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The Polyoxovanadate-Based Carboxylate Derivative $K_6H[V_{17}V_{12}^{V}(OH)_4O_{60}(OOC(CH_2)_4COO)_8] \cdot nH_2O$: Synthesis, Crystal Structure, and Catalysis for Oxidation of Sulfides

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Supporting Information

ABSTRACT: The high-nuclearity polyoxovanadate-based carboxylate derivative K₆H- $[V_{17}^V V_{12}^{IV}(OH)_4 O_{60}(OOC(CH_2)_4 COO)_8] \cdot nH_2 O$ (1) has been successfully synthesized by conventional aqueous methods and structurally characterized. The $[V_{17}^V V_{12}^{IV}(OH)_4 O_{60}(OOC(CH_2)_4 COO)_8]^7$ polyanion is built up from three cages: one $\{V_{17}^V (OH)_4 O_{44}\}$ cage and two identical $[(V_{3}^V O_6)_2 (OOC(CH_2)_4 COO)_4]^{8-}$ cages. Of the three cages, the $\{V_{17}^{V}(OH)_{4}O_{44}\}$ is a purely inorganic polyoxovanadate cluster, whereas each of the $[(V^{IV}_{3}O_{6})_{2}(OOC(CH_{2})_{4}COO)_{4}]^{8-}$ cages is a vanadium-based organic-inorganic hybrid cluster framed via four adipate ligands linking simultaneously to two triangular $\{V_3\}$ units. The two $[(V^{IV}_{3}O_{6})_{2}(OOC(CH_{2})_{4}COO)_{4}]^{8-}$ cages are covalently attached to the central $\{V_{17}^{V}(OH)_4O_{44}\}$ cage via V–O–V bonds in a linear arrangement, resulting in a $\{V_{29}\}$ -based hybrid cluster skeleton. The catalytic properties of compound 1 for the oxidation of sulfides by tert-butyl hydroperoxide were investigated, and the result indicates that 1 exhibits excellent catalytic activity for the oxidation of sulfides under mild conditions.



INTRODUCTION

Polyoxovanadates (POVs), as an important subclass of polyoxometalates (POMs), have attracted interest not only due to the different coordination geometries and versatile redox activities of vanadium ions but also due to their interesting molecular magnetism, good catalytic performance, bioactivity, and importance in medical chemistry.^{1–8}

As is known, vanadium has the ability to form many vanadium-oxygen clusters. The reported crystallographically characterized isopolyoxovanadates $[V_2O_7]^{4-9}$ $[V_3O_9]^{3-10}$ $[V_4O_{12}]^{4-,11}$ $[V_5O_{14}]^{3-,12}$ $[V_{10}O_{28}]^{6-,13}$ $[V_{12}O_{32}]^{4-,14}$ $[V_{13}O_{34}]^{3-,15}$ $[V_{15}O_{42}]^{9-,16}$ and $[V_{16}O_{42}]^{4-,17}$ form the class $[V_{13}O_{34}]^{\circ}$, $[V_{15}O_{42}]^{\circ}$, and $[V_{16}O_{42}]^{\circ-1}$ form the class of fully oxidized vanadium species.¹ Likewise, the cagelike clusters $[V_{10}O_{26}]^{4-,18} [H_{12}V_{13}O_{40}]^{4-,19} [V_{15}O_{36}]^{5-,20}$ $[V_{16}O_{38}]^{7-,21} [V_{16}O_{42}]^{7-,22} [V_{17}O_{42}]^{4-,23} [V_{18}O_{42}]^{n-}$ (n = 4, 10),²⁴ $[V_{18}O_{44}]^{6-,25} [V_{19}O_{49}]^{9-,26} [V_{22}O_{54}]^{6-,25}$ and $[V_{34}O_{82}]^{10-27}$ constitute the class of mixed-valent V^V/V^{IV} species. Only the $[V_{18}O_{42}]^{12-}$ polyanion belongs to the "fully reduced" POV species.²⁸ Among them, larger clusters are relatively few in number, probably due to the small size of the central templates, which determine the shape of the POV clusters.^{25,27} The introduction of oxygen-,^{29,30} nitrogen-,³¹ and phosphorus-containing^{32,33} donor ligands to POVs allows charge compensation via formal substitution of peripheral, bridging, or terminal oxo ligands, thus stabilizing initially unstable POV architectures, and further provides novel POV building units for the assembly of larger systems. Moreover, incorporation of organic groups into POV building blocks

would endow the POV-based organic-inorganic hybrids with additional functionality and promising applications.

