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Discrete spherical hexadecavanadates incorporating a bromide with oxidative bromination activity†

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Two discrete hexadecavanadates, $(n\text{-}Bu_4N)_4[V_{16}O_{38}(X)]$ (X = Cl^- (**1**) and X = Br^- (**2**)), were synthesized by a reaction of $[V_{10}O_{26}]^{4-}$ with a template anion resulting in the incorporation of chloride or bromide in the {V16} spherical cluster framework. The reaction of $[V_{10}O_{26}]^{4-}$ with *p*-toluenesulfonic acid proceeded under an aerobic environment to give **2** in the presence of an excess amount of bromide anion, which acted as both a template anion and a reducing reagent for the formation of the mixed-valence framework. For the synthesis of cluster **1**, additional reductive conditions were required due to the weak reducing ability of the chloride anion. The crystal structures of **1** and **2** were determined using single-crystal X-ray diffraction analysis. Both were found to consist of a discrete $[V^{V}{}_9V^{IV}{}_7O_{38}(X)]^{4-}$ framework by the linkage of VO_5 pyramidal units. Cyclic voltammetric studies of **1** and **2** in acetonitrile showed a series of stepwise reversible redox processes, which were due to the redox of the spherical polyoxovanadate frameworks. The oxidative bromination reactions of aromatic substrates were also investigated using cluster **2** as a catalyst under aerobic conditions.

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Introduction

Recent studies of vanadium chemistry reveal a wide range of functionality of vanadium coordination complexes, ranging from medicinal applications to catalytic organic syntheses.[1] Mimicking the vanadium bromoperoxidase functionality is a fundamentally important research subject in the chemistry of vanadium.[2] Indeed, the bromination reaction in organic synthesis has been studied extensively due to the great interest in bromoperoxidase activity.[3] In the biomimetic synthesis by vanadium catalysts for oxidative halogenation, H_2O_2 or O_2 is used as an oxidant and the typical catalysts employed are NH_4VO_3 and V_2O_5.[4]

Vanadium-substituted heteropolyoxometalates, $H_{3+n}[PMo_{12-n}V_nO_{40}]$, are also effective for the bromination of aromatic compounds and phenols, using dioxygen or air as an environmentally friendly oxidant.[5] The presence of multiple V^{5+} units in the cluster is essential to exhibit a reversible redox process in conjunction with utilizing dioxygen as an oxidant for the catalytic reaction. The reaction is believed to proceed through a stepwise redox process. The oxidation of a substrate by heteropolyoxometalates produced a reduced cluster, which then reoxidizes back to the original species by dioxygen in air.[6] However, the bromination reaction catalysed by pure polyoxovanadate species is unknown. Recently, an interesting application of V_2O_5 nanowires, which mimic vanadium bromoperoxidases, was reported, showing antibacterial activity for the prevention of marine biofouling.[7] This bromination ability of a simple oxide nanowire strongly suggests that an intrinsically nano-sized polyoxovanadate is a potential molecular catalyst for the bromination of organic substrates.

The versatile properties of polyoxovanadates arise from a wide variety of possible cluster geometries with robust oxide frameworks.[8] In polyoxovanadates, three types of basic building blocks are available. A tetrahedral, VO_4, a square pyramidal VO_5, and an octahedral VO_6 unit exhibit a variety of discrete cluster frameworks through the linkage of these polyhedral units by sharing vertices, corners or faces. The decavanadates, $[V_{10}O_{28}]^{6-}$, consisting of VO_6 units, are the predominant species in the acidic pH range.[9] Cyclic structures based on VO_4 units such as a tetravanadate, $[V_4O_{12}]^{4-}$, and VO_5 based bowl-type structures like a dodecavanadate, $[V_{12}O_{32}(CH_3CN)]^{4-}$, have also been investigated.[10]

In general, polyoxovanadates have oxidation states of vanadium atoms in the all-V(V) state. There is another type of complexes, known as reduced polyoxovanadates. It has partly reduced vanadium atoms with V(IV) oxidation state. The reduced polyoxovanadates are in a mixed valence state in a particular V^{V}/V^{IV} ratio and are redox active. The VO_6-based

