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Making one V^{IV} substitution for Mo on classical [Mo₂^VO₄]²⁺ group: the first heterobimetallic Mo–V subunit in polyoxomolybdate–bisphosphonate family†

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The development of a library of basic building units with distinct compositional and structural characteristics for the preparation of polyoxometalates remains a challenging and attractive endeavor. Herein, the first molybdovanadate cluster (**1**) modified by bisphosphonate (BP) ligands in a new [Mo^VV^{IV}O₄] building unit is successfully synthesized based on one V substituting for one Mo in the classical [Mo₂^VO₄] building unit. To compare the catalytic oxidation activity of the V-doped molybdovanadate cluster to that of other molybdovanadate clusters without V=O in an organic model reaction, a molybdovanadate cluster (**2**) free of V=O was prepared and using the atomically precise **1** and **2** as catalysts confirms the significance of the V-replaced model containing V=O. This work provides an insight into the assembly and catalytic activity site design of Mo–V clusters and enriches the basic building units of the polyoxomolybdate (POMos)–BP family.

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Introduction

Polyoxometalates (POMs) are a large exceptional class of oxygen cluster compounds mainly consisting of early transition metals of group V and VI (Mo, W, V, Nb, Ta, etc.) in their high oxidation states, which have a diverse structural and compositional range as well as a great variety of catalytic,^{1–5} electrochemical,^{6–8} medical,^{9–12} fluorescent^{13–15} and magnetic properties^{16–18} on the molecular level. Grafting organic moieties onto POMs by covalent bonds can unite the advantages of the inorganic metal oxide cluster and the organic components with rich functionalities to enrich the structure of POMs and enhance compatibility with other organic substrates or media.^{19–21} Recently, POMs incorporating BP have been an important subclass of POMs and possesses potential application prospects for the prominent work of many chemists.²² However, we find that the types of topological structures are

very limited and often only change the ligands in POMos–BP complexes, possibly due to the main precursor of most POMos–BP complexes being the dication [Mo₂^VO₄]²⁺²³ and the majority of the basic building units being the following: [Mo₂^VO₄],²⁴ [Mo₂^{VI}O₆],²⁵ [Mo₃^{VI}O₈] (Scheme 1a–l).²⁶ (Here, a basic building unit is well-defined as part of the integral structure rather than an isolated cluster.) These restricted basic building units hinder the generation of novel compounds within the POMos–BP family and significantly hamper the structural and preparative chemistry of the POMos–BP family, ultimately influencing the performance through structure–function relationships. It is a huge challenge to further boost the development of POMos–BP systems with desired structures.

To resolve the above-mentioned challenge, it is thus vastly essential to elaborate a library of basic building units with distinct compositional and structural characteristics. Inspired by previous reports about molybdenum/vanadium (Mo/V) or Mo–V mixed clusters for the similar coordination geometry, ionic radius and valence state between Mo and V,^{27–30} we deem it feasible and valuable to explore more new building units based on one V in place of one Mo in [Mo₂^VO₄] units in the family of POMos–BPs (Scheme 1). Meanwhile, the substitution pattern of V retaining the V=O with redox-active sites may have much better catalytic oxidation activity than the simple chelating coordination doping of V into Mo clusters like other transition metals.

The main objective of the present work is to investigate whether it is feasible to construct the hetero-metallic binuclear

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Scheme 1 The design concept of achieving a new heterobimetallic building unit in this work and previous works: (a–f) the classical wheel shaped clusters based on basic building unit $[\text{Mo}_2\text{O}_4]^{2+}$, (g) the transition metal element M doped $\text{Mo}_4(\text{BP})_2\text{M}$ ($\text{M} = \text{V}^{\text{IV}}$, Cr^{III} , Fe^{III} , Mn^{II}) based on $[\text{Mo}_2^{\text{VI}}\text{O}_6]$, (h–l) the various structures of POMos–BP members based on $[\text{Mo}_2^{\text{VI}}\text{O}_8]$ and our work.

building unit $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_4]$ in a POMos–BP system. Additionally, this work aims to confirm the significance of the V-replacing mode with $\text{V}=\text{O}$ by contrasting its catalytic oxidation activity with that of other V-doping without $\text{V}=\text{O}$ through an organic model reaction. Fortunately, by examining various reaction conditions, we were able to isolate novel Mo–V–BP clusters with an unusual building unit $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$ retaining $\text{V}=\text{O}$ (compound **1**), as well as a fresh illustration of straightforward V coordination doping free of $\text{V}=\text{O}$ (compound **2**) for comparison.