In various kinds of organic components, the covalent grafting of carboxylate ligands onto POV building units is a remarkable approach for the construction of POV-based carboxylate derivatives.²⁹ To date, a number of POV-based carboxylate derivatives have been reported, particularly based on monocarboxylate and aromatic multicarboxylates as structural modifiers. The monocarboxylic-functionalized POV clusters include the following examples that are based on $\{V_2\}$,³⁴ $\{V_3\}$,^{35–39} $\{V_4\}$,^{36,37,40–45} $\{V_5\}$,^{40,44,46} $\{V_6\}$,^{47,48} $\{V_8\}$,⁴⁹ $\{V_9\}$,⁴⁶ $\{V_{10}\}$,^{49,50} and $\{V_{11}\}$, $\{V_{13}\}$, $\{V_{16}\}$, and $\{V_{18}\}$.⁵¹ POVs incorporating aromatic multicarboxylate ligands have been successively reported by the groups of Zaworotko and Su. In their works, $\{V_6O_6(OCH_3)_9(SO_4)\}$, $\{V_6O_6(OCH_3)_9(VO_3)$ - (H_2O) , and the aforementioned $\{V_4\}$ and $\{V_5\}$ clusters act as secondary building units that assemble with rigid aromatic dicarboxylate or tricarboxylate linkers as edges or faces to form POV-based polyhedral cages.^{29,52-56} In comparison with monocarboxylic acids or rigid aromatic carboxylic acids, the number of POV-based aliphatic dicarboxylate derivatives is very limited. To our knowledge, only one compound has been reported, $[(n-C_4H_9)_4N]_2[V_8O_8(OCH_3)_{16}(C_2O_4)]$, with an oxalate ligand in the central cavity bridging eight vanadium ions with a ring-shaped core.⁵⁷ The reason for this is the

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random winding structure of the aliphatic dicarboxylic acids that are often present in the solvent and the O-donor groups of the acids are rather difficult to coordinate to metal ions. However, aliphatic dicarboxylic acids $HOOC(CH_2)_nCOOH$ acting as flexible multidentate O-donor ligands exhibit more coordination modes in comparison to other carboxylic acids, which benefits the construction of interesting vanadium-based cluster systems.

On the basis of these facts, we employed aliphatic dicarboxylic acids as ligands to construct POV-based inorganic–organic frameworks and obtained an unprecedented { V_{29} } - b a s e d a d i p at e d e r i v a t i v e, K₆ H - [$V_{17}^{V}V_{12}^{IV}(OH)_4O_{60}(OOC(CH_2)_4COO)_8$]·nH₂O (1). As far as we know, it is the largest carboxylic-functionalized POV cluster and first POV-based adipate derivative. The [$V_{17}^{V}V_{12}^{IV}(OH)_4O_{60}(OOC(CH_2)_4COO)_8$]^{7–} polyanion can be isolated as discrete potassium salts and has approximate dimensions of 2.1 nm × 1.1 nm (Figure S1 in the Supporting Information).

EXPERIMENTAL SECTION

Materials and Methods. All chemical reagents were purchased from commercial sources and used without further purification. The FT-IR spectra were performed in the range 2500–450 cm⁻¹ using KBr pellets on a Bruker VERTEX 70 IR spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded ranging from 5 to 40° at room temperature on a Bruker D8 ADVANCE diffractometer with Cu K α radiation (λ = 1.54056 Å). The C and H elemental analyses were obtained with a PerkinElmer 2400-II CHNS/O elemental analyzer. Metal element analysis was conducted on a PerkinElmer Optima2100 DV inductively coupled plasma optical-emission spectrometer. Thermogravimetric-mass (TG-MS) analysis of the samples was performed using a NETZSCH STA 449 F5 analyzer heated from 30 to 900 °C under nitrogen at a heating rate of 10 °C min⁻¹. Variabletemperature magnetic susceptibility data were obtained in the temperature range of 2-300 K using a SQUID magnetometer (Quantum Design, MPMS-3) with an applied field of 1000 Oe. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS ULTRA XPS spectrometer with monochromated Al (1486 eV) exciting radiation source.