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†Electronic supplementary information (ESI) available: Infrared spectra (Fig. S1) and ORTEP views (Fig. S2 and S3) of cluster **1** and **2**; Table of vanadium-halogen distances (Table S1); Infrared spectra of recovered catalyst (Fig. S4). CCDC 925676 for **1** and 925677 for **2**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50521a

complexes such as $[V_{13}O_{34}]^{3-}$, and $[V_{17}O_{42}]^{4-}$ show multiple redox waves in cyclic voltammetry, which indicates partial NaCl type packing modules of a V/O framework.[11] Spherical anionic frameworks are typical structures in the reduced form. The spherical structures are possibly based on a VO_5 pyramidal unit through the linkage of the basal plane, where the apex of the unit points outward from the sphere.[12] The resulting ball-shaped cluster has a void at the center in which an anionic group is encapsulated through weak electrostatic interactions with positively charged vanadium atoms. The valence state of vanadium is a mixed valence of V^{IV}/V^{V} or all V^{IV} states. The encapsulated anion at the center is believed to act as a template to maintain the spherical structure. Oxidation of the reduced framework may interfere with the formation of the spherical structure and produce a lacunary-type spherical structure such as $[HV_{12}O_{32}(Cl)]^{4-}$ with all V^{V} valence states.[13] Since these reduced polyoxovanadates are redox active species having multiple vanadium atoms in an oxygen-bridged cluster framework, these series of polyoxovanadates may also possess catalytic activity for various reactions in organic synthesis.

Here we report the first halide-incorporated discrete hexadecavanadate with the general formula $(n\text{-}Bu_4N)_4[V_{16}O_{38}(X)]$ ($X = Cl^-$, Br^-). The general purpose of the present study is to find possible catalysis candidates for the oxidative bromination reaction by polyoxovanadate species. We first isolated the polyoxovanadate species that survived under similar conditions for the aerobic bromination reaction of organic substrates. The synthetic condition we employed was a reductive acid condensation scheme with excess strong acid and bromide ion under aerobic oxygen. The resulting isolated $[V_{16}O_{38}(X)]^{4-}$ structure was determined using crystallographic studies. Catalytic bromination reactions of aromatic substrates were performed under aerobic conditions.

Experimental

Materials, methods and instrumentation

All reagents were used as purchased without purification under ambient reaction conditions. Solvents were dried and distilled and then stored under an atmosphere of nitrogen. Carbon, nitrogen and hydrogen contents were determined by the Research Institute for Instrumental Analysis at Kanazawa University. Elemental analyses of Cl and Br were performed by the Center for Organic Elemental Microanalysis Laboratory at Kyoto University. ^1H NMR spectra were recorded using a JEOL JNM-LA400 Spectrometer (400 MHz) in $CDCl_3$. Infrared spectra were measured using a Horiba FT-720 IR spectrometer in mineral oil or KBr pellets. The UV-visible spectra were recorded using a Hitachi U-3500 spectrophotometer. GC measurements were carried out using a Shimadzu GC 2014. The eluent gas was helium. $(n\text{-}Bu_4N)_4[V_{10}O_{26}]$ and $[Pd(COD)Cl_2]$ (COD = 1,5-cyclooctadiene) were synthesized according to literature procedures.[14]

Synthesis of compounds

Preparation of $(n\text{-}Bu_4N)_4[V_{16}O_{38}(Cl)]$ (1). $(n\text{-}Bu_4N)_4[V_{10}O_{26}]$ (190 mg, 0.10 mmol), $n\text{-}Bu_4NCl$ (139 mg, 0.50 mmol), $[Pd(COD)Cl_2]$ (11 mg, 0.04 mmol), and *p*-toluenesulfonic acid monohydrate (95 mg, 0.50 mmol) were dissolved in 2 ml of acetonitrile. After adding COD (87 mg, 0.8 mmol), the mixture was refluxed overnight. To the resulting blue solution was added 40 ml of diethylether, and the precipitate was collected and washed several times with a 1 : 1 mixed solvent of dichloromethane–diethylether to give a deep green powder. Yield: 98 mg, 65% based on V. Elemental analysis for $((n\text{-}C_4H_9)_4N)_4[V_{16}O_{38}(Cl)]\cdot 1/2C_8H_{12}$, $M_w = 2482.4$ g mol^{-1}, calcd (found)%: C 32.90 (32.89), H 6.09 (6.18), N 2.26 (2.32), Cl 1.43 (1.47). FT IR (KBr pellet), cm^{-1}: 997(s), 876(w), 820(m), 750(m), 668(m), 620(m). UV/Vis/NIR absorption spectrum in acetonitrile (nm): $\lambda = 876$ ($\varepsilon = 4120$ M^{-1} cm^{-1}) (IVCT).