Even though the classical dication building block $[\text{Mo}_2^{\text{VI}}\text{O}_4]^{2+}$ is recurrent for the design of various Mo–oxygen clusters³⁰ and the incorporation of transition metal elements M into $\text{Mo}_4(\text{BP})_2\text{M}$ ($\text{M} = \text{V}^{\text{IV}}$, Cr^{III} , Fe^{III} , Mn^{II}) has previously been reported,^{31–36} herein the unprecedented heterometallic binuclear building unit $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$ was first obtained in the POMs–BP family (Scheme 1). Notably, the desired compound **1** containing the fundamental heterobimetallic building unit $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$ obtained by substituting one Mo in the traditional $[\text{Mo}_2^{\text{VI}}\text{O}_4]^{2+}$ dimer was characterized by single-crystal X-ray diffraction (SXRD), powder X-ray diffraction (PXRD), FT-IR, XPS, and TGA. Furthermore, as a proof-of-concept, the catalytic oxidation activities of **1** and **2** for the oxidation of dibenzothiophene (DBT) using H_2O_2 as an oxidant were examined. By using the molecular models **1** and **2** as atomically precise building blocks, this study enriches the POMos–BP family's basic building blocks and opens new possibilities for the design of catalytic activity sites for Mo–V clusters.

Results and discussion

The treatment of $[\text{Mo}_2^{\text{VI}}\text{O}_4(\text{H}_2\text{O})_4]^{2+}$ aqueous media and risedronic acid (H_5L : $\text{H}_2\text{PO}_3\text{C}(\text{OH})(\text{CH}_2-3-\text{C}_5\text{NH}_4)\text{PO}_3\text{H}_2$) with different V precursors at 60 °C for 3 h afforded two polyoxomo-

lybdoanadates, **1** $[\text{N}(\text{CH}_3\text{CH}_2)_4]_7(\text{NH}_4)_{13}\{[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})\text{H}_2\text{L}^{3-}][\text{Mo}_5\text{O}_{15}\text{H}_2\text{L}^{3-}]_2\}_3 \cdot 2\text{Cl} \cdot 24\text{H}_2\text{O}$ and **2** $(\text{NH}_4)_9\text{Na}(\text{H}_2\text{O})_2[\text{NaV}^{\text{III}}(\text{Mo}_2^{\text{VI}}\text{O}_6)_2\text{L}_2\text{Cl}(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$, by adjusting the pH with different alkaline substances and counter cations. (The synthetic details are shown in the ESI.†) The polyanions in **1** can be briefly described as a centrosymmetric cluster in which a novel heterometallic binuclear unit $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})\text{H}_2\text{L}^{3-}]$ is united to two pentamolybdate cluster-based building units $[\text{Mo}_5\text{O}_{15}\text{H}_2\text{L}^{3-}]^{3-}$ on a mirror plane (Fig. 1a). The dimer of $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$ can be viewed as a substitution of one V on $[\text{Mo}_2^{\text{VI}}\text{O}_4]^{2+}$ for one Mo. Bond valence sums (BVS) of **1** confirm that the oxidation states of V and Mo in the dinuclear unit are +4 and +5, which is consistent with the results of XPS (Fig. S4–S6†). It is important to emphasize that BVS supports the assignment of two $\mu_2\text{-O}$ between Mo and V of $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$ as OH, demonstrating that the two $\mu_2\text{-O}$ have relatively stronger basicity than the other oxygen atoms. This, in turn, leads to a new trivalent $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$ dimer unit. The V^{IV} ion bearing one terminal $\text{V}=\text{O}$ bond adopts a square-pyramidal geometry with two V–O bonds from two phosphonato groups of one BP ligand and two V–O bonds from $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$. The Mo^{V} with $\text{Mo}=\text{O}$ of $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$ ion is coordinated by four $\mu_2\text{-O}$ atoms and one H_2O molecule to furnish a distorted octahedral geometry. Remarkably, the protonation of two doubly bridging oxygen atoms prolonged the associated Mo–O distances (0.208 nm) and induced conspicuous *trans* influences, resulting in the formation of two shorter $\mu_2\text{-O}$ doubly bridging Mo–O(Mo) (0.177 nm) distances, which is exceedingly unusual for *trans* influence in POMos chemistry. Meanwhile, the shorter $\text{Mo}=\text{O}$ (0.172 nm) double bonds *trans* to a long Mo–OH₂ (0.235 nm) bond are also attributed to *trans* influences. The successful replacement of Mo with V indicates that $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_4]^+$ is a possible basic building block (in some ways similar to the second building units of metal–organic

