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Synthesis of a phosphomolybdate with a tetranuclear vanadium core by installing vanadium atoms in a lacunary template using protecting group strategy

Chifeng Li, Kazuya Yamaguchi* and Kosuke Suzuki*

Vanadium-containing phosphomolybdates have outstanding catalytic and electrochemical properties. However, their traditional one-pot synthesis in aqueous media generates a mixture of randomly distributed isomers and undesirable impurities, has hampered the in-depth study of the catalysis and reaction mechanism of these compounds. Here, the selective synthesis of a tetranuclear vanadium-containing phosphomolybdate $[PV_3Mo_9O_{40}(VO)]^{3-}$ was achieved for the first time by using a pyridine-protected $[A-\alpha-PMo_9O_{31}(py)_3]^{3-}$ (py = pyridine) as a template.

Polyoxometalates (POMs) are a class of anionic metal oxide clusters with diverse structures and unique properties originating from their structures. Thus, their properties, such as redox potentials and acidities, can be tuned at the atomic level by selecting their structures, composition, and oxidation states. Therefore, these materials can be used in several applications and fields, including catalysis, analytical chemistry, medicine, and optical materials.[1,2] Among POMs, the Keggin-type vanadium-containing "mixed-addenda" phosphomolybdates $[PV_nMo_{12-n}O_{40}]^{(3+n)-}$ have demonstrated outstanding catalytic and electrochemical properties.[3] Typically, their catalytic activities in oxidation reactions are superior to those of the vanadium-containing tungsten-based analogs because of their higher redox potentials.[4] Mixed-addenda vanadium-containing phosphomolybdates are typically synthesized via a one-pot method using precursors, such as Na_2HPO_4, Na_2MoO_4, and $NaVO_3$, in aqueous media.[5] However, this traditional method generates a mixture of randomly distributed vanadium atoms in the skeleton of POMs as well as undesirable impurities, which hinders in-depth studies of the catalytic process and reaction mechanism (Fig. 1a). Conventionally, a controlled synthesis of multinuclear transition metal-containing "polyoxotungstates" using multivacant lacunary polyoxotungstates as templates (or inorganic ligands) has been developed.[6,7] However, this strategy

is largely limited to "polyoxotungstates", and the precise synthesis of multinuclear transition metal-containing "polyoxomolybdates" is still quite difficult because of the low stability of the multivacant lacunary polyoxomolybdates in both aqueous and organic media (Fig. 1b).[8]

Recently, our group has developed a method to significantly stabilize the metastable Keggin-type trivacant lacunary phosphomolybdate $[A-\alpha-PMo_9O_{34}]^{9-}$ by simply coordinating the pyridine molecules at the vacant sites. In addition, $[A-\alpha-PMo_9O_{34}]^{9-}$ can be isolated as a tetra-n-butylammonium (TBA) salt of $[A-\alpha-PMo_9O_{31}(py)_3]^{3-}$
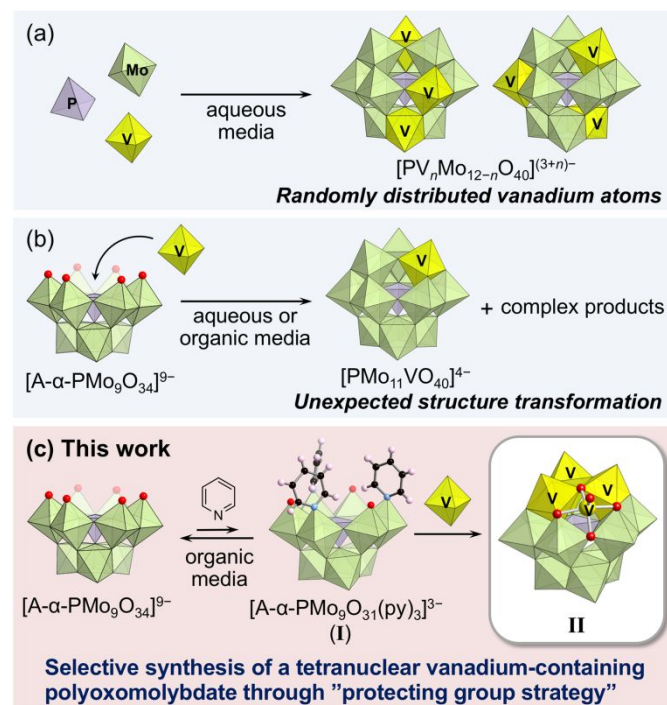