Preparation of $(n\text{-}Bu_4N)_4[V_{16}O_{38}(Br)]$ (2). $(n\text{-}Bu_4N)_4[V_{10}O_{26}]$ (190 mg, 0.10 mmol), $n\text{-}Bu_4NBr$ (161 mg, 0.50 mmol), and *p*-toluenesulfonic acid monohydrate (190 mg, 1.00 mmol) were dissolved in 2 ml of acetonitrile. The mixture was refluxed overnight. To the resulting blue solution was added 40 ml of diethylether, and the precipitate was collected and washed several times with a 1 : 1 mixed solvent of dichloromethane–diethylether to give a deep green powder. Yield: 98 mg, 63% based on V. Elemental analysis for $((n\text{-}C_4H_9)_4N)_4[V_{16}O_{38}(Br)]$, $M_w = 2472.8$ g mol^{-1}, calcd (found)%: C 31.09 (30.60), H 5.87 (5.81), N 2.27 (2.34), Br 3.23 (3.31). FT IR (KBr pellet), cm^{-1}: 999(s), 877(w), 823(m), 750(m), 671(m), 646(m). UV/Vis/NIR absorption spectrum in acetonitrile (nm): $\lambda = 878$ ($\varepsilon = 3120$ M^{-1} cm^{-1}) (IVCT).

Single-crystal X-ray diffraction

Well-shaped crystals were mounted in Hamilton cryoloops under a constant nitrogen flow. Attempts to collect reflection data were made several times in order to select a good quality crystal, and the best results are presented here. Intensity data were collected at −150 °C using a Rigaku/MSC mercury diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), by 0.5° ω-scans at 0° and 90° in ϕ. The crystal data are summarized in Table 1. Data were collected and processed using the CrystalClear program (Rigaku). Absorption corrections were applied based on face-indexing. Direct methods were used to solve the structures and to locate the heavy atoms. The light atoms were found through successive refinements by the full-matrix least-squares methods using the *SHELXL*-97 program.[15] The program PLATON[16] was used to evaluate the accuracy of the refinements, the space group choice, and the lack of higher symmetry. CCDC reference numbers: 925676(**1**) and 925677(**2**).

Oxidation reactions

Reactions under aerobic conditions were carried out using 100 ml glass pressure tubes with a vacuum pressure valve. The tubes were charged with appropriate amounts of the substrate, cluster, acids, and solvent. The solution was then brought to

Table 1 Crystallographic data for compounds **1** and **2**

	1	**2**
Formula	$C_{64}H_{144}N_4V_{16}O_{38}Cl$	$C_{64}H_{144}N_4V_{16}O_{38}Br$
M_w/g mol^{-1}	2428.4	2472.8
T/°C	−150(2)	−150(2)
Wavelength/Å	0.7107	0.7107
Crystal system	Tetragonal	Orthorhombic
Space group	$P4_22_12$	$P2_12_12$
Unit cell		
a/Å	16.409(2)	15.996(2)
b/Å	—	16.885(3)
c/Å	18.059(3)	18.218(3)
V/Å^3	4862.6(12)	4920.6(12)
Z	2	2
Collected reflections	49 575	54 121
Unique reflections	4774	11 222
Parameters	280	555
R_{int}	0.071	0.054
μ/mm^{-1}	1.563	1.924
R_1^{a}	0.099	0.070
wR_2^{b}	0.275	0.191
GOF	1.101	1.091
Flack parameter	0.00(8)	−0.04(2)

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2\}^{1/2}$.

the appropriate temperature in a thermostated oil bath. The reaction solution was stirred for 24 h. For the reaction of *p*-cresol, aliquots were withdrawn from the tube, and the products were quantified by gas chromatography by the internal standard method after being passed through a short silica gel column. Iodobenzene was added as an internal standard for gas chromatography. For the reaction of 1,3,5-trimethoxybenzene, bromination products were quenched with 1 N HCl, and extracted by diethylether three times. The extract was washed with a $NaHCO_3$ solution and then the mixture was dried over $MgSO_4$. The concentrated mixture was analysed by ^{1}H NMR through a comparison of integration ratios using durene ($C_6H_2(CH_3)_4$) as an internal standard.