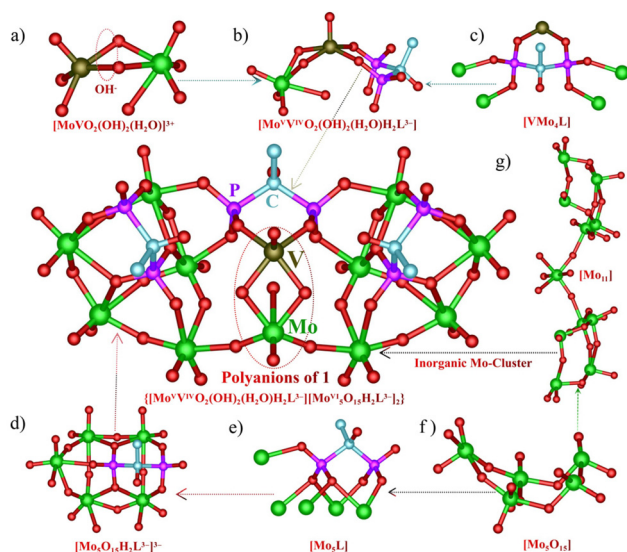


Fig. 1 Schematic illustration of the structures of the polyanions in **1** and its subunits (the pyridine ring of **L** was deleted for clarity): (a) $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$, (b) $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})\text{H}_2\text{L}^{3-}]$, (c) $[\text{VMo}_4\text{L}]$, (d) $[\text{Mo}_5\text{O}_{15}\text{H}_2\text{L}^{3-}]^{3-}$, (e) $[\text{Mo}_5\text{L}]$, (f) $[\text{Mo}_5\text{O}_{15}]$, (g) $[\text{Mo}_{11}]$.

frameworks) for the synthesis of novel Mo–V mixed clusters functionalized by BP or other organic groups. The anion cluster skeleton can also be viewed as two $[\text{Mo}_5\text{O}_{15}\text{H}_2\text{L}^{3-}]^{3-}$ building units systematically linked to a binuclear unit $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})\text{H}_2\text{L}^{3-}]$. The $[\text{Mo}_5\text{O}_{15}\text{H}_2\text{L}^{3-}]^{3-}$ subunit is composed of five Mo octahedra in a corner- and edge-sharing arrangement and forms a hollow shell occupied by the H_2L^{3-} ligand (Fig. 1d and g). As far as we know, these fascinatingly structured subunit $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_2(\text{OH})_2(\text{H}_2\text{O})]^{3+}$ dimer and pentamolybdate cluster basic building block $[\text{Mo}_5\text{O}_{15}]$ are both first reported here. In POMs chemistry, the pure inorganic hendeca-nuclear Mo-clusters with one Mo atom bridging two $[\text{Mo}_5\text{O}_{15}]$ are novel. The two types of H_2L^{3-} ligands exhibit distinct penta-coordination modes, as shown in Fig. 1e and f, in

which two phosphonato groups from another H_2L^{3-} ligand adopt the 2.110 mode and 5.221 bridging mode (Harris notation).³⁷ To compare the catalytic activity of the Mo–V–BP clusters with distinct V doping modes, the chelating-coordinating compound **2** devoid of $\text{V}=\text{O}$ double bonds was synthesized by varying the reaction conditions. As depicted in Fig. 2, the cluster anion **2** can be described as two units of $[(\text{Mo}_2^{\text{VI}}\text{O}_6)\text{C}_6\text{H}_5\text{NCH}_3\text{C}(\text{O})(\text{PO}_3)_2]^{4-}$ linked by one V^{III} cation and exhibits isostructural characteristics with two previous POMs–BP derivatives based on different BPs.³⁸ The V–O bond lengths in this anion range from 0.194 to 0.204 nm, meaning that vanadyl ($\text{V}=\text{O}$) is not present.³⁹ The $[\text{Mo}_2^{\text{VI}}\text{O}_6]$ structural unit is composed of two Mo octahedra in a face-sharing mode which are stabilized by two phosphonato groups and the hydroxyl of HL^{4-} ligands *via* P–O–Mo and C–O–Mo covalent bonding. The PO_3 group adopts the 3.120 coordination mode and the OH group bound to the C atom is found to be deprotonated, which was probably from the higher pH value of the solution.

