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Article

Structure Transformation among Deca-, Dodeca- and Tridecavanadates and Their Properties for Thioanisole Oxidation

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Abstract: The transformation of three types of polyoxovanadates, $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$, $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ and $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ have been investigated according to the rational chemical equations, and the best transformation conditions were reported. By the reaction of $[H_3V_{10}O_{28}]^{3-}$ with 0.33 equivalents of $\{(n\text{-}C_4H_9)_4N\}OH$ in acetonitrile at 80 °C, $[V_{12}O_{32}]^{4-}$ was formed with 92% yield. The reaction in nitroethane with 0.69 equivalents of *p*-toluenesulfonic acid gave $[V_{13}O_{34}]^{3-}$ with 91% yield. The ^{51}V NMR observation of each reaction suggests the complete transformations of $[H_3V_{10}O_{28}]^{3-}$ to $[V_{12}O_{32}]^{4-}$ and to $[V_{13}O_{34}]^{3-}$ proceeded without the formation of any byproducts and it provides the reliable synthetic route. Decavanadates were produced by the hydrolysis of $[V_{12}O_{32}]^{4-}$ or $[V_{13}O_{34}]^{3-}$. While the direct transformation of $[V_{13}O_{34}]^{3-}$ to $[V_{12}O_{32}]^{4-}$ partly proceeded, the reverse one could not be observed. For the thioanisole oxidation, $[V_{13}O_{34}]^{3-}$ showed the highest activity of the three.

Keywords: polyoxometalates; structure transformation; dodecavanadate; tridecavanadate; thioanisole oxidation

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1. Introduction

Polyoxometalates have been attracting much attention in broad fields such as catalyst chemistry, magnetochemistry, and pharmaceutical chemistry [1–3]. Polyoxovanadates have a unique structural chemistry due to the availability of various coordination environments of tetrahedral $\{VO_4\}$, square-pyramidal $\{VO_5\}$ and octahedral $\{VO_6\}$ units [4]. Due to the high reactivity, the chemistry of polyoxovanadates is limited in decavanadate species. The only stable example of isopolyoxovanadates in aqueous solution is decavanadates, which consist of $\{VO_6\}$ units, in addition to the metavanadate species, $[VO_3]_n^{n-}$ with $\{VO_4\}$ units [5]. The employment of non-aqueous solvent increases the diversity of the polyoxovanadates. Up to now, various isopolyoxovanadates with only fully oxidized V^{5+}, such as $[V_3O_9]^{3-}$, $[V_4O_{12}]^{4-}$ and $[V_5O_{14}]^{3-}$ with $\{VO_4\}$ units; $[V_{11}O_{29}F_2]^{4-}$, $[HV_{12}O_{32}(Cl)]^{4-}$, $[V_{12}O_{32}]^{4-}$, $[V_{12}O_{32}(Cl)]^{5-}$ and $[H_2V_{14}O_{38}(Cl)]^{5-}$ with $\{VO_5\}$ units; $[V_7O_{19}F]^{4-}$ with both $\{VO_4\}$ and $\{VO_5\}$ units; and $[V_6O_{19}]^{8-}$ derivatives, $[H_nV_{10}O_{28}]^{(6-n)-}$ and $[V_{13}O_{34}]^{3-}$ with $\{VO_6\}$ units have been synthesized [6–19]. Since the properties such as redox and optics of polyoxovanadates depend on the anion structures, it is crucially important to control those cluster frameworks [14,19].

The half spherical dodecavanadates $[V_{12}O_{32}]^{4-}$ consist of twelve $\{VO_5\}$ units and have an open cavity into which several molecules and anions, such as nitriles, dichloromethane, NO^- and Cl^-, are incorporated and the host-guest interactions have been theoretically investigated (Figure 1) [9,10,20–23]. To clarify the role of an electron-rich guest and the anion, further investigations including systematic synthesis are required.

Tridecavanadate $[V_{13}O_{34}]^{3-}$ was reported as an oxidation catalyst for a number of organic substrates (Figure 1) [19]. After the pioneering work on the chemistry of $[V_{13}O_{34}]^{3-}$, few further investigations were reported. Our group successfully synthesized the four electron reduced tridecavanadate $[H_4V_{13}O_{34}]^{3-}$ [24]. During our investigation, the electrochemical oxidation of $[H_4V_{13}O_{34}]^{3-}$ gave $[V_{12}O_{32}]^{4-}$ instead of $[V_{13}O_{34}]^{3-}$. The protonation may prevent the oxidation of $[H_4V_{13}O_{34}]^{3-}$ to form $[V_{13}O_{34}]^{3-}$. Cronin's group synthesized the manganese-substituted polyoxovanadate with the same anion structure of $[V_{13}O_{34}]^{3-}$ [25]. The hetero-metal containing polyoxometalates have the potential to show unique catalytic and magnetic properties [26–29]. As like synthesis of Cronin's cluster from the related manganese-containing polyoxovanadate, the control of the structure transformation is important.

In this work, we report on the structure transformation among $[H_3V_{10}O_{28}]^{3-}$, $[V_{12}O_{32}]^{4-}$ and $[V_{13}O_{34}]^{3-}$, including the improved synthesis of $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$. In addition, oxidation of thioanisole using these polyoxovanadates is discussed.