Electrochemistry

An ALS/CH Instruments Electrochemical Analyzer Model 600A was used for all voltammetric experiments. Acetonitrile and tetrabutylammonium perchlorate were used as the solvent and electrolyte, respectively. Solutions were degassed with nitrogen gas prior to electrochemical experiments. A single-compartment three-electrode cell was used with a glassy carbon electrode. Prior to all experiments, the working electrode was polished with alumina slurries (BAS, 0.05 μm). The electrode was rinsed with deionized water, then rinsed with acetone and used after air-drying. The auxiliary electrode was a 1 mm diameter platinum wire. Potentials are recorded *versus* the Ag^+/Ag electrode (BAS RE-7). The redox potential of ferrocene (Fc/Fc^+) *versus* the Ag^+/Ag reference electrode was 75 mV with a 90 mV peak separation in our experiments.

Bulk electrolysis was performed by using a BAS glassy carbon gauze electrode as the working electrode, which was placed in a porous frit cylinder immersed in CH_3CN with a platinum wire as the auxiliary electrode (0.1 M n-Bu_4NClO_4). Those electrodes were placed symmetrically and filled with 1 mmol of a V16 cluster solution. The reference electrode was the same as that used for cyclic voltammetry.

Results and discussion

Synthetic strategy

The predominant polyoxovanadate species in acidic solution are the decavanadates, $[H_nV_{10}O_{28}]^{(6-n)-}$. Under stronger acidic conditions, precipitation of V_2O_5 solids is often observed through a sequence of acid condensation reactions.[17] In the catalytic bromination reaction, a strong acid such as trifluoroacetic acid is often employed to facilitate the oxidation reaction. To develop catalytic species under such extreme acidic conditions, we investigated polyoxovanadate species that can be isolated under conditions identical to a typical catalytic bromination reaction. Thus, the required synthetic conditions are (i) the presence of a strong acid, (ii) an excess amount of bromide anion, and (iii) an excess amount of an oxidant. We employed *p*-toluenesulfonic acid as an acid, with an excess amount of tetra-*n*-butylammonium bromide in acetonitrile in the presence of atmospheric dioxygen, one of the most environmentally friendly oxidants. The decavanadates are known to precipitate during acidification, because various types of oligomers are formed through hydrogen bridged species.[18] Thus, we used reduced decavanadate, $[V_{10}O_{26}]^{4-}$ as a starting material for the synthesis of redox active species. By the synthesis of the above mentioned conditions,[19] we isolated complex **2**. The valence state of the isolated cluster was in the form of $[V^{V}{}_9V^{IV}{}_7O_{38}(Br)]^{4-}$. Here, a bromide anion acted as a template. **2** was not isolated using only one equivalent of bromide anion, demonstrating that an excess amount of bromide anion is required to act as a reducing reagent for the reduction of $[V_{10}O_{26}]^{4-}$. In fact, when we synthesized a chloride derivative for comparison, by using an excess amount of chloride anion, complex **1** was not formed due to the weaker reducing ability of the chloride anion. We employed relatively mild reducing condition for the synthesis of **1** through the reductive coupling scheme.[20] Instead of typical reducing reagents, we employed a more mild reduction of the polyoxovanadate by utilizing a catalytic oxidation reaction of olefin by a palladium complex. The catalytic oxidation of COD (1,5-cyclooctadiene) by $[Pd(COD)Cl_2]$ with $[V_{10}O_{26}]^{4-}$ is possible, contrary to the polyoxovanadates that have to be reduced in an inert atmosphere. By using this reduction scheme, **1** was successfully synthesized. The typical reducing reagents were not effective for the synthesis of **1**. In both syntheses, the resulting mixtures were precipitated by the addition of diethyl ether and the organic or organometallic residues were washed thoroughly using a mixed solvent of dichloromethane and diethylether. Both complexes **1** and **2** can be recrystallized in a normal laboratory atmosphere from acetonitrile.