Preparation of K₆H[V^V₁₇V^{IV}₁₂(OH)₄O₆₀(OOC(CH₂)₄COO)₈]nH₂O (1). A solution of KVO₃ (3.45 g, 25.0 mmol) in H₂O (50 mL) was treated at 90 °C with hydrazine hydrate (N₂H₄·H₂O; 80%, 200 \muL, 3.30 mmol) and maintained for 1 h at this temperature with stirring. Thereafter, adipic acid (3.00 g, 20.5 mmol) was added to the brown solution at 90 °C and the mixture was stirred until the solid was completely dissolved. The solution turned black. After addition of N₂H₄·H₂O (80%, 200 \muL, 3.30 mmol) once again to the reaction mixture, the solution was heated at 90 °C for 5 h with consistent stirring and then filtered hot. The filtrate was left to slowly evaporate at room temperature for 2 weeks, and then the precipitated dark green rodlike crystals were filtered off. Yield: calculated 0.743 g (19.8% based on vanadium). Anal. Calcd for C₄₈H₁₂₁O₁₂₂V₂₉K₆: C, 13.22; H, 2.80; V 33.86; K 5.38. Found: C, 13.47; H 2.58; V, 34.90; K 5.40. FT-IR (KBr, cm⁻¹): 3431, 2927, 2856, 1579, 1545, 1455, 1426, 1361, 989, 969, 954, 815, 765, 681.

X-ray Crystallography. A suitable single crystal of 1 was carefully selected under an optical microscope and sealed into a capillary glass tube. Crystal data were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 296 K. The structures were solved by direct methods, and non-hydrogen atoms were refined by full-matrix least-squares methods on F^2 using the SHELX program suite.⁵⁸ The hydrogen atoms of the organic groups were placed in calculated positions and then refined using a riding model with a uniform value of $U_{iso} = 1.2U_{eq}$. All H atoms of water molecules were directly added to the molecular formula but not included in the structural model. Non-hydrogen

atoms were refined anisotropically. The crystal data and structure refinement results revealed that the empirical formula was K6H- $[V_{17}^{V}V_{12}^{V}(OH)_4O_{60}(OOC(CH_2)_4COO)_8] \cdot 20H_2O$ $(C_{48}H_{109}O_{116}V_{29}K_6)$, which is composed of an adipate-functionalized POV cluster and 20 water molecules. The SQUEEZE program performed in PLATON was further used to calculate and evaluate the possible numbers of the disordered solvent water molecules in the two accessible voids of the crystal structure. A total of 43 extra disordered solvent water molecules should be added to the chemical formula $K_{6}H[V_{17}^{V}V_{12}^{IV}(OH)_{4}O_{60}(OOC(CH_{2})_{4}COO)_{8}]\cdot 63H_{2}O$ $(C_{48}H_{195}O_{159}V_{29}K_6)$ on the basis of the calculation results. However, the TGA and CHN elemental analysis results showed that the number of water molecules might be 26 for the empirical formula $K_6H[V_{17}^VV_{17}^{1V}(OH)_4O_{60}(OOC(CH_2)_4COO)_8] \cdot 26H_2O(C_{48}H_{121}O_{122}V_{29}K_6)$. This might be attributed to the weathering of crystals of 1. Gradually, most of the highly disordered water molecules are lost in the process of drying and storing at room temperature. Crystallographic data in this paper have been deposited at the Cambridge Crystallographic Data Centre with CCDC number 1551856 for 1. Selected crystallographic data of compound 1 are given in Table S1 in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis. The following four aspects are worth mentioning in the synthesis process of 1. (1) Compound 1 was synthesized in aqueous solution, but almost all of the reported POV-based carboxylate derivatives were prepared in organic solvent or mixed solvent. $^{34,46-49,51-57}$ (2) Due to the utilization of simple and stable potassium metavanadate (KVO₃) as a precursor, the reaction was carried out under aerobic conditions rather than rigorous anaerobic conditions. (3) In comparison with monocarboxylic acids, long-chain dicarboxylic acids HOOC- $(CH_2)_n$ COOH as multidentate O-donor ligands exhibit more coordination modes and good flexibility and conformational freedom and preferably link covalently to the hard vanadium atom, thus forming interesting structures. Among the aliphatic dicarboxylic acids HOOC(CH₂)_nCOOH (n = 1-4, 6), we finally found that only HOOC(CH₂)₄COOH could covalently link to the POV skeleton, resulting in an unprecedented adipate-functionalized POV structure. Analogous reactions using the dicarboxylic acids HOOC(CH₂)_nCOOH (n = 1-3, 6) as raw materials give unknown brown powders. (4) Hydrazine hydrate serves as a reducing agent. The V/N₂H₄ molar ratio is crucial to the formation of 1. Single crystals of 1 can be obtained when the V/N_2H_4 ratio is increased from 3.0:1 to 3.8:1, but the crystallization of 1 becomes difficult with further addition of hydrazine hydrate beyond the above range.

