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A Novel Octanuclear Vanadium(V) Oxide Cluster Complex Having an Unprecedented Neutral V_8O_{20} Core Functionalized with 4,4′-Di-*tert*-butyl-2,2′-bipyridine

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Supporting Information

ABSTRACT: A novel octanuclear vanadium(V) oxide cluster complex, $[V_8O_{20}(4,4'\text{-}{}^tBubpy)_4]$ (**1**), was synthesized and characterized by single-crystal X-ray structure analysis to reveal that **1** has an unprecedented neutral V_8O_{20} core. An unexpected interconversion between **1** and the methoxo(oxo)vanadium(V) cluster complex, $[V_4O_8(OMe)_4(4,4'\text{-}{}^tBubpy)_2]$ (**2**), was observed upon changes in the solvent systems.

Anionic vanadium oxide clusters (polyoxovanadates) are known to possess rich structural diversity, and considerable efforts have been devoted to their application in various areas, including catalysts, medicine, and materials for electronic devices.[1] *Neutral* vanadium oxide clusters[2] have also attracted much attention in recent years, not only because they serve as model compounds for partial structures of vanadium oxide (V_2O_5)[3] but also because of their potential of exhibiting activities in catalysis (in a gas-phase study[2a−c,4]) distinct from those of polyoxovanadates. However, examples of isolated neutral vanadium oxide clusters are still limited in number, which prevents investigation into their properties in detail. Functionalization of polyoxovanadates with organic groups[5] is one of the methods to obtain neutral vanadium oxide clusters.[6] Anionic organic ligands are often used to substitute an oxo group of polyoxovanadates and link organic groups directly to the vanadium centers, whereas there are few examples of the neutral vanadium oxide clusters functionalized only with neutral organic ligands.[6e] In addition, unfortunately, most of neutral vanadium oxide cluster complexes are quite insoluble in water and organic solvents as well, and therefore their reaction behavior in solution has been poorly investigated. Herein, we report the synthesis, characterization, and solvent-dependent core conversion of an octanuclear vanadium(V) oxide cluster complex, $[V_8O_{20}(4,4'\text{-}{}^tBubpy)_4]$ (**1**; 4,4′-^{t}Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine),[7] having a neutral V_8O_{20} core. It is noteworthy that the structure of the V_8O_{20} core in **1** has not been known, although some stable structures of neutral V_8O_{20} clusters were suggested to exist by using density functional theory (DFT) calculations.[2h]

Complex **1** was obtained in 75% yield from the reaction of vanadium(IV) oxide sulfate ($VOSO_4$) with 4,4′-^{t}Bubpy in the presence of sodium benzoate under an aerobic atmosphere.[8] Single-crystal X-ray structure analysis indicates that **1** contains a windmill-shaped[9,10] $V_8O_{20}N_8$ cluster unit with crystallographic S_4 symmetry, where the S_4 axis goes through the midpoints of V1···V1^{i} and V1^{ii}···V1^{iii} (Figures 1 and 2).

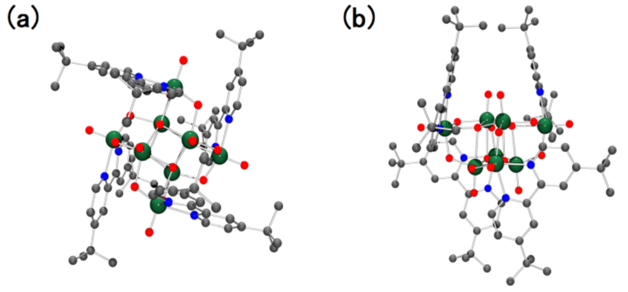

Figure 1. Ball-and-stick representations of a $V_8O_{20}N_8$ cluster unit in **1**: (a) top view of **1**; (b) side view. Color code: green, V; red, O; blue, N; gray, C. H atoms have been omitted for clarity.

