

Novel Heterotetranuclear V_2Mo_2 or V_2W_2 Complexes with 4,4'-Di-*tert*-butyl-2,2'-bipyridine: Syntheses, Crystal Structures, and Catalytic Activities

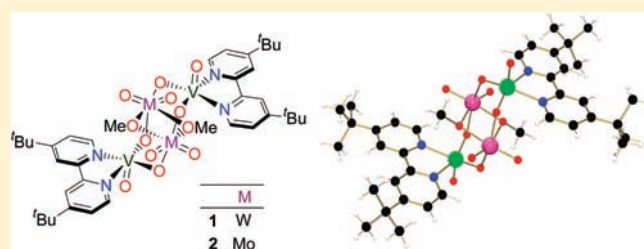
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S Supporting Information

ABSTRACT: Two novel heterotetranuclear complexes [$V_2O_2(\mu\text{-MeO})_2(\mu\text{-WO}_4)_2(4,4'\text{-}^t\text{Bubpy})_2$] (**1**) and [$V_2O_2(\mu\text{-MeO})_2(\mu\text{-MoO}_4)_2(4,4'\text{-}^t\text{Bubpy})_2$] (**2**) were synthesized, and the solid state structures of these complexes were revealed by single crystal X-ray crystallography. The heterotetranuclear complexes **1** and **2** are centrosymmetric building blocks, considered as consisting of two [$VO(4,4'\text{-}^t\text{Bubpy})$]³⁺ units bridged by $\mu\text{-MO}_4^{2-}$ ($M = W$ or Mo) anions connected with methoxy groups. Furthermore, catalytic activities of **1** and **2** in the alcohol oxidation with hydrogen peroxide as terminal oxidants in water as solvent were investigated.



INTRODUCTION

Development of new heteropolynuclear complexes is of great importance in many fields of catalysis and materials chemistry because complexes with different metals are known to modify the properties of the individual metals.¹ The heteropolynuclear complexes as catalysts are known to have potential to exhibit distinct activity different from the one shown by mononuclear complexes.² However, it is often difficult to combine different metals together in a single molecule without controlling their individual chemical properties. Complexation of the cationic metal complexes by metal oxyanions, such as WO_4^{2-} and MoO_4^{2-} , is an attractive method for the synthesis of heteropolynuclear complexes, but the examples of such simple anions used as ligands to the cationic metal complexes are still limited, compared with those of complexation by polyoxoanions.³ Also, most of heterometallic complexes bridged by metal oxyanions are used for the investigation of their magnetic properties,⁴ and the catalysis of those complexes is not investigated sufficiently. Here, we report the development of new heterotetranuclear complexes from a cationic vanadium complex bearing appropriate organic ligands and metal oxyanions (WO_4^{2-} or MoO_4^{2-}). In addition, the catalytic activity of these heterotetranuclear complexes was investigated.

RESULTS AND DISCUSSION

In a typical procedure, to an aqueous suspension of the vanadium(IV) complex, [$VO(4,4'\text{-}^t\text{Bubpy})_2$] SO_4 , prepared from $VOSO_4$ and 4,4'-di-*tert*-butyl-2,2'-bipyridine ($4,4'\text{-}^t\text{Bubpy}$),⁵ an aqueous solution of Na_2WO_4 was added, and the mixture was

stirred at ambient temperature to form a brown precipitate. A heterotetranuclear V_2W_2 complex (vanadium(V)–tungsten(VI) complex), [$V_2O_2(\mu\text{-MeO})_2(\mu\text{-WO}_4)_2(4,4'\text{-}^t\text{Bubpy})_2$] (**1**), was obtained as a yellow crystal by recrystallization of the precipitate from a mixture of methanol and chloroform. A heterotetranuclear V_2Mo_2 complex (vanadium(V)–molybdenum(VI) complex), [$V_2O_2(\mu\text{-MeO})_2(\mu\text{-MoO}_4)_2(4,4'\text{-}^t\text{Bubpy})_2$] (**2**) was also obtained by the reaction of [$VO(4,4'\text{-}^t\text{Bubpy})_2$] SO_4 with Na_2MoO_4 .⁶ The use of $4,4'\text{-}^t\text{Bubpy}$ as a bipyridyl ligand was necessary for the syntheses of this type of heterotetranuclear V_2W_2 or V_2Mo_2 complexes.⁷ The structures of these complexes **1** and **2** were characterized by NMR, IR, ESI-MS, and elemental analysis (see Experimental Section). The solid state structures of **1** and **2** were determined by single crystal X-ray crystallography. Crystal data for complexes **1** and **2** are summarized in Table 1. The crystal structures of **1** and **2** are shown in Figures 1–3. They have similar structures. Vanadium, tungsten, and molybdenum atoms in **1** and **2** are present in octahedral coordination. The heterotetranuclear complexes **1** and **2** are centrosymmetric building blocks, considered as consisting of two [$VO(4,4'\text{-}^t\text{Bubpy})$]³⁺ units bridged by $\mu\text{-MO}_4^{2-}$ ($M = W$ or Mo) anions connected with methoxy groups. Selected bond lengths (Å) and angles (deg) for **1** and **2** are listed in Table 2. The $V=O$ distances in **1** and **2** are almost the same (1.60 Å). The $W=O$ distances in **1** and the $Mo=O$ distances in **2** are 1.73 Å and 1.71 Å, respectively. The cyclic tetranuclear eight-membered structures exist in these complexes **1** and **2**. The $V-O$ distances within the eight-membered