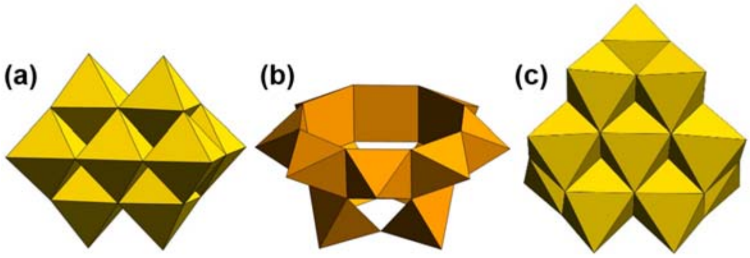


Figure 1. Anion structures of (**a**) $[H_3V_{10}O_{28}]^{3-}$, (**b**) $[V_{12}O_{32}]^{4-}$ and (**c**) $[V_{13}O_{34}]^{3-}$. Yellow octahedra and orange square-pyramids represent $\{VO_6\}$ and $\{VO_5\}$ units, respectively.

2. Results and Discussion

2.1. Structure Transformation among Deca-, Dodeca- and Tridecavanadates

The structure of decavanadates, $[H_nV_{10}O_{28}]^{(6-n)-}$, consists of ten octahedral $\{VO_6\}$ units stacked together in one molecule (Figure 1). While tridecavanadate $[V_{13}O_{34}]^{3-}$ also has a similar structure with three additional $\{VO_6\}$ octahedra in a triangular arrangement as add-on units on one of the surfaces of the decavanadate. Dodecavanadate $[V_{12}O_{32}]^{4-}$ has a totally different structure which is based on twelve square-pyramidal $\{VO_5\}$ units in a cage arrangement that has a cavity to incorporate a small molecule like acetonitrile at the center of the anion (Figure 1). These three complexes have distinct structures, yet the size of the anions are similar, and we tried to find the reaction conditions which can transform one molecule into another by adjusting the stoichiometry according to the molecular formula. The transformation process is monitored through ^{51}V NMR since all chemical shifts for each of those complexes were already reported [17,19,30]. In the transformation process, the employment of decavanadates as a starting material is especially beneficial because they are one of the most widely available species and thoroughly investigated in water as well as acetonitrile [8,31].

2.1.1. Transformation between Deca- and Dodecavanadates

The synthesis of the dodecavanadates was achieved in two different routes, even if the precursors are different in oxidation states, formulas and total charges on the cluster. In the first report by Klemperer's group, $[V_{12}O_{32}]^{4-}$ was prepared by refluxing an acetonitrile solution of the decavanadate with only two protonation sites, $\{(n\text{-}C_4H_9)_4N\}_4[H_2V_{10}O_{28}]$, for 1–2 min with >80% yield [10]. Later, by our group, $[V_{12}O_{32}]^{4-}$ was prepared by the oxidation of another type of decavanadate $\{(n\text{-}C_4H_9)_4N\}_4[V_{10}O_{26}]$ for 1 h at room temperature with 90% yield [9]. While $\{(n\text{-}C_4H_9)_4N\}_4[H_2V_{10}O_{28}]$ consists ten $\{V^{5+}O_6\}$ units, $\{(n\text{-}C_4H_9)_4N\}_4[V_{10}O_{26}]$ consists eight $\{V^{5+}O_4\}$ and two $\{V^{4+}O_5\}$ units. These differences show that the precursors are not important and provide us an opportunity to investigate the transformation of polyoxovanadates in accordance with the reaction equations. The triprotonated decavanadate $[H_3V_{10}O_{28}]^{3-}$ was selected as a precursor for investigation since the solution state of $[H_3V_{10}O_{28}]^{3-}$ in acetonitrile and water is well discussed before [17]. The conventional equation for the synthesis of $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ from $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ can be written by adjusting the stoichiometry as expressed in Equation (1).

$$6\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}] + 2\{(n\text{-}C_4H_9)_4N\}OH \rightleftarrows 5\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}] + 10H_2O \quad (1)$$

By the reaction of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ with 0.33 equivalents of $\{(n\text{-}C_4H_9)_4N\}OH$ in acetonitrile at room temperature for 24 h, ^{51}V NMR spectra showed signals due to $[H_3V_{10}O_{28}]^{3-}$ and $[H_2V_{10}O_{28}]^{4-}$, and $[V_{12}O_{32}]^{4-}$ as a minor product (Figure A1). The transfer reaction was slow at room temperature, and to accelerate the reaction, heating the solution was necessary. After refluxing for 1 h, only signals due to $[V_{12}O_{32}]^{4-}$ were observed with >99% chemoselectivity, and the isolated yield was 92% (Figure 2). IR spectrum of the isolated product show a perfect match with that of $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ (Figure 3).

In the presence of a stoichiometric amount of water, $[V_{12}O_{32}]^{4-}$ was stable with retention of the structure. An excess amount of water leads to the transformation of $[V_{12}O_{32}]^{4-}$ to decavanadates.

This is consistent with the established distribution study in aqueous media that dodecavanadates are not involved in the complicated equilibrium of polyoxovanadates [5]. In a mixed solvent of acetonitrile and water (3:1, *v*/*v*), the mixture of $[H_3V_{10}O_{28}]^{3-}$ and $[H_2V_{10}O_{28}]^{4-}$ was obtained (Figure A2). By addition of 0.4 equivalents of *p*-toluenesulfonic acid (TsOH) with respect to $[V_{12}O_{32}]^{4-}$, only $[H_3V_{10}O_{28}]^{3-}$ was detected by ^{51}V NMR and the isolated yield was 83% (Figure 2). IR spectrum of the isolated product shows convincing agreement with that of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ (Figure 3).