Structure of Compound 1. Single-crystal X-ray diffraction analysis demonstrates that compound 1 crystallizes in the tetragonal space group *P4/mnc* with the central V4 atom through the C_2 symmetry axis of the polyanion. Compound 1 is composed of one $[V_{17}^V V_{12}^I (OH)_4 O_{60}(OOC(CH_2)_4 COO)_8]^{7-}$ polyanion, six potassium cations, and 63 lattice water molecules. Two K⁺ cations are encapsulated by two identical $[(V_{3}^{IV}O_{6})_2(OOC(CH_2)_4COO)_4]^{8-}$ cages and connect to the interior oxygen atoms of the cages, respectively. The other four K⁺ ions are situated on one side of the polyanion and link to the adjacent cluster through O–K–O bridging bonds, leading to the formation of a one-dimensional belted structure along the crystallographic *c* axis (Figure 1).

The polyanion of compound 1 consists of one $\{VO_4\}$ tetrahedron, four $\{VO_5\}$ trigonal bipyramids, eight $\{VO_5\}$ tetragonal pyramids, 16 $\{VO_6\}$ octahedra, and eight adipate ligands (Figure 2e). As shown in Figure 2a, two $\{V_2O_{10}\}$ dimers and two $\{VO_5\}$ trigonal bipyramids are linked alternately in a



Figure 1. Polyhedral/ball and stick view of the belted structure of **1** along the crystallographic *c* axis. $\{VO_x\}$ (x = 4-6) groups are shown as orange polyhedra. Hydrogen atoms are omitted for clarity (as is the case for subsequent figures).



Figure 2. Polyhedral graphical representation of 1: (a) {V₆} moieties and VO₄ tetrahedron; (b) {V₁₃O₄₀} fragment; (c) {V^V₁₇(OH)₄O₄₄} cluster; (d) 29-nuclear vanadium-based cluster skeleton; (e) polyanion of 1. Color codes: {VO₄}, pink tetrahedron; {VO₆}, orange octahedra; {VO₅}, gray tetragonal pyramids; {VO₅}, blue trigonal bipyramids.

corner-sharing mode to form a cyclic {V₆} moiety. Two {V₆} moieties are interlinked perpendicularly via sharing edges and at the same time connect to the O13, O13A and O13B, O13C atoms of the central {VO₄} unit, respectively, thus facilitating a wheel-shaped {V₁₃O₄₀} cluster. The {V₁₃O₄₀} unit (Figure 2b), as a novel type of oxovanadate building block, has an architecture similar to that of the {Mo₈V₅O₄₀} unit except that the sites of four {VO₅} trigonal bipyramids and eight {VO₆} octahedra were formally exchanged for four {VO₄} tetrahedra and eight {MoO₆} octahedra, respectively (Figure S2 in the Supporting Information).⁵⁹ Additionally, we note that a highly protonated [H₁₂V₁₃O₄₀]^{4–} anion with a pseudo-Keggin-type structure was obtained by Wang's group.¹⁹

The {V₁₃O₄₀} framework is capped above and below by two {V₂O₈} units through sharing corners, leading to a spherical {V^V₁₇(OH)₄O₄₄} assembly with $C_{2\nu}$ symmetry (Figure 2c). Of interest in the spherical {V^V₁₇(OH)₄O₄₄} cluster are the two capping {V₂O₈} units, which are rotated by 90° with respect to each other and are arranged on the spherical surface of the