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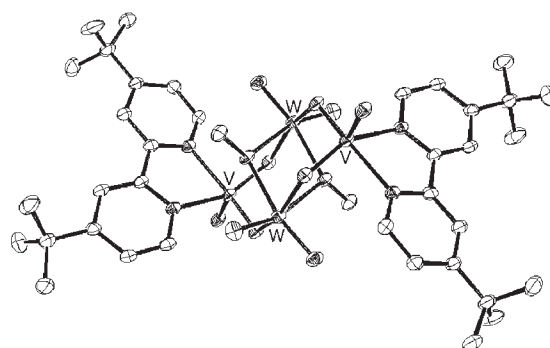
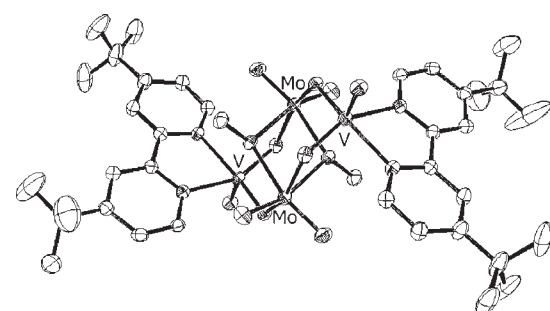
Table 1. Crystallographic Data and Structure Refinement of Complexes **1** and **2**

	1	2
formula	C ₃₈ H ₅₄ N ₄ O ₁₂ V ₂ W ₂	C ₃₈ H ₅₄ N ₄ O ₁₂ V ₂ Mo ₂
T (K)	113	123
cryst syst	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.1338(3)	10.2163(2)
<i>b</i> (Å)	15.6779(5)	16.2648(4)
<i>c</i> (Å)	19.7520(6)	19.0493(4)
α (deg)	72.9803(9)	105.0638(7)
β (deg)	80.3509(9)	97.1994(7)
γ (deg)	88.1885(9)	93.2327(7)
<i>V</i> (Å ³)	2957.75(15)	3019.4(1)
<i>Z</i>	1	1
<i>D</i> _{calcd} (g/cm ³)	1.644	1.672
μ (MoK α) (cm ⁻¹)	44.149	12.911
<i>F</i> (000)	1434.50	1516.00
2 θ max (deg)	50.6	55.0
<i>N</i> _{measured}	24398	52629
<i>N</i> _{unique}	10737	13821
GOF	1.05	1.03
<i>R</i> ₁	0.0335	0.0597
<i>wR</i> ₂	0.0960	0.1651