Fig. 1 Schematic diagram of the vanadium-containing polyoxomolybdate synthesis: (a) conventional one-pot synthesis of phospho-vanadomolybdates; (b) reaction between trivacant lacunary polyoxomolybdate and vanadium cations; and (c) this work: selective synthesis of a tetranuclear vanadium-containing polyoxomolybdate by the "protecting group strategy" using a pyridine-protected trivacant lacunary polyoxomolybdate

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† Electronic Supplementary Information (ESI) available: Experimental details, Tables S1–S7, and Fig. S1–S5. See DOI: 10.1039/x0xx00000x

(denoted "compound I", py = pyridine).[9] The moderately labile pyridine–molybdenum bonds in compound I enabled the selective synthesis of phosphomolybdates with different types of multinuclear manganese clusters using the "protecting group strategy".[10] In addition, a novel type of lacunary phosphomolybdate $[\gamma\text{-}PMo_{10}O_{36}]^{7-}$ was developed via the ligand-directed approach[11] using compound I as a precursor. Here, a new vanadium-containing phosphomolybdate was synthesized through a controlled installation of vanadium cations on the pyridine-protected lacunary precursor (compound I) as a template. In the process, compound I reacted with vanadyl acetylacetonate $(VO(acac)_2)$ in an organic medium to successfully synthesize a TBA salt of a tetranuclear vanadium-containing phosphomolybdate $[PV_3Mo_9O_{40}(VO)]^{3-}$ (compound II). The results indicated that compound II has a trinuclear vanadium core within the vacant site and one capping square-pyramidal vanadyl cation on the surface of the POM skeleton (Fig. 1c).

The cold-spray ionization (CSI) mass, ^{31}P nuclear magnetic resonance (NMR), and [51]V NMR spectroscopy analyses revealed that a commercially available Keggin-type vanadium-containing phosphomolybdate $H_6[PV_3Mo_9O_{40}]$ is composed of a complex mixture of products, with vanadium atoms distributed randomly at various positions (Figs. 2a, S1a, and S1b) because it is synthesized by simply mixing the starting compounds in an aqueous medium;[12] For example, the CSI-mass spectrum showed a series of peaks corresponding to $[H_{4+n}PV_nMo_{12-n}O_{40}(CH_3CN)_1]^+$ (n = 1, m/z = 1823; n = 2, m/z = 1779; n = 3, m/z = 1735; n = 4, m/z = 1691; n = 5, m/z = 1648; n = 6, m/z = 1604). The authors recently discovered that the installation of metal cations at multivacant lacunary "polyoxotungstates" in organic media is an effective approach to develop multinuclear metal-oxo (or metal) clusters while avoiding undesirable isomerization, structure transformation, and decomposition of the original polyoxotungstate frameworks and/or dissociation of the installed metal cations that occurs frequently in aqueous media.[7] Thus, the authors initially attempted to install vanadium at the vacant site of the Keggin-type trivacant lacunary phosphomolybdate $TBA_3H_6[PMo_9O_{34}]$ in acetonitrile using $VO(acac)_2$. However, the trivacant lacunary phosphomolybdate has low stability even in organic solvents; hence, the findings with polyoxotungstates were not directly applicable. The CSI-mass spectrometry of the reaction solution revealed that several undesirable by-products, including the fully occupied structure $[PMo_{12}O_{40}]^{3-}$ (m/z = 2792), the mononuclear vanadium-containing structure $[PMo_{11}VO_{39}]^{4-}$ (m/z = 2748), and other unidentified species (m/z = 2726 and 2678) were formed (Fig. 2b). The ^{31}P and [51]V NMR spectra of the reaction solution indicated a complex mixture of different vanadium species (Fig. S1c and S1d). Therefore, our recently developed "protecting group strategy" was used for the controlled installation of vanadium to multivacant lacunary phosphomolybdates, which were used as templates.