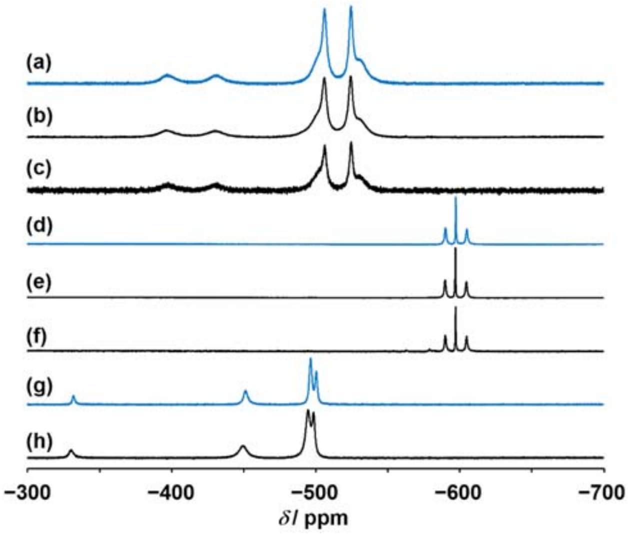


Figure 2. ^{51}V NMR spectra of (**a**) $[H_3V_{10}O_{28}]^{3-}$, (**d**) $[V_{12}O_{32}]^{4-}$ and (**g**) $[V_{13}O_{34}]^{3-}$ crystals dissolved in acetonitrile and of the reaction solution after the transformations of (**b**) $[V_{12}O_{32}]^{4-}$ to $[H_3V_{10}O_{28}]^{3-}$, (**c**) $[V_{13}O_{34}]^{3-}$ to $[H_3V_{10}O_{28}]^{3-}$, (**e**) $[H_3V_{10}O_{28}]^{3-}$ to $[V_{12}O_{32}]^{4-}$, (**f**) $[V_{13}O_{34}]^{3-}$ to $[V_{12}O_{32}]^{4-}$ and (**h**) $[H_3V_{10}O_{28}]^{3-}$ to $[V_{13}O_{34}]^{3-}$.

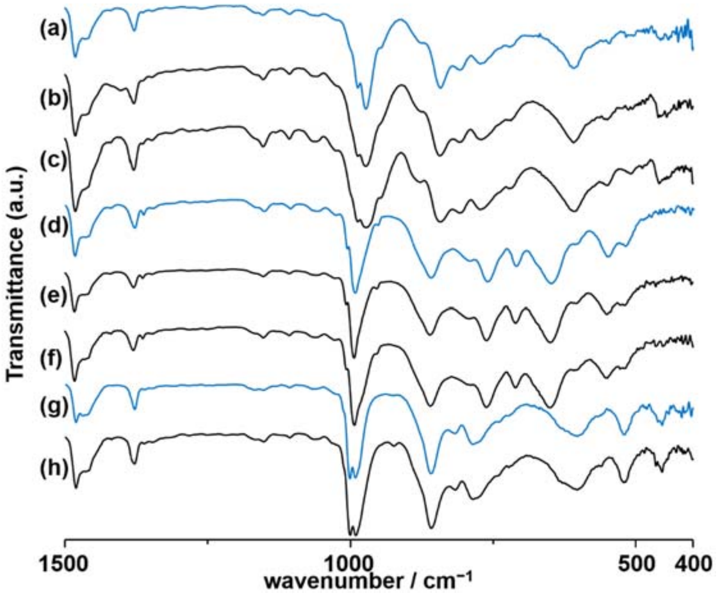


Figure 3. IR spectra of (**a**) $[H_3V_{10}O_{28}]^{3-}$, (**d**) $[V_{12}O_{32}]^{4-}$ and (**g**) $[V_{13}O_{34}]^{3-}$ crystals and of the powder obtained after the transformations of (**b**) $[V_{12}O_{32}]^{4-}$ to $[H_3V_{10}O_{28}]^{3-}$, (**c**) $[V_{13}O_{34}]^{3-}$ to $[H_3V_{10}O_{28}]^{3-}$, (**e**) $[H_3V_{10}O_{28}]^{3-}$ to $[V_{12}O_{32}]^{4-}$, (**f**) $[V_{13}O_{34}]^{3-}$ to $[V_{12}O_{32}]^{4-}$ and (**h**) $[H_3V_{10}O_{28}]^{3-}$ to $[V_{13}O_{34}]^{3-}$.

2.1.2. Transformation between Deca- and Tridecavanadates

In the reported procedure, $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ was obtained by refluxing 2.6 M $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ acetonitrile solution for 7 h under dry nitrogen [19]. In our investigation under the same condition, $[V_{13}O_{34}]^{3-}$ was formed as a minor product. The time dependent observation of ^{51}V NMR spectra at 80 °C reveals that the formation of $[V_{12}O_{32}]^{4-}$ is faster than that of $[V_{13}O_{34}]^{3-}$ (Figure A3). Once $[V_{12}O_{32}]^{4-}$ is formed, $[V_{13}O_{34}]^{3-}$ is no longer obtained in acetonitrile (see below). Although the solubility of $[V_{13}O_{34}]^{3-}$ is lower than $[V_{12}O_{32}]^{4-}$ and $[V_{13}O_{34}]^{3-}$ is selectively obtained by crystallization, the synthesis of $[V_{13}O_{34}]^{3-}$ is difficult in our hands. Therefore, the improved synthesis of $[V_{13}O_{34}]^{3-}$ is suggested in this paper. Since acetonitrile acts as a template to stabilize the host anion $[V_{12}O_{32}]^{4-}$, the choice of the appropriate solvent is important for the rational synthesis of $[V_{13}O_{34}]^{3-}$. $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ was dissolved in nitroethane and stirred for 3 h at 80 °C. Despite the indication that $[V_{13}O_{34}]^{3-}$ is selectively formed by ^{51}V NMR, the solution color turned to green during the reaction, suggesting that some of the vanadium atoms are reduced by hot nitroethane. The reduced byproducts are no longer detectable by ^{51}V NMR. After the removal of $[V_{13}O_{34}]^{3-}$ as crystals, addition of diethyl ether gave green precipitates. IR spectrum of this precipitate was in agreement with that of reported $[V_{18}O_{46}(NO_3)]^{5-}$ (Figure A4) [32]. The transformation of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ into $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ may be accomplished according to Equation (2).