ring are longer (1.78–1.79 Å) compared with the V=O distances. The W–O distances within the eight-membered ring are in the range 1.95–1.96 Å, and the Mo–O distances within the eight-membered ring are in the range 1.95–1.97 Å, which are longer than the M=O (M = W or Mo) distances. In **1**, the O2–V1–O4#1 angle and the O2–W1–O4 angle are 102.34(17)° and 153.56(16)°, respectively. Also, in **2**, the O2–V1–O4#1 angle and the O2–Mo1–O4 angle are 102.77(14)° and 153.71(13)°, respectively. These complexes also have the four-membered ring structure (M₂(μ -MeO)₂ (M = W or Mo)) and two kinds of six-membered ring structures (VM₂O₂(μ -MeO) (M = W or Mo)). The tungsten or molybdenum centers are connected through methoxy groups. The W1–O3 and W1–O3#1 distances are 2.26 Å and 2.24 Å, respectively, and the Mo1–O3 and Mo1–O3#1 distances are almost the same (2.25 Å). In **1**, the O3–W1–O3#1 angle, the W1–O3–W1#1 angle, the O3–W1–O4 angle, and the O3#1–W1–O4 angle are 70.64(12)°, 109.36(13)°, 82.38(13)°, and 75.66(15)°, respectively. In **2**, the O3–Mo1–O3#1 angle, the Mo1–O3–Mo1#1 angle, the O3–Mo1–O4 angle, and the O3#1–Mo1–O4 angle are 70.85(11)°, 109.15(12)°, 81.88(11)°, and 75.38(12)°, respectively.

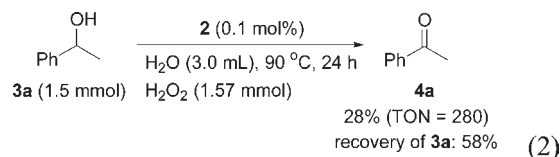
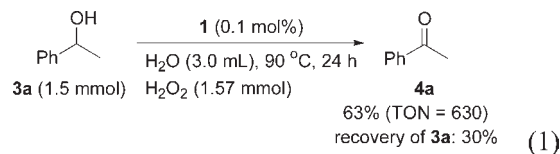
Oxoperoxo vanadium(V), molybdenum(VI), and tungsten(VI) complexes are known to serve as useful oxidation catalysts.⁸ Therefore, we next investigated the catalytic activity of these heterotetranuclear complexes, **1** and **2**, for the oxidation of alcohols with hydrogen peroxide as terminal oxidants.

Oxidation of 1-phenylethanol (**3a**) was examined with hydrogen peroxide in the presence of **1** or other metal complexes using water as solvent. The results are shown in Table 3. VOSO₄ and VO(Hhpic)₂⁹ exhibited moderate catalytic activity in the oxidation of **3a** (entries 1 and 2). 4,4'-Di-*tert*-butyl-2,2'-bipyridyl (4,4'-*t*-Bubpy) was not effective as an additional ligand to VOSO₄ (entry 3). Na₂WO₄ was not effective as catalysts for the oxidation (entries 4 and 5). The complex **1** was found to be an effective

**Figure 1.** Crystal structure of **1** (symmetry-expanded structures). Ellipsoids are shown at the 50% probability level.**Figure 2.** Crystal structure of **2** (symmetry-expanded structures). Ellipsoids are shown at the 50% probability level.

precatalyst for the oxidation reaction in Table 3, and **4a** was produced selectively in a good yield (entry 6).^{10,11}

Furthermore, when the oxidation of **3a** (1.5 mmol) was conducted using H₂O₂ (1.57 mmol) at 90 °C for 24 h in the presence of **1** (0.1 mol %), the turnover number (TON) of **1** increased from 292 (see, Table 3, entry 6) to 630 (eq 1).^{12,13} V₂Mo₂ complex **2** could also be employed as a precatalyst for the oxidation of **3a**, but the yield of **4a** and TON were lower compared with the case using **1** as a precatalyst (eq 2).



The results of the oxidation of various secondary alcohols using **1** are shown in Table 4. Diphenylmethanol (**3b**) was oxidized under the reaction condition to afford benzophenone (**4b**) in a moderate yield (entry 2). The oxidation of cyclohexyl(phenyl)methanol (**3c**) proceeded very slowly (entry 3). From these results, steric hindrance may influence the reactivity of **1**. Oxidations of 1-(*p*-substituted phenyl)ethanols **3d** and **3e**

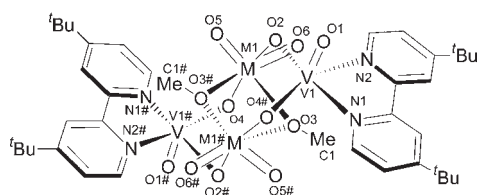


Figure 3. Numbering of selected atoms of heterotetranuclear V_2M_2 ($M = W$ or Mo) complexes **1** or **2**.

proceeded selectively to afford the corresponding ketones **4d** and **4e**, respectively (entries 4 and 5). Furthermore, 4-*tert*-butylcyclohexanol (**3f**) could be oxidized by prolonging the reaction time (entry 6).¹⁴