 $\{V_{17}^V(OH)_4O_{44}\}$ cluster at a distance of 4.2458(14) Å from the V4 atom of the central $\{VO_4\}$ tetrahedron of the cluster. Unlike most known POV clusters that display a closed-sphere-like structure, this spherical $\{V_{17}^{V}(OH)_{4}O_{44}\}$ cluster contains four openings at the surface. Thus, two kinds of vanadium ions, socalled "cap" and "belt" vanadium centers, exist in the $\{V_{17}^{V}(OH)_{4}O_{44}\}$ cores (Figure S3 in the Supporting Information). It is worth noting that three different $\{VO_x\}$ (x = 4-6) units but four types of coordination modes around the V^V ions exist in the $\{\bar{V^V}_{17}(OH)_4O_{44}\}$ cages. The V1 center adopts a five-coordinate {VO₅} trigonal-bipyramidal configuration. V2 and V3 ions employ $\{VO_6\}$ octahedral coordination geometries. A $\{VO_4\}$ regular tetrahedron is formed around the central V4 atom. The other {VO₅} unit is determined as a tetragonal-pyramidal configuration for the capping vanadium (V5) (Figure S4 in the Supporting Information). Therefore, compound 1 is expected to have versatile activities due to its rich coordination chemistry. Furthermore, the V-O framework bonds define four distinct types of environments within the $\{V_{17}^V(OH)_4O_{44}\}$ cage for the five crystallographically independent vanadium atoms. One of these atoms (V1) is bound to three μ_3 -O atoms (V-O = 1.743(4)-1.789(4) Å) and one μ_4 -O atom (V–O = 2.435(5) Å). Two vanadium atoms (V2 and V3) are linked to one μ_4 -O atom (V–O = 1.939(4) and 1.911(4) Å), three μ_3 -O atoms (V-O = 1.962(4) - 2.281(4) Å) and one μ_2 -O atom (V-O = 1.809(5)and 1.707(5) Å). The central V4 atom forms bonds to four μ_3 -O atoms (V–O = 1.705(4) Å). Finally, V5 is bound to four μ_2 -O atoms with V–O distances ranging from 1.904(5) to 1.958(5) Å. The terminal V–O distances for these metal atoms all lie within the narrow range of 1.582(5) - 1.608(4) Å. The $[V_{5}^{IV}V_{12}^{V}O_{42}]^{4-}$ anionic cluster, composed of a close-packed distorted-supercubane {V₁₃O₁₄} core and four capping V=O groups, has been observed in the compound (n- $Bu_4N)_4[V_{17}O_{42}]^{23}$

The $\{V_{17}^V(OH)_4O_{44}\}$ cage is further expanded by four $\{V_3\}$ fragments via V-O-V bonds, forming an unprecedented crablike 29-nuclearity POV cluster skeleton (Figure 2d). Obviously, a 29-nuclearity purely inorganic POV cluster cannot exist solely due to its high negative charge. Actually, two of the four $\{V_3\}$ moieties are covalently bridged by four adipate ligands via sharing oxygen sites to build up a cage with a scaffold structure (denoted $[(V^{IV}_{3}O_{6})_{2}(OOC (CH_2)_4COO)_4]^{8-}$ (Figure 3a). Four oxo groups of each adipate anion acting as pillars within the scaffold structure bridge three V centers from two $\{V_3\}$ moieties (Figure 3b). As reported previously,⁶⁰ the introduction of adipate ligands serves to reduce the charge of the polyanion, thus stabilizing the rare POV skeleton. Then the two identical $[(V_{3}^{IV}O_{6})_{2}(OOC (CH_2)_4COO)_4]^{8-}$ cages are covalently attached to the central $\{V_{17}^{V}(OH)_{4}O_{44}\}$ cage via V–O–V bonds in a linear arrangement, resulting in a $\{V_{29}\}$ -based hybrid cluster structure. Therefore, the entire $[V_{17}^VV_{12}^V(OH)_4O_{60}(OOC-(CH_2)_4COO)_8]^{7-}$ polyanion can be regarded as a "cage to cage" architecture constructed from three cages (Figure 2e). However, the V- μ_2 -O(adipate) bond distances (2.007(6)-2.236(6) Å) are longer than those of V- μ_2 -O(V) (1.707(5)-1.958(5) Å).

