

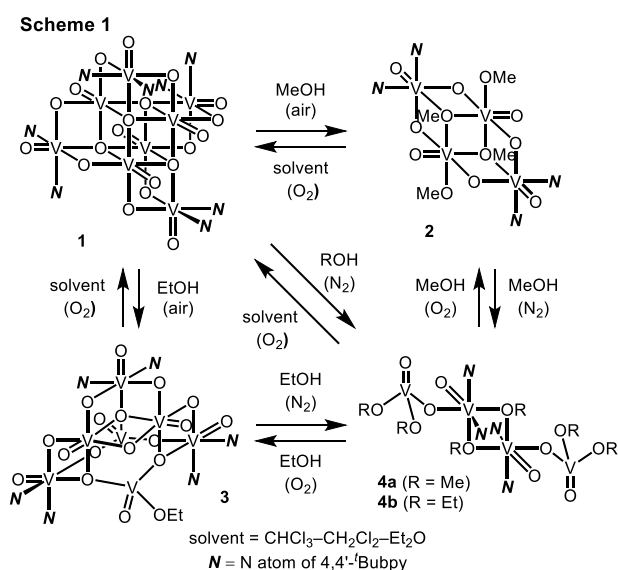
非イオン性混合原子価バナジウム(IV/V)酸化物クラスター錯体の合成とその性質

Synthesis and Properties of Nonionic Mixed-Valent
Vanadium(IV/V) Oxide Cluster Complexes応用化学専攻 井上 裕太
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1. Introduction

Anionic vanadium oxide clusters (polyoxovanadates: POVs)¹ have been attracting much attention because of their rich structural and chemical diversities leading to wide applications such as catalysts, drugs, and magnetic materials. In particular, structural changes and reaction behaviors of oxidovanadium anions in aqueous and organic solutions have been well studied, and a variety of POVs have been synthesized and characterized. By contrast, examples of nonionic vanadium oxide clusters are still limited in number, although they have potential to exhibit new properties distinct from those of POVs.

Recently, the nonionic octanuclear vanadium(V) oxide cluster $[\text{V}_8\text{O}_{20}(4,4'\text{-}^t\text{Bubpy})_4]$ (**1**; $4,4'\text{-}^t\text{Bubpy}$ = $4,4'\text{-di-tert-butyl-2,2'-bipyridine}$) was successfully synthesized by our research group.² Although cluster **1** maintains its structure in CHCl_3 , splitting of its core takes place in MeOH or EtOH under air to form the tetranuclear vanadium(V) oxide cluster $[\text{V}_4\text{O}_8(\text{OMe})_4(4,4'\text{-}^t\text{Bubpy})_2]$ (**2**) or the heptanuclear vanadium(V) oxide cluster $[\text{V}_7\text{O}_{17}(\text{OEt})(4,4'\text{-}^t\text{Bubpy})_3]$ (**3**), respectively. In contrast, when an alcohol (MeOH, EtOH) solution of **1** was refluxed for 24 h under N_2 , the nonionic mixed-valent tetranuclear $\text{V}^{\text{IV}}\text{V}^{\text{V}}$ oxide clusters $[\text{V}_4\text{O}_6(\text{OR})_6(4,4'\text{-}^t\text{Bubpy})_2]$ (**4a**, R = Me; **4b**, R = Et) were formed. In this reaction, the alcohol was confirmed to act as a reductant. Furthermore, interconversion among clusters **1–4** was observed, which provides a rare example in the solution chemistry of nonionic vanadium oxide clusters (Scheme 1).



In this study, to broaden the scope of reductive conversion of nonionic vanadium(V) oxide clusters, the author examined the reaction of **1** with PPh_3 as a reducing agent.

2. Experimental Section

All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. Products were characterized by NMR, IR, X-ray diffraction, SQUID, and elemental analyses.

3. Results and Discussion

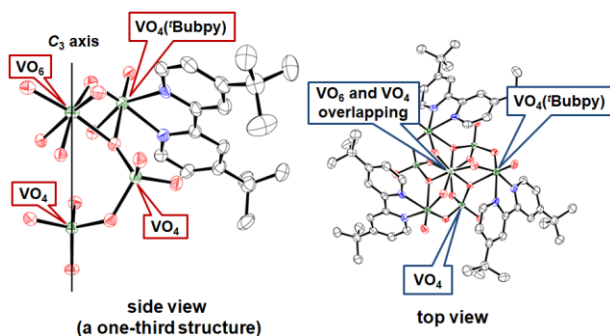
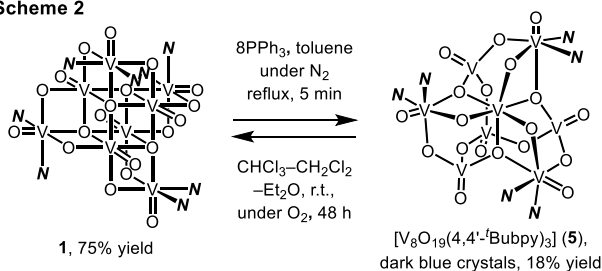
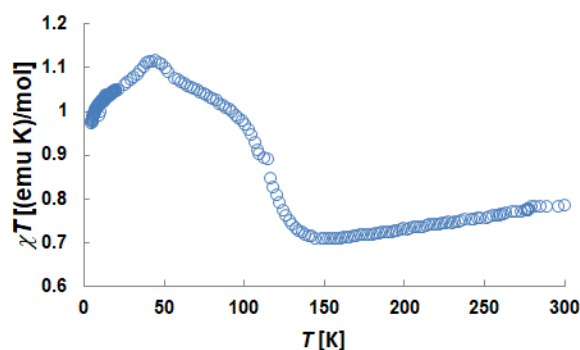
Partial reduction of **1** by PPh_3