The examples of metal-complex-catalyzed oxidation of alcohols with H_2O_2 using water as solvent are still limited,¹⁵ although oxidations using water as solvent could be cheaper, more eco-friendly, and safer than current oxidation processes in organic solvents.¹⁶ Also, oxidation of alcohols using water as solvent often proceeds in an organic–aqueous biphasic system, and therefore, phase transfer catalysts are often required. In our reaction system, however, the oxidation of alcohols with **1** proceeded without the addition of any phase transfer catalyst. The result suggests that affinity of **1** to organic substrates was improved by the selection of appropriate organic ligands, that is, 4,4'-*t*-Bubpy. In addition, from the result of Table 3, we believe that preparation of heteropolynuclear complexes enables us to develop new oxidation catalysts with improved catalytic activity to realize efficient oxidation reactions.¹⁷

CONCLUSIONS

Two new heterotetranuclear complexes **1** and **2** were synthesized, and the solid state structures of **1** and **2** were revealed by single crystal X-ray crystallography. These complexes had unique structures linked through μ - MO_4^{2-} ($M = W$ or Mo) and μ - MeO^- bridges, and contained two different metals known to have a potential to act as useful oxidants. Preliminary results of alcohol oxidation with H_2O_2 using water as solvent in the presence of **1** as a precatalyst suggest that polynucleation of the complex with appropriate organic ligands leads to the development of new catalysts for environmentally friendly oxidation systems.

EXPERIMENTAL SECTION

General Procedures. 1H NMR spectra were recorded on a JEOL JNM-AL-300 (300 MHz) spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained on a JEOL JNM-AL-400 (100 MHz) spectrometer using $CDCl_3$ as the solvent. Chemical shifts in ^{13}C NMR were measured relative to $CDCl_3$ by using δ 77.0 ppm. ^{51}V NMR spectra were obtained on a JEOL ECX-400 (105 MHz) spectrometer using $CDCl_3$ as the solvent with $VOCl_3$ (−4 ppm) as an external standard. IR spectra were determined on a Shimadzu FTIR 8400 infrared spectrometer. Substrates **3c**,¹⁸ **3d**,¹⁹ and **3e**²⁰ were prepared by reduction of the corresponding ketones with $NaBH_4$. Unless otherwise noted, other reactants and reagents were purchased from commercial source and used without further purification.

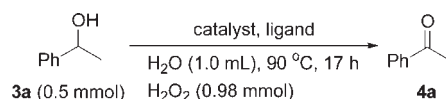
X-ray Crystallography. Crystals of **1** or **2** were mounted on a glass fiber and cooled in the cold stream of nitrogen gas. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated $Mo-K\alpha$ radiation. The structure was solved by direct methods (SHELX97). For **1**, the *tert*-butyl group was found disordered.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

	1 ($M = W$) ^a	2 ($M = Mo$) ^b
V1–O1	1.602(3)	1.602(4)
V1–O2	1.783(3)	1.787(3)
V1–O4#1	1.784(4)	1.783(4)
V1–N1	2.153(3)	2.165(3)
V1–N2	2.139(4)	2.150(4)
M1–O2	1.947(3)	1.948(3)
M1–O3	2.259(3)	2.254(3)
M1–O3#1	2.238(4)	2.247(4)
M1–O4	1.957(3)	1.972(3)
M1–O5	1.730(3)	1.714(3)
M1–O6	1.731(4)	1.709(4)
O3–C1	1.440(5)	1.437(5)
O1–V1–O2	103.27(17)	102.86(14)
O1–V1–O4#1	104.84(19)	104.95(16)
O1–V1–N1	95.34(17)	93.16(14)
O1–V1–N2	96.24(18)	96.74(16)
O2–V1–O4#1	102.34(17)	102.77(14)
O2–V1–N1	155.91(17)	158.29(15)
O2–V1–N2	89.33(17)	90.48(14)
O4#1–V1–N1	87.24(16)	86.82(14)
O4#1–V1–N2	152.62(15)	151.12(12)
N1–V1–N2	73.39(17)	72.97(14)
O2–M1–O3	75.20(13)	74.61(11)
O2–M1–O3#1	83.73(15)	85.78(12)
O2–M1–O4	153.56(16)	153.71(13)
O2–M1–O5	97.14(16)	98.19(14)
O2–M1–O6	99.15(17)	99.39(15)
O3–M1–O3#1	70.64(12)	70.85(11)
O3–M1–O4	82.38(13)	81.88(11)
O3–M1–O5	160.79(18)	159.81(15)
O3–M1–O6	93.15(16)	94.19(13)
O3#1–M1–O4	75.66(15)	75.38(12)
O3#1–M1–O5	91.22(17)	90.03(14)
O3#1–M1–O6	162.38(14)	162.43(12)
O4–M1–O5	99.64(15)	99.97(14)
O4–M1–O6	95.85(17)	93.83(15)
O5–M1–O6	105.6(2)	105.68(16)
M1–O2–V1	120.12(16)	119.58(14)
M1–O4–V1#1	119.1(2)	117.68(17)
M1–O3–M1#1	109.36(13)	109.15(12)
M1–O3–C1	118.3(3)	117.3(3)
M1#1–O3–C1	116.9(3)	116.8(3)