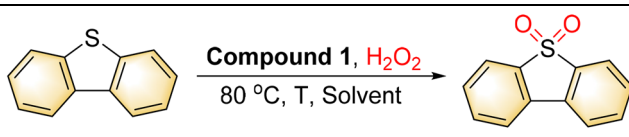
As in previous reports, the Mo/V mixed-addendum Keggin-type POMs $[\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}]$ show better catalytic activities than pure $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, which indicates that the V atom may play a key function during the catalytic reaction process.⁴⁰ The catalytic reaction route may also include the prevalent oxygen atom transfer (OAT) *via* the Mars–Van Krevelen mechanism.^{41–44} Hence, the remaining $\text{V}=\text{O}$ double bonds in Mo–V catalysts may have more activity than those in other Mo–V clusters. In view of this, the atomically precise Mo–V clusters **1** and **2** are chosen as model catalysts to check the catalytic activity by the oxidation of dibenzothiophene (DBT) with H_2O_2 as an oxidant. The target product was obtained by column chromatography and analyzed by ^1H NMR.

The effects of time and solvent on the product catalyzed by **1** were investigated using dibenzothiophene as a substrate. Table 1 provides an overview of the selected examples. The optimal conditions are 0.2 mmol of substrate, 0.001 mmol of catalyst, 0.8 mmol H_2O_2 (30% aqueous), 80 °C, 12 h, and 2 mL CH_3CN . The catalytic properties of compound **1** were assessed



Fig. 2 Schematic illustrations of the structures of (a) $[(\text{Mo}_2^{\text{VI}}\text{O}_6)\text{C}_6\text{H}_5\text{NCH}_3\text{C}(\text{O})(\text{PO}_3)_2]^{4-}$ in **2**, (b) the polyhedron of $[\text{Mo}_2^{\text{VI}}\text{O}_6]$ structural unit, and (c) the coordination mode of two phosphonato groups and hydroxyl of HL^{4-} ligand.

Table 1 Effect of reaction conditions for the oxidation of DBT with H_2O_2^a

				
Entry	Solvent	Time (h)	Conversion ^b (%)	Select for sulfone ^b (%)
1	CH_3CN	6	39	>99
2	CH_3CN	12	95	>99
3	CH_3CN	18	96	>99
4	H_2O	12	Trace	Trace
5	DMF	12	Trace	Trace
6	EtOH	12	57	>99
7	EA	12	68	72
8	DCM	12	27	9
9	1,4-Dioxane	12	90	63

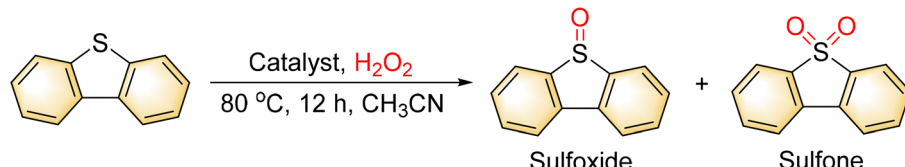
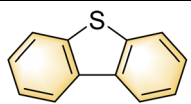
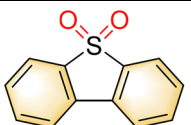
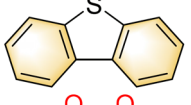
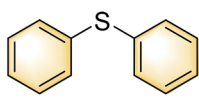
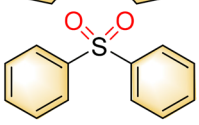
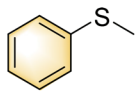
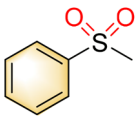
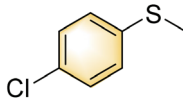
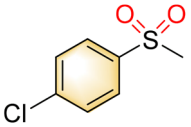
^a Reaction conditions: 0.2 mmol of dibenzothiophene, 0.001 mmol of compound **1**, 0.8 mmol H_2O_2 (30% aqueous), 80 °C, 2 mL of solvent.

^b Conversion: isolated yield.