When a toluene solution of **1** and PPh_3 (8 equiv) was heated at reflux for 5 min under N_2 and cooled to room temperature, an octanuclear vanadium(IV/V) oxide cluster $[\text{V}_8\text{O}_{19}(4,4'\text{-}^t\text{Bubpy})_3]$ (**5**) was obtained in 18% yield as

dark blue crystals (Scheme 2). Also, the formation of OPPh_3 and free 4,4'-Bubpy was confirmed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR. These results suggest that PPh_3 reduces **1** to produce OPPh_3 , free 4,4'-Bubpy, and **5**. The molecular structure of **5** was confirmed by single-crystal X-ray analysis (Figure 1). The core of **5** has a C_3 axis and contains four VO_4 , one VO_6 , and three $\text{VO}_4(4,4'\text{-Bubpy})$ units, and its formal oxidation state is $\text{V}^{\text{IV}}_2\text{V}^{\text{V}}_6$. Bond valence sum (BVS) calculations suggest that the oxidation state of V atom in VO_6 unit is +4, and V atoms in three $\text{VO}_4(4,4'\text{-Bubpy})$ units are mixed-valent ($\text{V}^{\text{IV}}\text{V}^{\text{V}}_2$).

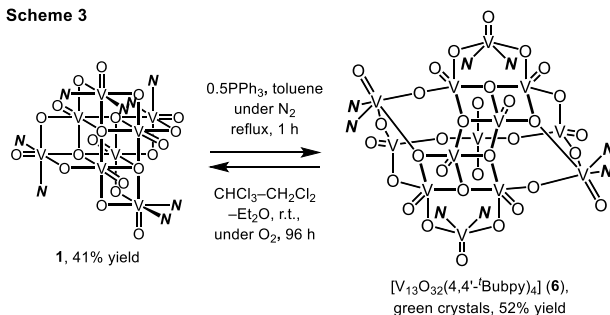
Magnetic measurement with SQUID showed that **5** exhibits ferro- and antiferromagnetic interaction at the temperature range of 50–150 and 150–300 K, respectively (Figure 2). Magnetic phase transition may occur at 150 K.

Scheme 2

Figure 1. ORTEP drawing for **5**Figure 2. χT vs T plot for **5**

Interestingly, a similar reaction of **1** using a half-equivalent of PPh_3 afforded a tridecanuclear vanadium(IV/V) cluster $[\text{V}_{13}\text{O}_{32}(4,4'\text{-Bubpy})_4]$ (**6**) in 52% yield, whose structure was confirmed by preliminary single-crystal X-ray analysis (Scheme 3).

Scheme 3



The core of **6** contains three VO_4 , six VO_5 , two $\text{VO}_3(4,4'\text{-Bubpy})$ and two $\text{VO}_4(4,4'\text{-Bubpy})$ units, and its formal oxidation state is $\text{V}^{\text{IV}}\text{V}^{\text{V}}_{12}$. BVS calculations suggest that the oxidation state of one of the V atoms in the $\text{VO}_3(4,4'\text{-Bubpy})$ units is +4.

SQUID measurement showed that **6** exhibits paramagnetism at the temperature range of 5–300 K. The low temperature part (5–100 K) of the inverse susceptibility (χ^{-1}) curve was fitted using the Curie–Weiss law to give a Curie constant $C = 0.33 \text{ emu mol}^{-1} \text{ K}$.

Finally, re-oxidation of **5** and **6** was examined. As expected, **5** and **6** was converted back to **1** when dissolved in $\text{CHCl}_3\text{-CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ mixture under O_2 .

4. Conclusion

Unprecedented nonionic mixed-valent vanadium(IV/V) oxide clusters **5** and **6** were synthesized, and its magnetic properties, together with interconversion among **1**, **5**, and **6**, were investigated.

5. References

- Hayashi, Y. *Coord. Chem. Rev.* **2011**, 255, 2270.
- Inoue, Y. *et al. Inorg. Chem.* **2016**, 55, 6712.

6. Presentation list

- 96th CSJ annual meeting **2016**, 2E5-02.
- 66th Conf. of JSCC **2016**, 2Ac-08.
- 97th CSJ annual meeting **2017**, 4G4-40.
- 67th Conf. of JSCC **2017**, 1Aa-01.
- 98th CSJ annual meeting **2018**, 1B1-01.