$$13\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}] \rightleftarrows 10\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}] + 9\{(n\text{-}C_4H_9)_4N\}OH + 15H_2O \qquad (2)$$

The formation of a base according to Equation (2) prompted the reductive condition for those polyoxovanadates. In the presence of 0.69 equivalents of TsOH with respect to $[H_3V_{10}O_{28}]^{3-}$ to neutralize $\{(n\text{-}C_4H_9)_4N\}OH$, the solution color remained brown. ^{51}V NMR spectrum of the reaction solution showed pure signals due to $[V_{13}O_{34}]^{3-}$ (Figure 2). IR spectrum of the brown precipitates formed by addition of an excess amount of diethyl ether into the reaction solution, was the same as that of $[V_{13}O_{34}]^{3-}$ crystals, suggesting that the complete transformation of $[H_3V_{10}O_{28}]^{3-}$ to $[V_{13}O_{34}]^{3-}$ is achieved with 91% isolated yield (Figure 3). We find this reaction useful for further investigation of $[V_{13}O_{34}]^{3-}$ chemistry.

By the reaction of $[V_{13}O_{34}]^{3-}$ with 0.9 equivalents of $\{(n\text{-}C_4H_9)_4N\}OH$ in a mixed solvent of acetonitrile and water (2:1, *v*/*v*), quantitative formation of $[H_3V_{10}O_{28}]^{3-}$ was detected by ^{51}V NMR and IR spectra (Figures 2 and 3). The transformation of $[V_{13}O_{34}]^{3-}$ to $[H_3V_{10}O_{28}]^{3-}$ was *ca.* 10 times faster than that of $[V_{12}O_{32}]^{4-}$ partly due to the structural resemblance between $[H_3V_{10}O_{28}]^{3-}$ and $[V_{13}O_{34}]^{3-}$. Both of the structures of $[H_3V_{10}O_{28}]^{3-}$ and $[V_{13}O_{34}]^{3-}$ consist of $\{VO_6\}$ units sharing the edge of the octahedra. Only difference in the $[V_{13}O_{34}]^{3-}$ structure from $[H_3V_{10}O_{28}]^{3-}$ is the successive capping of the additional three $\{VO_6\}$ octahedra in a triangular arrangement as add-on units on top of the same decavanadate framework.

2.1.3. Transformation between Dodeca- and Tridecavanadates

In addition to the transformation between $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ and $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ or $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$, transformation between $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ and $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ was investigated based on the Equation (3).

$$13\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}] + 8H_2O \rightleftarrows 12\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}] + 16\{(n\text{-}C_4H_9)_4N\}OH \quad (3)$$

In acetonitrile, $[V_{12}O_{32}]^{4-}$ was not converted to $[V_{13}O_{34}]^{3-}$ even by addition of water and TsOH with heating. The resemblance of stoichiometry between Equations (1) and (3) also make it difficult to control the selective conversion of $[V_{12}O_{32}]^{4-}$ to $[V_{13}O_{34}]^{3-}$. Decavanadates are thermodynamically stable in the presence of water and $[V_{12}O_{32}]^{4-}$ is hardly transformed to other species in acetonitrile without water even when a stoichiometric amount of acid was added. To stimulate the formation of $[V_{13}O_{34}]^{3-}$, we tried to use a different solvent from acetonitrile and nitroethane was successful in converting $[V_{12}O_{32}]^{4-}$ into other forms. However, only the decomposition reaction was observed under the reaction condition with 1.2 equivalents of TsOH in nitroethane at 80 °C, and the formation of $[V_{13}O_{34}]^{3-}$ could not be detected by ^{51}V NMR.

Without any additives, $[V_{13}O_{34}]^{3-}$ was stable even in the refluxing condition in acetonitrile. According to Equation (3), the addition of 1.3 equivalents of $\{(n\text{-}C_4H_9)_4N\}OH$ to the solution of $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ was investigated. From ^{51}V NMR spectrum, decavanadates and $[V_{12}O_{32}]^{4-}$ were formed in 2 h at room temperature (Figure 4). The formation of decavanadates could be proceeded via Equation (2). Without heating, $[V_{12}O_{32}]^{4-}$ was hardly obtained via Equation (1) for 2 h (Figure A1). Therefore, $[V_{13}O_{34}]^{3-}$ was directly converted to $[V_{12}O_{32}]^{4-}$ via Equation (3). To achieve high yield of $[V_{12}O_{32}]^{4-}$, the reaction solution was refluxed and the formation of $[V_{12}O_{32}]^{4-}$ was detected by ^{51}V NMR with >95% chemoselectivity (Figure 2). The isolated yield was 86%. IR spectrum of the isolated product was identical to that of $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ (Figure 3).