The $[(V^{IV}_{3}O_{6})_{2}(OOC(CH_{2})_{4}COO)_{4}]^{8-}$ fragments of the polyanion present an unusual structure, the appreciation of which is facilitated by a comparison with other structurally characterized triangular trinuclear vanadium-based carboxylate complexes. In the reported compounds $[V_{3}(\mu_{3}-O)(\mu_{2})]^{8-}$



Figure 3. Polyhedral/ball and stick views: (a) $[(V^{IV}_{3}O_6)_2(OOC-(CH_2)_4COO)_4]^{8-}$ moieties; (b) coordination mode of the adipate ligand; (c) $\{(V_3O_6)(OOC)_4\}$ unit.

OOCCH₂CH₃)₆(OH₂)₃]Cl·2H₂O,³⁶ [V₃(μ_3 -O)(μ -OOCCH₃)₆(OH₂)₃]Cl·3.5H₂O,³⁷ and V₃(O)₃(THF)-(C₆H₅CO₂)₆,³⁹ the mean V···V distances are 3.312, 3.332, and 3.714 Å (Table S2 in the Supporting Information), respectively. In contrast, the average V···V distance of the [(V₃O₆)₂(OOC(CH₂)₄COO)₄]⁸⁻ fragment is 3.259 Å, which is significantly shorter than those of {V₃O}-based compounds. In particular, the V6···V7 distances are 2.841 Å (Figure 3c). According to the reported values, the neutral {V₄O₄}O₄ cubane unit forms two covalent V–V bonds that are 2.65 Å in length;²⁷ in comparison, a kind of strong metal–metal interaction exists between V6 and V7 metal ions. Additional bond distances are V=O(terminal)(av) = 1.583 Å, V– μ_3 -O(centered)(av) = 1.913 Å, and V–O(adipate)(av) = 2.087 Å.

The oxidation states of all V centers were established by a combination of bond valence sum (BVS) calculations and X-ray photoelectron spectroscopy (XPS). BVS values reveal that 12 vanadium centers range from 4.213 to 4.272 with an average of 4.235 and the other 17 vanadium centers range from 4.668 to 5.222 with an average of 5.098, indicating that the respective valences are +4 and +5 (Table S3 in the Supporting Information), attributed to V^{V}/V^{IV} -POV species. In addition, XPS measurements of 1 were performed to further prove the above results. They exhibit two peaks of ca. 517.13 and ca. 516.15 eV in the energy region of V $2p_{3/2}$, which can be attributed to V⁵⁺ $2p_{3/2}$ and V⁴⁺ $2p_{3/2}$, respectively (Figure S5 in the Supporting Information).⁵⁶ Furthermore, five protons should be added for charge-balance considerations and the BVS values of all oxygen atoms in Table S4 in the Supporting Information suggest that one proton delocalizes over the entire architecture, while O3, O3A, O3B, and O3C atoms are monoprotonated.

Magnetic Properties. The variable-temperature magnetic susceptibility of 1 was studied in the range of 2–300 K under an external magnetic field of 1000 Oe (Figure 4). The room-temperature value of $\chi_{\rm M}T$ of 12 uncoupled V⁴⁺ ions (4.50 emu mol⁻¹ K with g = 2.0, S = 1/2) is much higher than the experimental $\chi_{\rm M}T$ value of 3.21 emu mol⁻¹ K. Subsequently, the $\chi_{\rm M}T$ value of 1 decreases continuously with decreasing temperatures and at 2 K approaches 1.81 emu mol⁻¹ K, indicating the presence of strong antiferromagnetic exchange interactions within the clusters. The temperature dependence of the reciprocal susceptibilities $(1/\chi_{\rm M})$ fits to the Curie–Weiss law in the high-temperature region (160–300 K) with the



Figure 4. Temperature dependence of χ_M and $\chi_M T$ versus *T* plots of **1**.