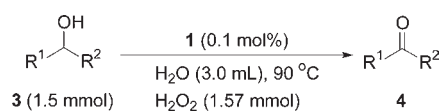
^aSymmetry operators: (#1) $-X+1, -Y+1, -Z+1$. ^bSymmetry operators: (#1) $-X+1, -Y, -Z$.

Synthesis of $[V_2O_2(\mu-MeO)_2(\mu-WO_4)_2(4,4'-t-Bubpy)_2]$ (1**).** To a solution of 4,4'-di-*tert*-butyl-2,2'-bipyridyl (4,4'-*t*-Bubpy) (930.4 mg, 3.5 mmol) in EtOH (40 mL) was added a solution of $VOSO_4 \cdot 5H_2O$ (437.6 mg, 1.7 mmol) in EtOH (20 mL). After stirring for 2.5 h at 40 °C, the solution was concentrated under reduced pressure, and the precipitate was filtered using diethyl ether and dried in vacuo to afford $[VO(4,4'-t-Bubpy)_2]SO_4$ as a green powder (700.6 mg). HR-ESI MS (MeOH) calcd for $C_{36}H_{49}N_4O_5SV$

Table 3. Catalytic Activities for Oxidation of 1-Phenylethanol with **1** and Other Metal Complexes

entry	catalyst (mol %)	ligand (mol %)	yield (%) ^a	selectivity (%) ^b	conversion (%) ^c	TON ^d
1	VOSO ₄ (1)	none	44	66	67	44
2	VO(Hhpic) ₂ (1)	none	43	65	66	43
3	VOSO ₄ (1)	4,4'-t-Bubpy (2)	33	50	66	33
4	Na ₂ WO ₄ (1)	none	7	70	10	7
5	Na ₂ WO ₄ (1)	4,4'-t-Bubpy (2)	8	42	19	8
6	1 (0.25)	none	73	82	89	292

^aDetermined by ¹H NMR. ^bSelectivity = (formed **4a**)/(converted **3a**). ^cConversion of **3a** to **4a**. ^dThe turnover number (TON) of the catalyst = (mmol of **4a**)/(mmol of catalyst).

Table 4. Oxidation of Various Secondary Alcohols in the Presence of **1**

entry	substrate	product	time (h)	yield (%) ^a	selectivity (%) ^b	TON ^c		
1	R ¹ = Ph, R ² = Me	3a	4a	24	63	90	630	
2	R ¹ = Ph, R ² = Ph	3b	4b	24	25	86	250	
3	R ¹ = Ph, R ² = ^c Hex	3c	4c	24	6	100	60	
4	R ¹ = 4-BrC ₆ H ₄ , R ² = Me	3d	4d	24	33	83	330	
5	R ¹ = 4-NO ₂ C ₆ H ₄ , R ² = Me	3e	4e	24	43	83	430	
6		3f		4f	90	18	55	180

^aDetermined by ¹H NMR. ^bSelectivity = (formed **4**)/(converted **3**). ^cThe turnover number (TON) of the catalyst = (mmol of **4**)/(mmol of catalyst).