The $V_8O_{20}N_8$ cluster unit is composed of four VO_6 and four VO_4N_2 octahedra, and the main body of the V_8 cluster may be viewed as a combination of two ribbonlike V_4 units lying perpendicular to each other. Thus, the connecting part of the ribbonlike V_4 units forms a cuboidal V_4O_4 structure. The $V{=}O_{terminal}$ bond distances are nearly 1.6 Å, whereas the distances for the $V{-}O_{bridging}$ bonds cis or trans to a terminal oxo ligand are 1.79−2.01 or 2.21−2.41 Å, respectively. These values are within the range expected for these bonds,[6m,11] although the V1−O4^{iii} distance at 2.4101(18) Å is among the longest V−O bonds of this type. These situations make the cuboidal V_4O_4 moiety at the center of the cluster elongated along the S_4 axis. On the other hand, the V1−V1^{i} distance at 2.8653(6) Å in the central cubane is much shorter than the nearest V−V distances (ca. 3.11−3.12 Å) observed in the isolated neutral vanadium(IV/V)[6f,i] and vanadium(V)[6m] oxide cluster complexes.

Bond-valence-sum (BVS) calculations of all V atoms in **1** indicate that **1** is a vanadium(V) oxide cluster complex (Table S3 in the Supporting Information, SI). To the best of our knowledge, this complex provides the first example of an isolated neutral octanuclear vanadium(V) oxide cluster complex. In addition, the windmill-shaped V_8O_{20} core in **1** is unprecedented; a neutral V_8O_{20} cluster with an S_4 symmetry (a cubelike V_8O_{20} isomer) has been suggested to exist by using DFT calculations,[2h] but the latter structure is distinctly different from that of **1**.

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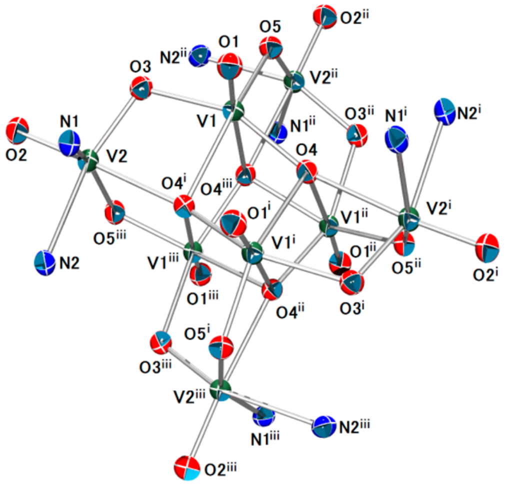
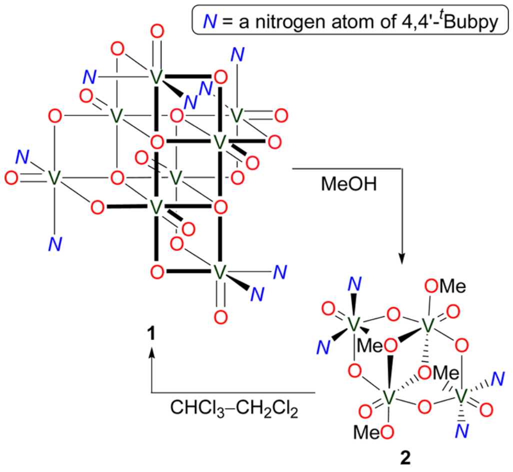


Figure 2. Crystal structure of **1** with numbered atoms. Ellipsoids are shown at the 50% probability level. H and C atoms are omitted for clarity. Symmetry operators: (i) $-x + 1, -y + {}^{1}/_{2} + 1, z$; (ii) $-y + {}^{1}/_{4} + 1, x + {}^{1}/_{4}, -z + {}^{1}/_{4} + 1$; (iii) $y + {}^{3}/_{4} - 1, -x + {}^{1}/_{4} + 1, -z + {}^{1}/_{4} + 1$. Selected interatomic distances (Å) and angles (deg): V1–O1 1.5991(18), V1–O4^{i} 2.0119(16), V1–O4 1.8483(16), V1–O3 1.9780(16), V1–O4^{iii} 2.4101(18), V1–O5 1.7927(17), V2–O2 1.6080(18), V2–O4^{i} 2.2128(16), V2–O3 1.7247(16), V2–O5^{iii} 1.8483(18), V2–N1 2.155(2), V2–N2 2.187(2), V1···V1^{i} 2.8653(6); V1–O3–V2 111.95(8), V1–O4–V1^{i} 95.76(7), V1–O4–V1^{ii} 106.59(8), V1–O4–V2^{i} 164.33(10), V1^{i}–O4–V1^{ii} 101.37(7), V1^{i}–O4–V2^{i} 93.17(7), V1^{ii}–O4–V2^{i} 84.13(6), V1–O5–V2^{ii} 116.77(9), O4–V1–O4^{i} 80.01(7), O4–V1–O4^{iii} 76.94(7), O4^{i}–V1–O4^{iii} 74.17(6), O3–V1–O4^{i} 77.37(7), O3–V2–O4^{i} 77.51(7), O4^{i}–V2–N1 79.36(7).