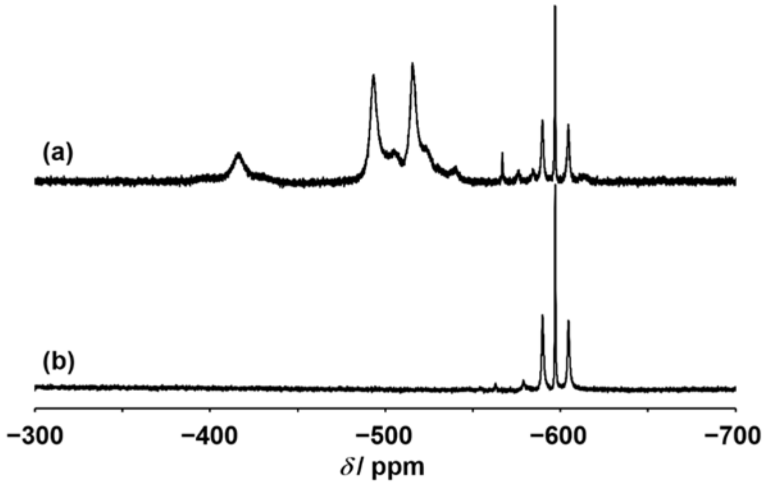


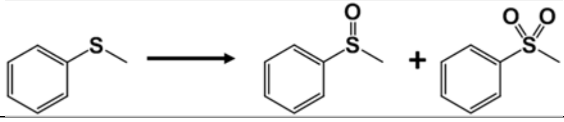
Figure 4. ^{51}V NMR spectra of the reaction solution of $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ with 1.3 equivalents of $\{(n\text{-}C_4H_9)_4N\}OH$ after 2 h (**a**) at room temperature and (**b**) in reflux condition.

2.2. Oxidation of Thioanisole

Next, to clarify the differences among $[H_3V_{10}O_{28}]^{3-}$, $[V_{12}O_{32}]^{4-}$ and $[V_{13}O_{34}]^{3-}$ in the activity for oxidation, the thioanisole oxidation with *t*-butyl hydroperoxide (TBHP) was carried out (Table 1). The oxidation of sulfides to sulfoxides and sulfones has been a widely researched subject due to the importance of products as intermediates in organic synthesis [33]. This method is also useful for oxidative desulfurization of oil [34]. TBHP and H_2O_2 are usual oxidants for the oxidation of sulfides.

It is reported that the redox properties of $[H_3V_{10}O_{28}]^{3-}$, $[V_{12}O_{32}]^{4-}$ and $[V_{13}O_{34}]^{3-}$ are different from one another [19]. Although there are some reports on oxidation catalysis for several organic substrates with $[H_3V_{10}O_{28}]^{3-}$ and $[V_{13}O_{34}]^{3-}$, the comparison of the activity in these compounds is not investigated [19,35,36].

Table 1. Oxidation of thioanisole with vanadium species [a].



Entry	Vanadium Species (μmol)	Total Yield (%)	Ratio of Sulfoxide:Sulfone
1	$\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ (7.7)	91	93:7
2	$\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ (8.4)	79	79:21
3	$\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ (10)	33	94:6
4 [b]	V_2O_5 (20)	67	97:3
5	-	3	-

[a] Reaction condition: thioanisole (1 mmol), TBHP (1 mmol), acetonitrile (2 mL), 25 °C, 2.5 h. Yields were determined by GC with an internal standard. Total yield (%) = {sulfoxide (mol) + sulfone (mol) × 2}/initial TBHP (mol) × 100; [b] V_2O_5 was suspended.

Each polyoxovanadate retains their anion structures in acetonitrile at 25 °C. In the presence of 20 equivalents of TBHP with respect to polyoxovanadates, their anion structures were maintained (Figure A5). In the presence of $[V_{13}O_{34}]^{3-}$, 91% total yield of methyl phenyl sulfoxide and methyl phenyl sulfone was achieved in 2.5 h (Table 1). The ratio of sulfoxide and sulfone was 93:7. Under the same reaction conditions, oxidation reaction hardly proceeded in the absence of vanadium species. $[H_3V_{10}O_{28}]^{3-}$ showed a lower activity for this reaction (33% yield in 2.5 h). The reactivity of $[V_{12}O_{32}]^{4-}$ was different from that of $[V_{13}O_{34}]^{3-}$. The yield with $[V_{12}O_{32}]^{4-}$ in 0.5 h (59%) was higher than that with $[V_{13}O_{34}]^{3-}$ (25%), and the reaction ended in 90 min with *ca.* 80% yield. Successive oxidation of sulfoxide to sulfone proceeded from the initial stage of the reaction in the presence of $[V_{12}O_{32}]^{4-}$. While the $[V_{12}O_{32}]^{4-}$ framework is closely related to layered V_2O_5, in which vanadium atoms adopt the square-pyramidal coordination geometry, $[V_{12}O_{32}]^{4-}$ showed the higher activity for the formation of sulfone than V_2O_5. The reactivity depends on the electrophilicity of the active oxidant [37].

After the reaction, the precipitates of polyoxovanadates were formed by addition of a large amount of ethyl acetate and the powder was collected by filtration. From IR and ^{51}V NMR spectra, $[H_3V_{10}O_{28}]^{3-}$ and $[V_{12}O_{32}]^{4-}$ retained their structures and $[V_{13}O_{34}]^{3-}$ was partly decomposed to decavanadates (Figures A6 and A7). Since decavanadates are less active for the oxidation of thioanisole, $[V_{13}O_{34}]^{3-}$ is contributed to the high activity.