The absorption spectra of clusters **1** and **2** in acetonitrile display an intense broad absorption in the Vis/NIR region (500–1400 cm^{-1}), which corresponds to intervalence bands

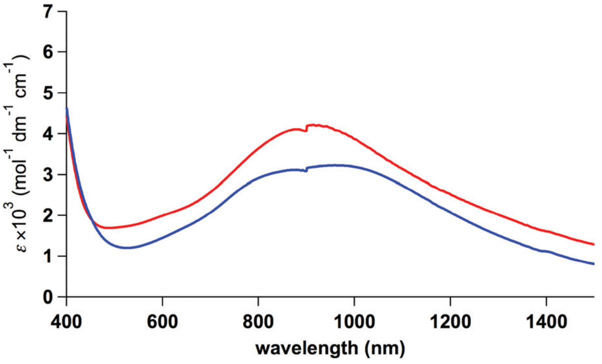

Fig. 1 UV/Vis/near-IR spectra of **1** and **2** in acetonitrile. Red: cluster **1**; blue: cluster **2**. The bump at 900 nm is due to detector switching.

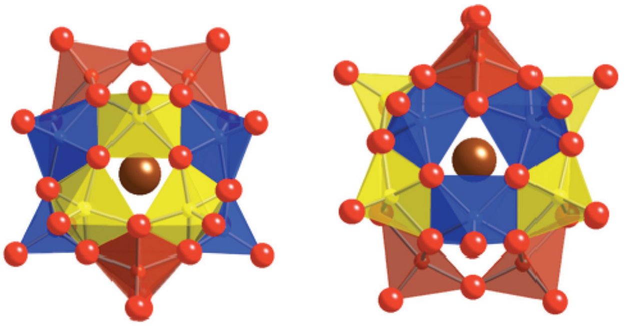

Fig. 2 Polyhedral view of the $[V_{16}O_{38}(X)]^{4-}$ cluster. Yellow, blue, red polyhedrons represent VO_5 units, color coded to label crystallographically independent units. Red spheres represent oxygen atoms and the brown circle represents the halogen anion. Left and right views are related by a 90° rotation through the four bar axis at the center of the anion.

between V^{IV} and V^V (Fig. 1). During the course of the synthesis, we observed a color change from purple for $[V_{10}O_{26}]^{4-}$ to deep blue for **2**. The absorption features of clusters **1** and **2** were similar due to the same V_{16} cluster framework with the same mixed valence state of $[V^V{}_9V^{IV}{}_7]$. The absorption coefficient was larger in cluster **1**, despite the same valence state. This was due to the smaller size of **1**, which enabled a more efficient interaction between V^{IV}/V^V intervalence transitions.

Structural analysis

The X-ray single crystal structure analyses of clusters **1** and **2** reveal the anionic {V16} spherical framework, which is constructed by the linkage of sixteen VO_5 pyramidal units. A chloride or bromide anion is encapsulated in the central cavity. This type of {V16} spherical polyoxovanadate has been reported to be the building block in an inorganic–organic hybrid material with secondary coordination complexes.[21] These previous examples reveal a wide variety of electrostatic charges on the {V16} cluster through −3 to −12 based on the diverse oxidation states, indicating a robust framework for multiple redox reactions. The previous examples are combined with a coordination entity as a cation to form a metal–organic framework, which is basically insoluble and unable to test the catalytic activity of the hexadecavanadate frameworks unless it breaks the coordination bonds between polyoxovanadates and the coordination entity. Clusters **1** and **2** are discrete analogues of those halogen incorporated {V16} clusters. By the employment of a large organic cation, n-Bu_4N^+, both clusters are readily soluble in acetonitrile. Potassium derivatives of the discrete framework which incorporate no anion, $[H_2V_{16}O_{38}]^{10-}$, or CN^- anion, $[V_{16}O_{38}(CN)]^{9-}$, have been reported as potassium salts.[22]

In **1**, the anion has a four-fold rotoinversion center at the chloride anion, and the vanadium polyhedra are color coded in Fig. 1. Red polyhedrons are related by S_4 symmetry and only one red unit is crystallographically independent. Three yellow and blue units are also related by S_4 symmetry, though only three yellow units are independent. In total, four VO_5 units, one red and three yellow units, are crystallographically independent. In cluster **2**, the symmetry was lowered and eight units, three yellow, three blue, and two red units, are independent (Fig. 2).