A green precipitate was obtained (yield = ca. 60%) from the reaction of pyridine-protected lacunary phosphomolybdate I
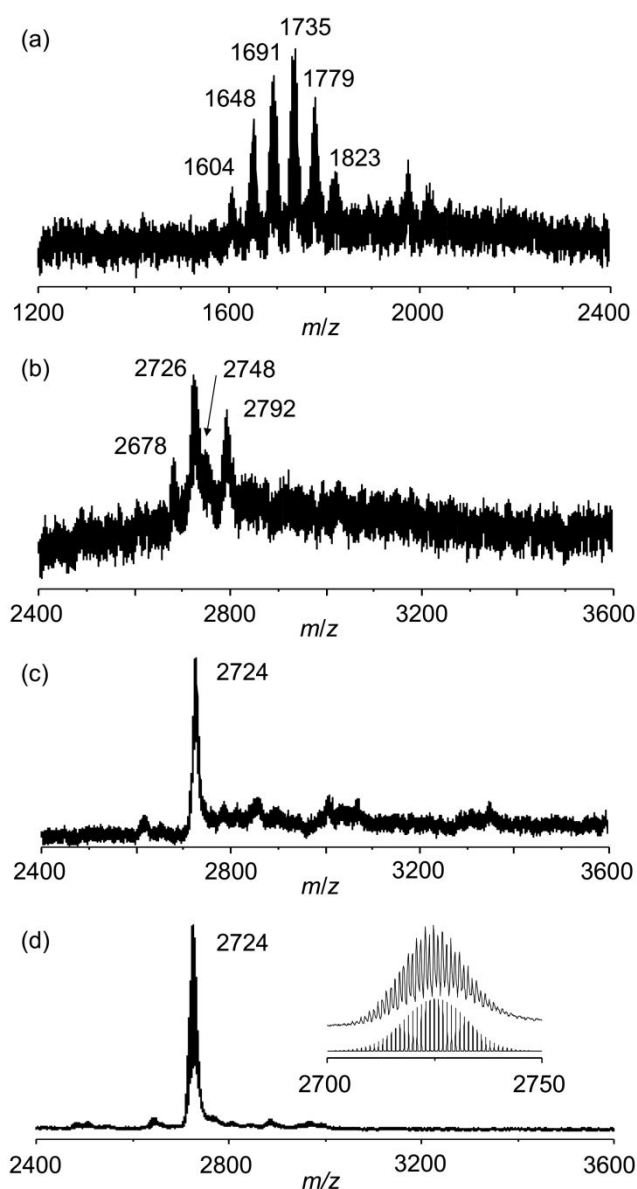

Fig. 2 Positive-ion CSI-mass spectra of (a) a commercially available Keggin-type vanadium-containing "mixed-addenda" phosphomolybdate $H_6[PV_3Mo_9O_{40}]$ in acetonitrile; (b) the reaction solution of $TBA_3H_6[PMo_9O_{34}]$ and $VO(acac)_2$ in a mixture of acetonitrile-d_3 and water (100/1, v/v) after stirring at room temperature for 1 h, followed by the addition of HNO_3 (70%) and stirring at room temperature for 10 min; (c) the reaction solution of compound I and $VO(acac)_2$ in a mixture of acetonitrile-d_3 and water (100/1, v/v) after stirring at room temperature for 1 h, followed by the addition of HNO_3 (70%) and stirring at room temperature for 10 min; and (d) compound II in acetonitrile. Inset: a spectrum within an m/z range of 2700–2750 and the simulated patterns for $[TBA_4PV^{5+}{}_4Mo_9O_{41}]^+$ (m/z = 2724)