3. Experimental Section

3.1. Chemicals and Instruments

All solvents were purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as received. *p*-Toluenesulfonic acid monohydrate (TsOH) and 40% tetra-*n*-butylammonium hydroxide aqueous solution were purchased from Wako Pure Chemical Industries and Sigma-Aldrich (Tokyo, Japan) and used after the dilution to 0.1 M solution with acetone (for the transformations to $[V_{13}O_{34}]^{3-}$) or acetonitrile (for the other transformations). Thioanisole, naphthalene, methyl phenyl sulfoxide, methyl phenyl sulfone and 5.5 M *t*-butyl hydroxide in decane were obtained from Wako Pure Chemical Industries, Tokyo Chemical Industry (Tokyo, Japan) and Sigma-Aldrich and used as received. $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ was synthesized according to the reported procedure [17].

IR spectra were measured on Jasco FT/IR-4200 (Hachioji, Japan) using KBr disks. NMR spectra were recorded with JEOL JNM-LA400 (Akishima, Japan). ^{51}V NMR spectra were measured at 105.15 MHz at 25 °C unless otherwise noted. The chemical shift reference standard for ^{51}V NMR spectroscopy is $VOCl_3$. Elemental analyses of C, H and N were performed by the Research Institute for Instrumental Analysis at Kanazawa University (Kanazawa, Japan). GC analyses were performed on Shimadzu GC-2014 (Kyoto, Japan) with a flame ionization detector (FID) equipped with a NEUTRABOND-1 capillary column (internal diameter = 0.25 mm, length = 30 m).

3.2. Transformation of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ to $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$

$\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ (100 mg, 0.06 mmol) was dissolved in acetonitrile (3 mL), followed by addition of 0.1 M $\{(n\text{-}C_4H_9)_4N\}OH$ (0.2 mL, 0.02 mmol) and refluxed for 1 h. After cooling, the solution was added to diethyl ether (40 mL) and stirred for 10 min. Then, the precipitates formed were collected and dried to afford 98 mg of $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ (92% yield based on vanadium atoms). ^{51}V NMR of the reaction solution: δ −590, −597, −605 ppm. Anal. Calcd. for $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$: C,36.72; H, 6.93; N, 2.68; found: C, 35.33; H, 6.62; N, 2.67. IR (KBr pellet; 1500–400 cm^{-1}): 1483, 1379, 994, 860, 792, 761, 711, 649, 609, 549, 519 cm^{-1}.

3.3. Transformation of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ to $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$

$\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ (100 mg, 0.06 mmol) was dissolved in nitroethane (3 mL), followed by addition of 0.1 M TsOH (0.4 mL, 0.04 mmol) and stirred for 3 h at 80 °C. After cooling, the solution was added to diethyl ether (40 mL) and stirred for 10 min. Then, the precipitates formed were collected and dried to afford 81 mg of $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ (91% yield based on vanadium atom). ^{51}V NMR of the reaction solution: δ −331, −451, −496, −500 ppm. Anal. Calcd. for $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$: C, 29.82; H, 5.63; N, 2.17; found: C, 29.64; H, 5.59; N, 2.34. IR (KBr pellet; 1500–400 cm^{-1}): 1482, 1379, 1001, 991, 859, 816, 786, 605, 523, 457 cm^{-1}.

3.4. Transformation of $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ to $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$

$\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ (106 mg, 0.05 mmol) was dissolved in a mixed solvent of acetonitrile and water (4 mL, 3:1, *v*/*v*), followed by addition of 0.1 M TsOH (0.2 mL, 0.02 mmol) and stirred for 10 h at 60 °C. After cooling, the solution was added to the mixed solution of diethyl ether and tetrahydrofuran (45 mL, 8:1, *v*/*v*) and stirred for 10 min. Then, the precipitates formed were collected and dried to afford 84 mg of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ (83% yield based on vanadium atom). ^{51}V NMR of the reaction solution: δ −397, −431, −506, −524 ppm. IR (KBr pellet; 1500–400 cm^{-1}): 1482, 1379, 987, 972, 876, 843, 808, 771, 721, 609, 550, 506, 461 cm^{-1}.

3.5. Transformation of $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ to $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$

$\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ (19 mg, 0.01 mmol) was dissolved in a mixed solvent of acetonitrile and water (3 mL, 2:1, *v*/*v*), followed by addition of 0.1 M $\{(n\text{-}C_4H_9)_4N\}OH$ (0.09 mL, 0.009 mmol) and stirred for 1 h at 60 °C. After cooling, the solution was added to the mixed solution of diethyl ether and tetrahydrofuran (45 mL, 8:1, *v*/*v*) and stirred for 10 min. Then, the precipitates formed were collected and dried to afford 19 mg of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ (86% yield based on vanadium atom). ^{51}V NMR of the reaction solution: δ −397, −430, −506, −525 ppm. IR (KBr pellet; 1500–400 cm^{-1}): 1482, 1379, 987, 973, 875, 843, 809, 770, 719, 609, 550, 507, 461 cm^{-1}.