[M + H]⁺ 700.2863, found 700.2881. Next, water (10 mL) was added to the green powder to form a suspension in a glass vessel. After addition of an aqueous solution of Na₂WO₄·2H₂O (494.3 mg, 1.5 mmol) in water (10 mL) to the suspension, the reaction mixture was stirred for 3 h at ambient temperature. After the reaction, the precipitate was filtered using water and dried in vacuo to afford a brown powder. Next, methanol was added to the brown powder, forming a brown suspension, followed by filtration of the suspension to give a yellow solution. Chloroform was added to the yellow solution, and the resulting mixture was let stand for recrystallization at room temperature for 2 weeks, affording **1** (428.4 mg, yield = 40% based on vanadium) as a yellow crystal. ¹H NMR (CDCl₃, 300 MHz) δ 9.15 (d, J = 6.1 Hz, 4H), 8.05 (d, J = 1.7 Hz, 4H), 7.70 (dd, J = 6.3, 1.7 Hz, 4H), 3.18 (s, 6H), 1.46 (s, 36H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.82, 154.01, 152.21, 124.78, 117.15, 57.38, 35.87, 30.34; ⁵¹V NMR (CDCl₃, 105 MHz) δ -544; IR (KBr, cm⁻¹) 3442, 2964, 1618, 1413, 977, 906, 758; HR-ESI MS (CHCl₃) calcd for C₃₈H₅₄N₄O₁₂V₂W₂Na [M + Na]⁺ 1251.153, found 1251.150. Anal. Calcd for C_{38.5}H_{54.5}Cl_{1.5}N₄O₁₂V₂W₂: C, 35.90; H, 4.26; N, 4.35. Found: C, 35.82; H, 4.18; N, 4.29.

Synthesis of [V₂O₂(μ-MeO)₂(μ-MoO₄)₂(4,4'-t-Bubpy)₂] (2**).** To a solution of 4,4'-di-*tert*-butyl-2,2'-bipyridyl (4,4'-t-Bubpy) (539.5 mg, 2.0 mmol) in MeOH (20 mL) was added a solution of VOSO₄·5H₂O (253.6 mg, 1.0 mmol) in MeOH (20 mL). After stirring for 2.5 h at 40 °C, the solution was

concentrated under reduced pressure to afford [VO(4,4'-t-Bubpy)₂]SO₄ as a green powder, and water (10 mL) was added to the green powder to form a suspension in a glass vessel. After addition of an aqueous solution of Na₂MoO₄·2H₂O (366.7 mg, 1.5 mmol) in water (10 mL) to the suspension, the reaction mixture was stirred for 3 h at ambient temperature. After the reaction, the precipitate was filtered using water and dried in vacuo to afford a brown powder. Next, methanol was added to the brown powder, forming a brown suspension, followed by filtration of the suspension to give a yellow solution. Chloroform was added to the yellow solution, and the resulting mixture was let stand for recrystallization at room temperature for 2 weeks, affording **2** (192.2 mg, yield = 37% based on vanadium) as a yellow crystal. ¹H NMR (CDCl₃, 300 MHz) δ 9.04 (d, J = 5.9 Hz, 4H), 8.05 (d, J = 1.7 Hz, 4H), 7.65 (dd, J = 6.0, 1.8 Hz, 4H), 3.10 (s, 6H), 1.45 (s, 36H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.34, 153.40, 152.20, 124.52, 117.06, 57.38, 35.80, 30.36; ⁵¹V NMR (CDCl₃, 105 MHz) δ -533; IR (KBr, cm⁻¹) 3442, 2962, 1618, 1411, 968, 904, 742; HR-ESI MS (CHCl₃) calcd for C₃₈H₅₄N₄O₁₂V₂Mo₂Na [M + Na]⁺ 1079.062, found 1079.058. Anal. Calcd for C_{38.8}H_{54.8}Cl_{2.4}N₄O₁₂V₂Mo₂: C, 40.70; H, 4.72; N, 4.98. Found: C, 40.59; H, 4.81; N, 4.88.

General Procedure for Oxidation of Alcohols with Hydrogen Peroxide in the Presence of **1 (Table 4).** The V₂W₂ complex **1** (1.8 mg, 0.0015 mmol) and alcohols **3** (1.5 mmol) were placed in a

25 mL two necked flask, and then water (3.0 mL) was added. The mixture was heated to 90 °C, 30% H₂O₂ aq. (0.16 mL, 1.57 mmol) was added to the mixture, and then the reaction was conducted with magnetic stirring for the appropriate time. After the reaction, the mixture was diluted with diethyl ether, and the organic phase was evaporated. The crude product was dissolved in CDCl₃, and an appropriate amount of 1,3,5-trioxane was added as an internal standard to determine the yield of the product by ¹H NMR spectroscopy.