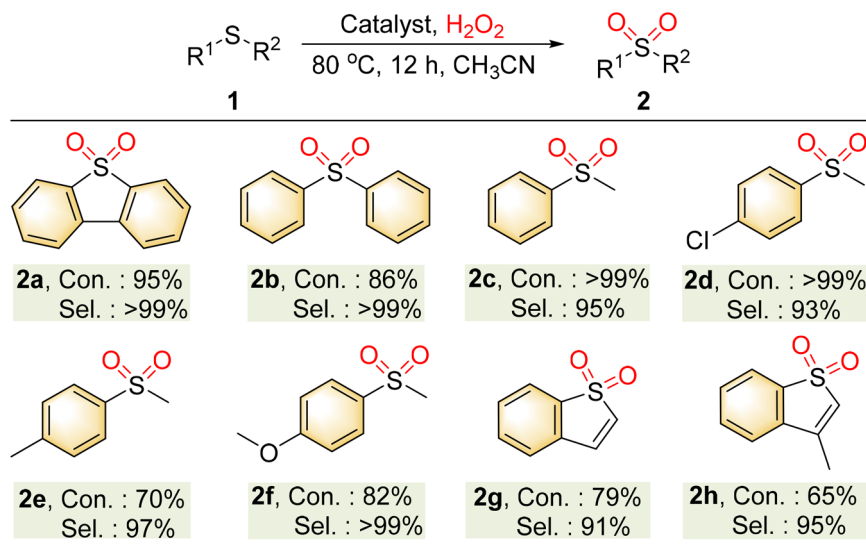
by screening compounds **1** and **2** and a blank under standard conditions (0.2 mmol thioether, thioanisole, and 4-chloro-thioanisole), as shown in Table 1. In entry 1 of Table 2, the blank reaction and compound **2** were performed on dibenzothiophene, with only 22% and 35% conversions and 0% and 25% selectivities, respectively. The conversion and selectivity were low. However, compound **1** has good conversion and selectivity for sulfone, which suggests that $\text{V}=\text{O}$ played a key role in the catalytic performance of POMos-BP. When expanded to diphenyl thioether, thioanisole, and 4-chloro-thioanisole, compound **1** still exhibits good conversion and selectivity.

To verify the universality of **1** under the optimized reaction conditions for the high selectivity of sulfone, different substituent sulfides were used as substrates in the catalytic reactions. As shown in Scheme 2, all substrate expansion experiments indicated that the selectivity for sulfone was higher than 90%. The conversion rate decreases slightly as the steric hindrance of the S atom increases and the selectivity stays high with the increasing steric hindrance of the S atom.

Table 2 The oxidation of sulfides using different catalysts^a

					
Entry	Substrate	Catalyst	Product	Conversion ^b (%)	Selectivity ^b (%)
1		1		95	>99
		2		35	25
		Blank		22	Trace
2		1		86	>99
		2		63	57
		Blank		37	17
3		1		>99	95
		2		>99	61
		Blank		26	Trace
4		1		>99	87
		2		82	67
		Blank		18	Trace

^a Reaction conditions: 0.2 mmol of substrate, 0.001 mmol of catalyst, 0.8 mmol H_2O_2 (30% aqueous), 80 °C, 12 h, 2 mL CH_3CN . ^b Conversion: isolated yield.



Scheme 2 Substrate expansion for catalytic oxidation of thioether by **1**.

Conclusions

In summary, the first molybdovanadate cluster (**1**) modified by BP with the unusual $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_4]$ building unit was successfully synthesized based on the substitution of one V for one Mo in the classical $[\text{Mo}_2^{\text{V}}\text{O}_4]$ building unit. More significantly, we demonstrated that the $\text{V}=\text{O}$ in **1** plays a pivotal role in the deep oxidation of dibenzothiophene into sulfone by comparing the atomically precise **1** and **2** as molecular model catalysts. This work enriches the basic building units of the POMos-BP family and may shed new light on the assembly and catalytic activity site design of Mo-V clusters. Further studies of the assembly mechanism, other novel Mo-V clusters containing the $[\text{Mo}^{\text{V}}\text{V}^{\text{IV}}\text{O}_4]$ building unit using this approach, and potential catalytic activities toward other organic model reactions are underway in our laboratory and will be reported in due course.

Author contributions

Y. F. Bi and B. K. Chen conceived and designed the project. X. Y. Ren, G. Zhang, and L. L. Dai performed the experiments and characterization. X. Y. Ren wrote the original draft. G. P. Yang, Y. F. Bi and B. K. Chen provided supervision, validated the experimental results, and reviewed and edited the manuscript. G. P. Yang and B. K. Chen provided funding support.

Conflicts of interest

The authors declare no competing financial interest.

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