The structural relationship between $[V_{15}O_{36}(X)]^{4-}$ and $[V_{16}O_{38}Cl]^{4-}$ is shown in Fig. 3.[23] The framework can be regarded as having two parts: one is a cylindrical $\{V_{14}O_{35}\}$ framework denoted by yellow and blue polyhedrons, and another is a red polyhedral group on the top and bottom of the cylinder which can be regarded as a capping group for the cylinder. Each of the capping groups is composed of a $\{V_2O_3\}$ unit and these four red polyhedrons are related in S_4 symmetry. To the cylindrical $\{V_{14}O_{35}\}$ cluster units, two capping groups can be accommodated at the bottom and the top of the cylinder. There are two possible capping units on the cylinder. One is a $\{V_2O_3\}$ unit, and capping from the top and bottom of the cylinder produces the {V16} clusters. The second capping unit is a vanadyl {VO} unit seen on the left in Fig. 3. A {V15} cluster is formed when the cluster is capped by one {VO} unit from the top and one $\{V_2O_3\}$ unit from the bottom. The O/V ratio is 2.4 in {V15}, and 2.375 in the {V16} cluster. This indicates that {V16} is a more acid condensed species than {V15}. Vanadium pentoxide has an O/V ratio of 2.5; thus these spherical polyoxovanadates are the end products of the acid condensation.

From the BVS (bond valence sum) calculation[24] combined with charge valance, the valence state of the cluster core was regarded as $[V^V{}_9V^{IV}{}_7O_{38}]$ in complexes **1** and **2**. The BVS values are in the range of 4.36–5.28 in **1** and 4.21–5.00 in **2**.[25] Thus

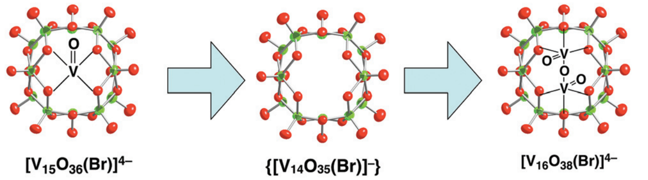

Fig. 3 Structural comparison of the $[V_{15}O_{36}Br]^{4-}$ cluster and the $[V_{16}O_{38}Br]^{4-}$ cluster viewed along the four bar axis. Green and red spheres represent vanadium and oxygen atoms, respectively. Left: the $[V_{15}O_{36}Br]^{4-}$ cluster looking down from the V=O group; middle: the hypothetical $\{V_{14}O_{35}\}$ cylindrical unit; right: the capping $\{V_2O_3\}$ group fitted in the cylindrical unit.

the electrons are delocalized over the spherical cluster framework. The average distance between vanadium atoms and the central halogen atom is 3.483 Å in **1** and 3.515 Å in **2**. The cluster size of **1** is smaller as expected from the smaller ionic radius of the chloride anion. In other words, the {V16} cluster shell shrinks to accommodate the smaller chloride anion, indicating a stronger inter-valence interaction between vanadium atoms by the shorter vanadium atom distances in the cluster. Fluoride or iodide did not form these {V16} cluster shells under our reaction conditions.

Redox properties

The cyclic voltammograms obtained for clusters **1** and **2** showed at least five redox processes including two overlapping oxidation waves and three well-resolved reduction couples in acetonitrile (Fig. 4). The $E_{1/2}$ values of three stepwise reduction waves were observed at −0.26, −0.74, and −1.40 V ($E_{1/2}$ *vs.* Fc/Fc$^+$) in cluster **1** and at −0.17, −0.76, and −1.41 V ($E_{1/2}$ *vs.* Fc/Fc$^+$) in cluster **2**. Bulk electrolysis with coulometric analysis showed each of the reduction processes as one-electron processes. The reductive electrochemical processes of the two clusters are summarized in the following reaction scheme in eqn (1a)–(1c):

$$[\mathrm{V^V}_9\mathrm{V^{IV}}_7] + \mathrm{e^-} \rightleftharpoons [\mathrm{V^V}_8\mathrm{V^{IV}}_8] \tag{1a}$$

$$[\mathrm{V^V}_8\mathrm{V^{IV}}_8] + \mathrm{e^-} \rightleftharpoons [\mathrm{V^V}_7\mathrm{V^{IV}}_9] \tag{1b}$$

$$[\mathrm{V^V}_7\mathrm{V^{IV}}_9] + \mathrm{e^-} \rightleftharpoons [\mathrm{V^V}_6\mathrm{V^{IV}}_{10}] \tag{1c}$$

The reversible multistep redox of these clusters suggests that the valence states are spread over the spherical cluster shell.

