. The reaction rate constant (k) can be obtained from 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 ²⁰ "y=mx - b", in which "m" is the reaction order of the

oxidovanadium 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;⁵⁵ c_2 and c_3 are known as 0.4 mol/L and 10⁻⁴ mol/L, respectively.

²⁵ Based on the equation of " $b=logk + ylogc_2 + zlogc_3$ ", so the reaction rate constant (k) can be obtained. Bromination of phenol red was monitored by measurement of the absorbance at 592 nm for reaction aliquots which were extracted at specific time points and diluted into phosphate buffer of pH=5.8.

30 Experimental set up for catalytic oxidation

The oxidation reactions were carried out under air condition (atmospheric pressure) in a two-necked glass flask, fitted with a water condenser. In a typical experiment, 0.0004 g of the catalyst (complexes 1 or 2) was dissolved in 3 mL of desired solvent. ³⁵ Then the required amounts of H_2O_2 (in a 30% H_2O solution) and

 HNO_3 were added in this order, followed by 0.34 g of cyclohexane. The reaction solution was stirred at chosen temperature for selected times.

For the products analysis, 0.05 g of methylbenzene (internal standard) and 3 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample (1.0 μ L) was taken from the organic phase and analyzed by a GC equipped with a capillary column and a flame ionization detector

⁴⁵ by the internal standard method. TON is moles of products (cyclohexanol and cyclohexanone)/mole of catalyst. Blank experiments confirmed that no cyclohexanol or cyclohexanone was formed in the absence of the metal catalyst under the same conditions.

50 Conclusions

Two novel vanadium(III) complexes were synthesized by hydrothermal reaction of starting materials $V_2(SO_4)_3$ with rigid carboxylate as ligands in the system of H₂O. In order to investigate their applicability, the bromination reaction activities

⁵⁵ of them were tested with phenol red as organic substrate in the presence of H₂O₂, KBr and phosphate buffer. By changing the

concentration of vanadium(III) complexes, the reaction rate constant (k) were obtained finally (k of 1.174×10³ and 2.054 ×10³, respectively), which indicated that they can be considered ⁶⁰ as a potential functional model of VHPO. In addition, the catalytic abilities of the vanadium(III) complexes were evaluated in the oxidation of cyclohexane. Various parameters as solvent, temperature, acid and oxidant concentration have been tested in order to optimize both activity and selectivity of the oxidative ⁶⁵ process. Under optimized conditions, cyclohexanol and cyclohexanone were obtained with good to excellent conversion catalyzed by the complexes **1** and **2** (TON of 395 for **1** and 279 for **2**, respectively).

It is found that vanadium complexes with N-, and O- donor 70 chelating aromatic ligands exhibited better catalytic activity by studying on the reactions of catalytic bromination and catalytic oxidation. Our group will investigate deeply the application of the vanadium complexes as catalysts in the future.

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Supporting information paragraph

Tables of atomic coordinates, isotropic thermal parameters, and complete bond distances and angles have been deposited with the

85 Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge, by quoting the publication citation and deposition numbers CCDC 858688 (1) and 858689 (2) from the Director, CCDC, 12 Union Road. Cambridge, CB2 1EZ, UK (fax+44-1223-336033; e-mail 90 deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Novel vanadium(III) complexes with rigid phenylpolycarboxylate ligands: synthesis, structures and application in C-H bond activation

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Two vanadium(III) complexes: V(dipic)(Hbdc)(H₂O)₂ (1) and $[V_2(dipic)_2(H_2btec)(H_2O)_4] \cdot 2H_2O$ (2) are synthesized and characterized. They exhibited catalytic bromination and cyclohexane oxidation activity.