ASSOCIATED CONTENT

S Supporting Information. X-ray crystallographic data in CIF format, NMR spectra, and IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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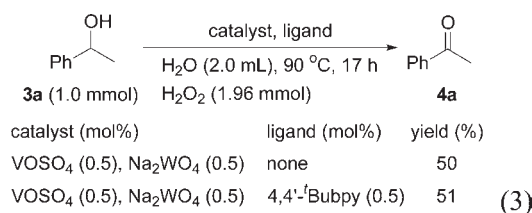
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- (6) We presume that the oxidation state of vanadium atoms changed from V(IV) to V(V) by air-oxidation during recrystallization to form **1** or **2**.
- (7) Other vanadium(IV) complexes with substituted 2,2'-bipyridyl (5,5'-dimethyl-2,2'-bipyridyl) or 1,10-phenanthroline were employed

for the syntheses of heterotetranuclear V₂W₂ or V₂Mo₂ complexes. However, the materials obtained in the reaction of the vanadium(IV) complexes with Na₂WO₄ or Na₂MoO₄ in water have low solubility to organic solvents such as methanol, and therefore, recrystallization using methanol have been so far unsuccessful. We feel that the selection of the appropriate ligands to increase the solubility to organic solvents is important to obtain heterotetranuclear V₂W₂ or V₂Mo₂ complexes in the present synthetic method.

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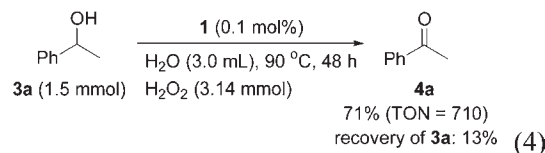
(10) The oxidation of **3a** was examined using both metal precursors (VOSO₄ and Na₂WO₄) with and without the ligand (4,4'-t-Bubpy) according to the reaction conditions of Table 3. As a result, the product of **4a** was formed in moderate yields, respectively (eq 3). Although the real active species is still unknown, we believe that the structure of **1** (Figure 1) is important as a precatalyst for the present oxidation reaction.



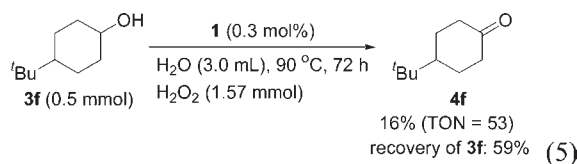
(11) When hydrogen peroxide was added to the reaction mixture of **1** and 1-phenylethanol (**3a**) at 90 °C, the color of the mixture turned from pale yellow to orange. This suggests that a peroxo complex was formed immediately by the addition of hydrogen peroxide. In addition, no significant induction period was observed in the oxidation of **3a** with **1** (Table 3, entry 6) varying the reaction time: the yield of **4a** (time) = 16% (2 h); 44% (6 h); 73% (17 h). Hydrogen peroxide was completely consumed after the reaction time of 17 h.

(12) Hydrogen peroxide was completely consumed after the reaction.

(13) Additional hydrogen peroxide (1.57 mmol) was added to the reaction mixture after 24 h, and the mixture was stirred at 90 °C for 24 h. As a result, the turnover number (TON) of **1** increased from 630 (see, eq 1) to 710, but the unchanged substrate **3a** (13%) was recovered and hydrogen peroxide was left at the end of the reaction (eq 4). We assume that the high concentration of substrate **3** in the reaction mixture is effective in the present oxidation reaction.¹⁴



(14) The oxidation of 4-tert-butylcyclohexanol (**3f**) was examined by changing only the amount of **3f** from 1.5 to 0.5 mmol, according to the condition of Table 4, entry 6. As a result, the turnover number (TON) of **1** decreased from 180 (see, Table 4, entry 6) to 53 (eq 5). From the results of eqs 4¹³ and 5, we consider that higher molar ratio of substrate **3** to **1** may be required in the oxidation reaction to maintain reaction efficiency.



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(17) We are interested in development of a reusable catalyst with high TON for oxidation reactions.^{9b} In the present work, we found the possibility that polynucleation of the complex was effective in improving its catalytic ability, because the yield of **4a** afforded by **1** and TON of **1** (Table 3) were difficult to achieve by using the mononuclear complexes in Table 3, although the TONs of **1** may not be very encouraging numbers at this stage. We believe that it is possible to further improve the ability of **1** as a precatalyst (or a catalyst) by preventing deactivation of catalysts with the selection of the appropriate reaction condition^{13,14} and the bulkier ligand.²¹

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