In addition to the reduction waves, two sets of oxidation waves were observed at 0.27 and 0.60 V ($E_{1/2}$ *vs.* Fc/Fc$^+$) in cluster **1** and overlapped oxidation waves at 0.47 V ($E_{1/2}$ *vs.* Fc/Fc$^+$) were observed in cluster **2**. The oxidation waves appear to be quasi-reversible, but the presence of overlapping waves makes a definitive assignment for the process difficult. For the oxidation of organic substrates by using these clusters, it may be important to compare the potential of the first available reduction wave, which may be utilized to oxidize the organic substrates resulting in the reduction of the cluster core. The $E_{1/2}$ value of the first reduction wave in cluster **2** was −0.17 V *vs.* −0.26 V ($E_{1/2}$ *vs.* Fc/Fc$^+$) in cluster **1**. This indicates that cluster **2** is a better oxidant, and is easier to be reduced than cluster **1**. The smaller size of cluster **1** makes the electron density of the cluster core higher, resulting in a cluster framework that is more difficult to reduce. Thus, we conclude that cluster **2** is more suitable for the oxidation reaction catalysis. The third reduction wave on cluster **2** appeared to be irreversible. It may be affected by the destabilization of the reduced spherical core caused by the interaction with the larger bromide. The small peak between the second and third reduction waves in cluster **1** may be attributed to slow redistribution of the negative charges on the cluster. These observations may suggest the charge redistribution after two-electron reductions (eqn (1c)) to compensate for the build up of the negative charges over the cluster. The additional charges on the cluster by the two-electron reduction have to be redistributed to compensate for the negative charge repulsions resulting in a different $\mathrm{V^{IV}/V^{V}}$ positional arrangement in the cluster.

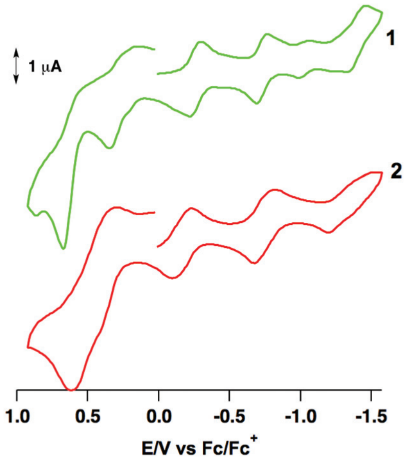

Fig. 4 Cyclic voltammograms of 0.1 mmol dm^{-3} **1** (green line) and **2** (red line) in CH_3CN (0.1 M *n*-Bu_4NClO_4).

This spherical polyoxovanadate **2** synthesized under strong acidic conditions is an active catalyst for the aerobic bromination of phenols and aromatic compounds. The smaller first redox potentials in cluster **2** predict that cluster **2** is susceptible to be reduced by the substrate and thus cluster **2** was subjected to the oxidative bromination of an aromatic substrate. We chose *p*-cresol as a substrate and the oxidative bromination reaction using cluster **2** as a catalyst was conducted under an aerobic environment (Table 2).

The reaction proceeded slowly using ambient air as an oxidant at reflux temperature of an acetonitrile solution. The catalytic reaction required an excess amount of bromide in the mixture. Without adding bromide externally, the reaction was totally inactive (entry 4). It was suggested that the bromide inside the {V16} cage was not involved in the catalytic process and only functioned as a template to maintain the {V16} cage structure. The control experiments conducted without cluster **2** show no activity (entry 5). In the initial stage of the reaction, 2-bromo-*p*-cresol was selectively produced but after consumption of the unreacted substrates, the formation of 2,6-dibromo-*p*-cresol increased. The use of pure oxygen as an oxidant increased the yield but also increased the formation of 2,6-dibromo-*p*-cresol (entry 2).

The catalyst can be recovered by precipitation using diethylether from the catalytic mixture and then purified by removing the organic residue by washing the precipitate with mixed solvents. The IR spectrum of the recovered catalyst was identical to the original sample, and it can even be recrystallized in acetonitrile. The reuse of the recovered catalyst showed nearly the same activity as the initial sample in the second run (entry 6). The turnover number (TON), based on cluster **2**, was *ca.* 12 in acetonitrile solution.