with $VO(acac)_2$ in a mixture of acetone and water (100/1, v/v) at room temperature (~25 °C). The CSI-mass spectrum of the product in acetonitrile exhibited a main set of peaks at m/z = 2967 that can be assigned to $[TBA_5PV^{5+}{}_3V^{4+}Mo_9O_{41}]^+$ (theoretical m/z = 2967, Fig. S2), showing that four vanadium atoms were incorporated in the lacunary {PMo_9} unit. In addition, this spectrum suggested that three of the four vanadium atoms were V^{5+} and the last one was V^{4+}. Further
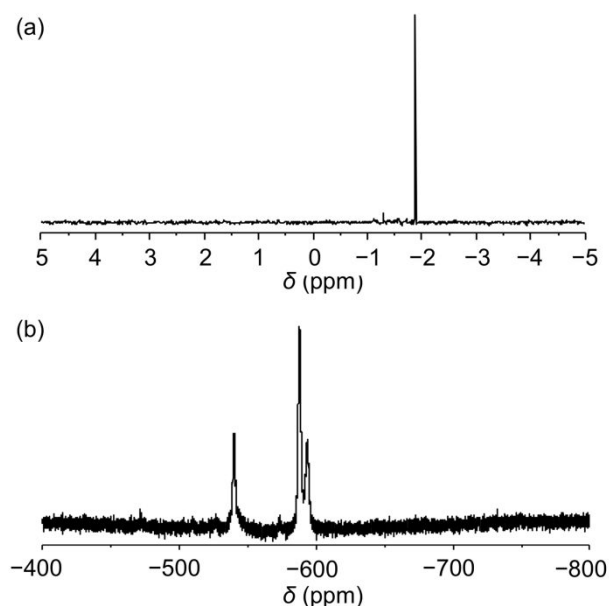
Fig. 3 (a) ^{31}P NMR and (b) ^{51}V NMR spectra of compound **II** in acetonitrile-d_3

Fig. 4 (a) Crystal structure of the anion part of compound **II**, in which the skeleton vanadium atoms **(V2**, **V3**, and **V4)** are located at the position adjacent to the vanadyl cation (**V1**). (b) The second possible arrangement (structure **II'**), in which the skeleton vanadium atoms (**V2**, **V3**, and **V4**) are located at the position opposite the vanadyl cation (**V1**). The yellow and red spheres represent V and O atoms, respectively. The light green, yellow, and light purple polyhedra represent [MoO_6], [VO_6], and [PO_4], respectively. The energy values for two possible structures are shown based on that of structure **II**.

reaction of the green precipitate with nitric acid (70%, as an oxidizing agent) in acetonitrile caused a change in the color of the solution from green to orange-yellow. Then, an orange-yellowish powder (compound **II**) was obtained by adding an excess of diethyl ether to the solution (yield = ca. 80%). The CSI-mass spectrum of both the reaction solution (in acetonitrile-d_3/water (100/1, v/v), Fig. 2c) and the powder obtained (compound **II**) in acetonitrile (Fig. 2d) exhibited a main set of peaks centered at m/z = 2724, which corresponds to [$TBA_4PV^{5+}_4Mo_9O_{41}$]$^+$ (theoretical m/z = 2724, Figs. 2c, 2d), indicating that the V^{4+} species was oxidized to V^{5+} during the nitric acid treatment. Notably, the CSI-mass spectrum of the reaction solution of lacunary phosphomolybdate with VO(acac)$_2$ using compound **I** as the template (Fig. 2c) exhibited much purer signals than the spectrum of the reaction solution using TBA$_3$H$_6$[PMo$_9$O$_{34}$] under the same reaction conditions (Fig. 2b), indicating that the side reactions were largely prohibited using the pyridine-protected compound **I**. This reveals the importance of using the "protecting group strategy." The elemental analysis of compound **II** indicated that the P/Mo/V ratio was 1/9/4.[13] The ^{31}P NMR spectrum of compound **II** showed a single peak at −3.75 ppm (Fig. 3a). These results indicate that compound **II** is a "single species," in which four vanadium atoms are installed in a template (compound **I**) at specific positions, that is, isomers with different substitution positions are not mixed together.