negative Weiss constant $\Theta = -110.9$ K, which further confirms the presence of antiferromagnetic coupling between vanadium-(IV) centers. In addition, a Curie constant of 4.35 emu mol⁻¹ K is highly consistent with the expected value for 12 uncorrelated V⁴⁺ ions at 300 K, further supporting the assignment of oxidation states (Figure S6 in the Supporting Information). Antiferromagnetic coupling between oxovanadium(IV) magnetic ions is common in mixed-valence vanadium(IV/V) clusters.^{49,51,55,56} In addition, the $\chi_{\rm M}$ value increases from 0.01 emu mol⁻¹ at 300 K to 0.09 emu mol⁻¹ at 25 K and then exponentially increases to reach a maximum of 0.90 emu mol⁻¹ at 2 K.

Catalytic Oxidation of Sulfides. The oxidation of organic sulfide has gained increasing interest owing to the various utilities of both sulfone and sulfoxide in organic synthesis.⁶¹ In the reaction system, vanadium-based POMs present good catalytic activity for desulfurization.^{62,63} Thus, we explored the oxidation of sulfides using $K_6H[V_{17}V_{12}V_{12}(OH)_4O_{60}(OOC-(CH_2)_4COO)_8]\cdot 26H_2O$ as a catalyst in dichloromethane (CH_2Cl_2) with *tert*-butyl hydroperoxide (TBHP) as the oxidant at room temperature/50 °C/60 °C.

The results of catalytic experiments with four kinds of sulfides as substrates (diphenyl thioether, alkyl thioethers, aryl alkyl thioethers, and thiophenes) along with blank experiments are presented in Table 1 and Table S5 in the Supporting Information. As shown in Table 1, TBHP dosage (entry 13), reaction temperature (entries 2 and 6), time (entries 2, 4, and 5), and dosage of catalyst (entries 2 and 7) were the important factors that influence the conversion of oxide products. Specifically, under optimized conditions, compound 1 exhibits extraordinary efficiency in converting diphenyl thioether to diphenyl sulfoxide with much higher conversion and barely satisfactory selectivity (entry 2, conversion 92%, selectivity 87%) in comparison to those reported under similar experimental conditions (Table S6 in the Supporting Information).^{61,64} Furthermore, alkyl thioethers were converted into sulfoxides with the maximum 99% conversion and more than 80% selectivity (entries 8-10) within 1/2 h at room temperature, which demonstrated the excellent activity of catalyst 1 at low catalytic dosage. Meanwhile the aryl alkyl thioethers (entries 11-13) also show higher conversion in comparison to diphenyl thioether and have high selectivity for sulfoxide products. Moreover, 1 was used as catalyst for the oxidation of thiophenes (entries 14-16) containing dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), and benzothiophene (BT), which reacted with the

Table 1. Results for Oxygenation of Different Sulfides with TBHP Catalyzed by 1 in CH_2Cl_2

Entry	Substrate	TBHP (mmol)	Time (h)	Con. (%) ^a	Selectivity (%) RR'SO/RR'SO;
1 ^b		1	1	58	97 3
2		2	1	92	87 13
3		3	1	96	78 22
4	\dot{Q}	2	0.5	80	89 11
5		2	2	94	85 15
6°		2	1	97	79 21
7^{d}		2	1	80	89 11
8	<u>_s</u>	2	0,5	94	92 8
9	~~~s~~~	2	0.5	99	80 20
10	~~~s~~~	γ_2	0.5	93	92 8
11 ^b	()	2	1	98	91 9
12	\dot{O}	2	1	98	73 27
13	\mathcal{O}^{\sim}	2	1	98.5	79 21
14 ^e		0.34	2	81	0 100
15	$\langle \nabla Q \rangle$	0.34	3	81	8 92
16	$\langle \mathcal{O} \rangle$	0.34	3	38	0 100

^{*a*}Conversion determined by using GC with dodecane as an internal standard. The products were identified by GC-MS. ^{*b*}Reaction conditions for entries 1–5 and 11–13: 1 mmol of substrate; 3 μ mol of catalyst; 3 mL of CH₂Cl₂; 25 °C. ^{*c*}Conditions as in footnote b but reaction at 50 °C. ^{*d*}Reaction conditions for entries 7–10: 2 μ mol of catalyst. ^{*e*}Reaction conditions for entries 14–16: 0.1 mmol of substrate; 3 μ mol of catalyst; 2 mL of CH₂Cl₂; 60 °C.