3.6. Transformation of $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ to $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$

$\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ (39 mg, 0.02 mmol) was dissolved in acetonitrile (3 mL), followed by addition of 0.1 M $\{(n\text{-}C_4H_9)_4N\}OH$ (0.26 mL, 0.026 mmol) and refluxed for 1 h. After cooling, the solution was added to diethyl ether (40 mL) and stirred for 10 min. Then, the precipitates formed were collected and dried to afford 40 mg of $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ (86% yield based on vanadium atom). ^{51}V NMR of the reaction solution: δ −590, −597, −605 ppm. IR (KBr pellet; 1500–400 cm^{-1}): 1483, 1380, 993, 860, 789, 762, 711, 649, 605, 553, 519 cm^{-1}.

3.7. Oxidation of Thioanisole

The oxidations of thioanisole were carried out in an 18 mL glass tube reactor containing a magnetic stir bar. A procedure was as follows: Vanadium species, thioanisole, naphthalene as internal standard, acetonitrile and TBHP were successively placed into the glass tube reactor. The reaction mixture was stirred at 25 °C. The yields of the products were periodically determined by GC analysis using an internal standard technique. All products are known and confirmed by comparison of their GC retention times with the authentic samples.

4. Conclusions

The quantitative conversions among deca-, dodeca- and tridecavanadates were established by monitoring through ^{51}V NMR to determine the optimized transformation conditions. The inorganic host cage complex $[V_{12}O_{32}]^{4-}$ is converted from $[H_3V_{10}O_{28}]^{3-}$ by adjusting the amount of base. Decavanadate is self-condensed into $[V_{13}O_{34}]^{3-}$ in nitroethane by utilizing proton on the decavanadate for the dehydration condensation and the further addition of the controlled amount of acid helps to prevent the byproduct formation. The quantitative formation of $[V_{13}O_{34}]^{3-}$ was achieved with one of the most available $[H_3V_{10}O_{28}]^{3-}$ as a starting material. Transformation of $[V_{12}O_{32}]^{4-}$ or $[V_{13}O_{34}]^{3-}$ to decavanadates proceeded by the hydrolysis reaction. While the direct transformation of $[V_{13}O_{34}]^{3-}$ to $[V_{12}O_{32}]^{4-}$ proceeded by addition of base, conversion of $[V_{12}O_{32}]^{4-}$ to $[V_{13}O_{34}]^{3-}$ could not be observed during our investigation. These transformation reactions proceeded according to the equations and provide the reliable synthetic pathway for the synthesis of $[V_{13}O_{34}]^{3-}$. The studies shows that a careful control of the amount of acid or base in appropriate solvents is able to achieve the transformation among those isopolyoxovanadates, which is fundamentally important species in polyoxovanadate chemistry.

We also demonstrated that $[V_{13}O_{34}]^{3-}$ shows the highest activity for the oxidation of thioanisole among these polyoxovanadates.

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Author Contributions

This work was conceived by Y. Hayashi and Y. Kikukawa. The rational structural transformation experiments and oxidation of sulfide were undertaken by K. Ogihara and Y. Kikukawa, respectively. The manuscript was written with contributions from all authors. Y. Kikukawa and K. Ogihara contributed equally.

Conflicts of Interest

The authors declare no conflict of interest.

Appendix

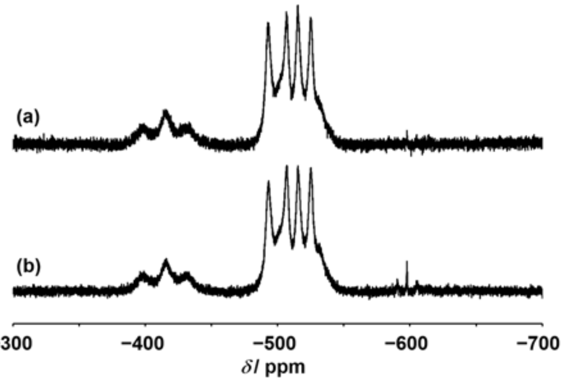

Figure A1. ^{51}V NMR spectra of the forward reaction solution in Equation (1) for the conversion of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ to $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ in acetonitrile at room temperature after (**a**) 12 h; (**b**) 24 h.

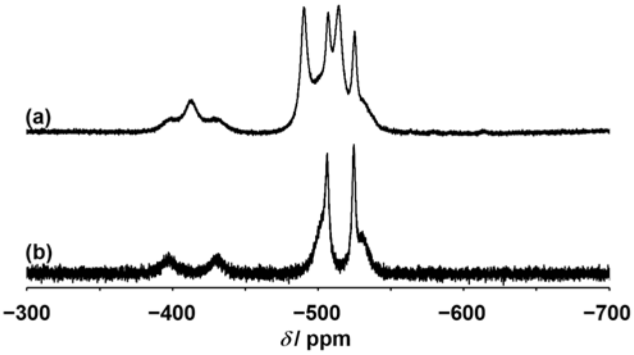

Figure A2. ^{51}V NMR spectra of the reverse reaction solution in Equation (1) for the conversion of $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$ to $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ in a mixed solvent of acetonitrile and water (3:1, *v*/*v*) (**a**) without TsOH; (**b**) with 0.4 equivalents of TsOH.