Table 2 Oxidative bromination of *p*-cresol by aerobic dioxygen catalysed by cluster **2**[a]

Entry	**2** (mmol)	*n*-Bu_4NBr (mmol)	Acid (mmol)	Atmosphere	Yield[b] [%] a	Yield[b] [%] b	TTON[c]
1	0.02	0.6	1.2	Air	54	2	11
2	0.02	0.6	1.2	O_2	64	19	17
3	0.02	0.6	0.1	Air	6	0	1
4	0.4	0	1.2	Air	0	0	0
5	0	0.6	1.2	Air	0	0	0
6[d]	0.02	0.6	1.2	Air	59	4	12

[a] Reaction conditions: in acetonitrile (1.5 ml), 80 °C, 24 h with CF_3COOH as an acid. The concentration of *p*-cresol is 0.4 mmol for entries 1–6. [b] a represents 2-bromo-*p*-cresol, and b represents 2,6-dibromo-*p*-cresol. [c] TTON corresponds to moles of products per mole of **2**. [d] Entry 6 uses recovered catalyst.

Interestingly, when other types of polyoxovanadates that are stable under modest pH conditions and soluble in acetonitrile, such as $[H_3V_{10}O_{28}]^{3-}$ and $[HV_{12}O_{32}(Cl)]^{4-}$, were employed in the catalytic reaction, they showed similar activity in bromination ability. These results indicate that under strong acidic conditions in the presence of excess trifluoroacetic acid and bromide anion, vanadium cluster frameworks are very likely to be converted to spherical cluster **2**. The high O/V ratio of $[H_3V_{10}O_{28}]^{3-}$ allowed them to be further condensed by strong acids into a spherical framework that has a low O/V ratio. To prove this point, we recovered polyoxovanadate species from the catalytic reaction conducted using $[H_3V_{10}O_{28}]^{3-}$ that were soluble in acetonitrile. The IR spectra of the recovered catalytic species were identical to that of cluster **2**. This indicated that cluster **2** was sustained under this reaction condition and also some polyoxovanadate species in acetonitrile tended to convert into cluster **2** under highly acidic conditions with excess bromide anion present.

We also performed the oxidative bromination reaction of 1,3,5-trimethoxybenzene as a benchmark for the bromination ability of the catalysts (Table 3).

This type of an aromatic substrate makes the catalytic activity comparison feasible, due to the lack of selectivity in the reaction and higher sensitivity to the oxidative bromination reaction. The employment of hydrogen bromide as a bromide source and also as an acid dramatically improves the TTON under these reaction conditions. The bromination reaction of 1,3,5-trimethoxybenzene gave monobrominated species selectively with TTON 75. These results are comparable to the oxidative bromination catalysts previously reported by using vanadium coordination complexes as catalysts.[26] Cluster **2** is the main polyoxovanadate product under strong acid conditions with excess bromide and is a good precatalyst for the bromination reaction. It should also be emphasized that after the catalytic reaction, cluster **2** can be recovered and reused, because the catalytic reaction condition is exactly the same as the synthetic condition.

Table 3 Oxidative bromination of 1,3,5-trimethoxybenzene by aerobic dioxygen catalysed by cluster **2**[a]

	Solvent	Substrate (mmol)	*n*-Bu_4NBr (mmol)	HBr[b] (mmol)	TTON[c]
1	Acetonitrile	0.4	0.6	1.2	17
2	1,4-Dioxane	1.0	2.0	3.0	75

[a] Reaction conditions: 0.02 mmol of cluster **2** in 1.5 ml of solvent, 80 °C, 24 h under aerobic conditions. Bromo-1,3,5-trimethoxybenzene was an only product. [b] 33% HBr solution in acetic acid is used. [c] TTON corresponds to moles of products per mole of **2**.

Conclusions

Under the oxidative bromination condition, *i.e.*, the presence of a strong acid and excess bromide under aerobic dioxygen, spherical polyoxovanadates $[V_{16}O_{38}(Br)]^{4-}$ were isolated and characterized through X-ray structure determination and cyclic voltammetry studies. The structure of the cluster was a discrete spherical type cluster in a mixed valence state of $[V^V{}_9V^{IV}{}_7]$ unlike precedences in which the hexadecavanadate core were buried in a metal–organic framework, unable to dissolve in organic solution. The redox chemistry shows stepwise multiple reversible waves, typical of a spherical cluster framework in a reduced polyoxovanadate cluster. Cluster **2** can be recrystallized in a strong acid under aerobic conditions. The oxidative bromination reactions of aromatic substrates by air were performed using cluster **2**. After the catalytic reaction, cluster **2** can be readily recovered and used again without loss of activity. Further studies of the ambient bromination process using discrete polyoxovanadates may reveal potential value for a versatile vanadium chemistry.

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