oxidant TBHP in CH_2Cl_2 medium at 60 °C. The maximum substrate conversions were 81% achieved after 2 h for DBT, 81% after 3 h for 4,6-DMDBT, and 38% after 3 h for BT. The three substrates were finally oxidized into the corresponding sulfones with 100%, 92%, and 100% selectivity, which was superior to the aforementioned three kinds of sulfides in selectivity of oxidation products. Most of the oxidation reactions could happen without catalyst 1 (Table S5 in the Supporting Information), but the conversion of the catalytic oxidation reactions was very low; the highest conversion of the blank experiment was just about 13%. In contrast, we speculated that the catalytic reaction might be concentrated on the POV-based organic—inorganic units.

The catalyst was recovered by simple centrifugal separation, washed with CH_2Cl_2 , dried, and reused directly without being replenished or reconditioned. A comparative study of the conversion and sulfoxide selectivity for the 1-catalyzed sulfoxidation of diphenyl thioether in CH_2Cl_2 across three runs is presented in Figure S7 in the Supporting Information. The catalytic oxidation reaction in the final run gave 60% substrate conversion. In comparison with the initial catalytic activity, there was evident loss of catalytic activity. In order to

investigate the stability of the catalyst, IR spectra of the catalyst 1 before and after the catalytic reaction have been studied. The differences in the IR spectra are the extra peaks at 1703 cm⁻¹ of the samples after the catalytic reaction, which may be attributed to the carbonyl stretching vibration of carboxyl (Figure S8 in the Supporting Information). The results suggest that the V-O(adipate) bonds might partially ruptured but the adipate ligands remains intact within the framework, so that the structure of POV is still retained. In order to authenticate this, elemental analysis have been performed for compound 1 before and after the catalysis experiment. The chemical formula of 1 indicates that the theoretical C/V molar ratio is 1.655. According to the results of elemental analysis, the ratios of carbon atoms to vanadium atoms before and after the catalytic reaction are 1.636 and 1.642, respectively, which further confirms that the adipate ligands do not fall off from the framework. In addition, XPS measurements were performed to identify the oxidation states of V centers in compound 1 after the first run, second run, and third run. The XPS data of the samples after each run give three peaks, all at about 517.17 eV, which should be attributed to V^{5+} $2p_{3/2}$. The results confirm that the samples after the first run have been completely oxidized to the fully oxidized vanadium species (Figure S9 in the Supporting Information). Future work will be dedicated to improving the activity and selectivity for oxidation of organic sulfide with nontoxic solvent and eco-friendly oxidant and improving the stability of the catalyst.

CONCLUSION

In conclusion, the high-nuclearity vanadium-based compound $K_6H[V_{17}^VV_{12}^V(OH)_4O_{60}(OOC(CH_2)_4COO)_8] \cdot nH_2O$ has been synthesized under reducing conditions in aqueous solution. Interestingly, compound 1 features a "cage to cage" architecture via a pure inorganic V-based $\{V_{17}^{V}(OH)_4O_{44}\}$ cluster, which is expanded by two identical $[(V_{3}^{VV}O_6)_2(OOC$ architecture via a pure inorganic V-based $\{V^V$ $(CH_2)_4COO)_4$ ⁸⁻ hybrid cages through V-O-V bridges in a linear arrangement, yielding a 29-nuclearity V-based discrete structure. Magnetic studies indicate that 1 shows antiferromagnetic behavior. Furthermore, compound 1 shows excellent activity at low catalytic dosage for the oxidation of thioethers with high sulfoxide selectivity. In comparison with the main interest in the rational design and basal synthesis of novel POVbased carboxylate derivatives, the exploitation of catalytic performance of POV-based carboxylate derivatives has not been explored until now, and it is still a challenging task for us now and in the near future.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02207.

Structural and catalytic figures, crystallographic data and catalytic oxidation of sulfides, TGA, X-ray powder diffraction patterns, IR comparison spectra, XPS spectrum, and TG-MS curves (PDF)

Accession Codes

CCDC 1551856 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge

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Notes

The authors declare no competing financial interest.

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