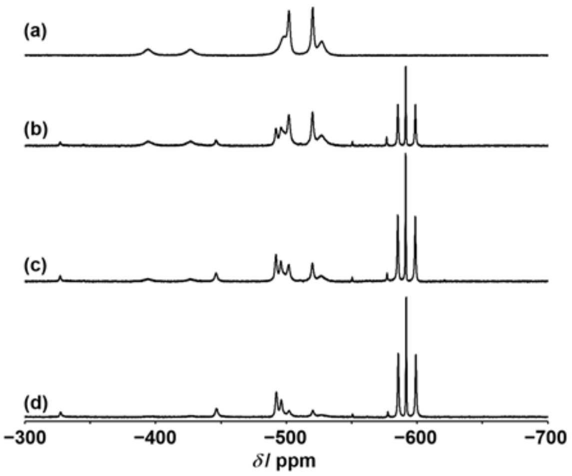

Figure A3. ^{51}V NMR spectra of the forward reaction solution in Equation (2) for the conversion of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ to $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ in acetonitrile at 80 °C under dry nitrogen atmosphere after (**a**) 0 h; (**b**) 1 h; (**c**) 3 h; (**d**) 7 h.

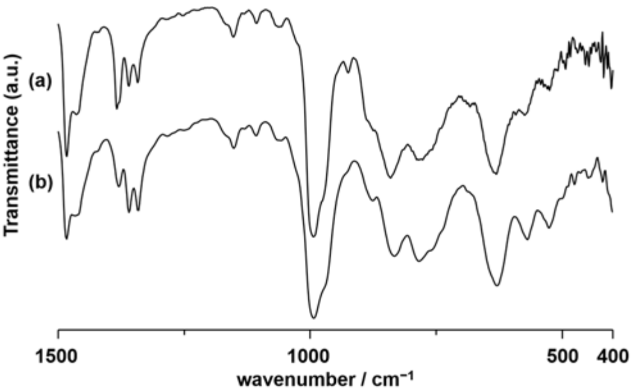

Figure A4. (**a**) IR spectrum of the pale-green precipitated samples after the separation of $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$. The powder was obtained from the forward reaction solution in Equation (2) for the conversion of $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$ to $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ without addition of acid in nitroethane at 80 °C. (**b**) IR spectrum of the authentic samples of $\{(n\text{-}C_4H_9)_4N\}_5[V_{18}O_{46}(NO_3)]$ [32].

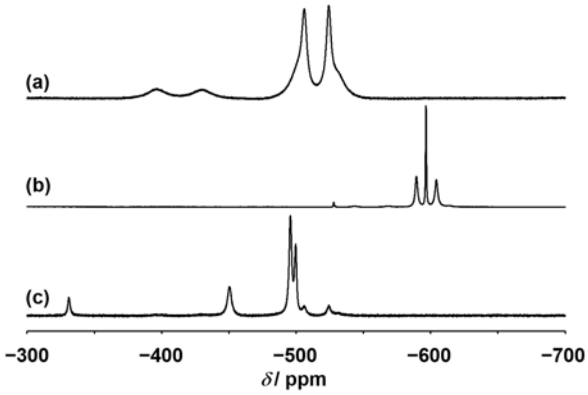

Figure A5. ^{51}V NMR spectra of (**a**) $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$; (**b**) $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$; (**c**) $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$ in the presence of 20 equivalents of TBHP. No spectral change was observed after 23 h.

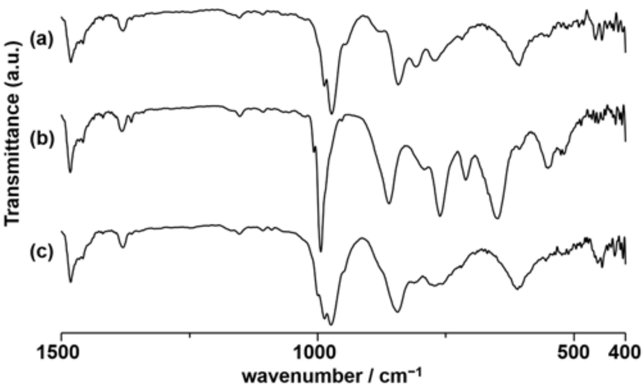

Figure A6. IR spectra of the samples obtained after the oxidation reaction with (**a**) $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$; (**b**) $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$; (**c**) $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$.

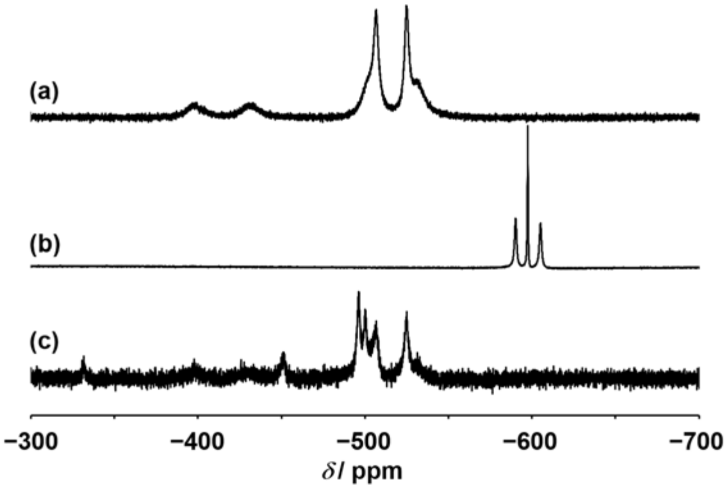

Figure A7. ^{51}V NMR spectra of the samples obtained after the oxidation reaction with (**a**) $\{(n\text{-}C_4H_9)_4N\}_3[H_3V_{10}O_{28}]$; (**b**) $\{(n\text{-}C_4H_9)_4N\}_4[V_{12}O_{32}]$; (**c**) $\{(n\text{-}C_4H_9)_4N\}_3[V_{13}O_{34}]$. Samples were dissolved in acetonitrile.

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