Single crystals of compound **II** suitable for X-ray crystallographic analysis were obtained by vapor diffusion of ethyl acetate into a dichloromethane solution of compound **II**. The anion structure of compound **II** was found to be a monomeric Keggin-type structure, in which a disordered 5-coordinated vanadyl cation ([VO]$^{3+}$, **V1**) was observed clearly on the surface of the skeleton structure (Fig. 4a, S3b, Table S1, on the top and bottom surface of the skeleton with the optimized occupancy of 70% and 30%). X-ray analysis could
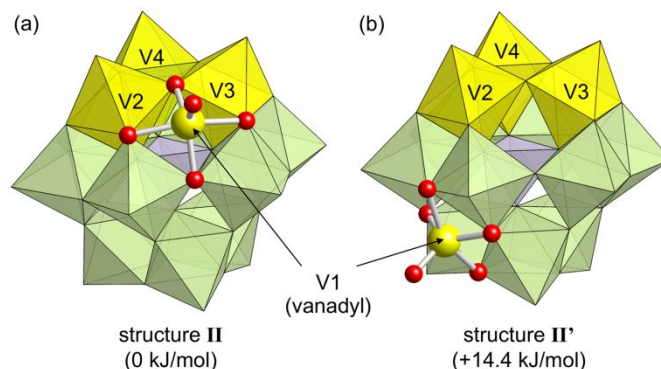
not distinguish the vanadium and molybdenum atoms in the skeleton structure. However, the positions of the vanadium atoms in the skeleton structure could be determined based on the experimental results (i–iii). (i) The ^{31}P NMR spectrum, CSI-mass spectrum, and elemental analysis revealed that compound **II** is the single species in which the four vanadium atoms are installed in the {PMo$_9$} structure. (ii) The ^{51}V NMR spectrum of compound **II** showed three peaks at −539.8, −587.8, and −593.3 ppm, with a respective intensity ratio of 1:2:1 (Fig. 3b). The peak observed at −539.8 ppm can be assigned to a capping vanadyl cation ([VO]$^{3+}$, **V1**).[14b] Therefore, the other three skeleton vanadium atoms (**V2**, **V3**, and **V4**) can be assigned as 6-coordinated vanadium atoms installed at the three vacant sites of the A-α-Keggin trivacant lacunary phosphomolybdate template.[14] In addition, the capping vanadyl cation (**V1**) caused the splitting of the ^{51}V NMR signals of the three skeleton vanadium atoms (**V2**, **V3**, and **V4**) into two sets of peaks at an intensity ratio of 2:1. However, there are still two possible arrangements of the three skeleton vanadium atoms (**V2**, **V3**, and **V4**), that is, they could be located in positions adjacent to or opposite the **V1** atom (structures **II** or **II'**; Figs. 4a or 4b). (iii) The density functional theory calculations of the two possible anionic structures revealed that structure **II** was significantly stable compared to structure **II'** (energy difference = 14.4 kJ/mol), suggesting the preferable formation of structure **II** (for details, refer to ESI). Therefore, the four vanadium atoms are probably installed in adjacent positions, with the **V1** atom as a vanadyl cation capping at the surface of the skeleton and the **V2**, **V3**, and **V4** atoms in the vacant sites of the A-α-Keggin trivacant lacunary phosphomolybdate template (Fig. 4a). Due to the disorder of the capping vanadyl cation (**V1**), **V2**, **V3**, and **V4** atoms are also disordered (Fig. S3b, see ESI experimental sections for detail). *Structure **II** is the first multinuclear vanadium-containing phosphomolybdate in which the vanadium atoms are introduced at the specific positions designed at the vacant sites.*[13]

Conflicts of interest

There are no conflicts to declare.

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