The high solubility of **1** in chloroform enabled us to perform the structural investigation of **1** in solution.[12] In the ^{1}H NMR spectrum of **1** in chloroform-*d*, six resonances at δ 8.94 (d, J = 4.5 Hz, 4H), 8.81 (d, J = 5.5 Hz, 4H), 8.11 (s, 4H), 7.95 (s, 4H), 7.81 (d, J = 4.5 Hz, 4H), and 6.91 (d, J = 4.0 Hz, 4H) are observed in the aromatic region, which suggests the existence of six chemically nonequivalent protons in the aromatic rings of the 4,4′-^{t}Bubpy ligands. In addition, the ^{51}V NMR spectrum of **1** in chloroform-*d* displays two resonances at δ −501 and −535 with the intensity ratio of 1:1. These results are consistent with the S_4-symmetric solid-state structure of **1**, which contains two types of chemically unequivalent V atoms (VO$_6$ and VO$_4$N$_2$ octahedra; Figures 1 and 2).

In contrast, when **1** was dissolved in methanol instead of chloroform at room temperature, the color of the solution turned slowly from yellow to orange yellow, and yellow crystals were deposited upon standing overnight.[13] Single-crystal X-ray structure analysis has revealed that splitting of the core of **1** takes place to form the methoxo(oxo)vanadium(V) cluster complex, [V$_4$O$_8$(OMe)$_4$(4,4′-^{t}Bubpy)$_2$] (**2**), in 66% yield (Figure S1 in the SI).[14] While the bpy analogue of **2**, [V$_4$O$_8$(OMe)$_4$(bpy)$_2$], has already been known for some time, its synthesis was based on the reactions between bpy and oxovanadium(IV) complexes with organic ligands, i.e., [VO(sal-gly)(H$_2$O)] (sal-gly = *N*-salicylideneglycinate)[6m] or [VO(acac)$_2$] (Hacac = acetylacetone).[6f] Hence, the present conversion of **1** to **2** provides a new straightforward route to the construction of this type of methoxo(oxo)vanadium(V) cluster.[15] Complex **2** is easily dissolved in a chloroform–dichloromethane mixture, and slow diffusion of diethyl ether into this yellow solution of **2** afforded yellow crystals in moderate yield, which were confirmed to be **1**, in turn, by X-ray diffraction analysis (Scheme 1).[16]

Scheme 1. Interconversion of 1 and 2 by Changes in the Solvent Systems



To our knowledge, interconversion of different types of neutral vanadium oxide cluster complexes has not been confirmed experimentally so far. Further investigation into the reaction behavior of **1** in alcoholic solvents, together with its use as homogeneous catalysts for hydrocarbon oxidation,[1b,2b,3c,f,i] is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format for **1** and **2**, experimental details, and ^{1}H, ^{13}C{^{1}H}, and ^{51}V NMR spectra of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) A dark-brown suspension was obtained by the addition of sodium benzoate to a biphasic mixture of an aqueous solution of $VOSO_4$ and a dichloromethane solution of 4,4′-^{t}Bubpy. The organic layer was separated and layered with diethyl ether. The color of the solution turned slowly (over a few weeks) to yellow under aerobic conditions, and **1** was deposited as yellow solids (see SI). We presume that oxidation of oxovanadium(IV) species generated at first by O_2 diffused from air, and aggregation of vanadium(V) species thus formed gave rise to **1**. For recent literature concerning oxidation-driven vanadate cluster assembly using vanadium(IV) precursors, see: Forster, J.; Rösner, B.; Fink, R. H.; Nye, L. C.; Ivanovic-Burmazovic, I.; Kastner, K.; Tucher, J.; Streb, C. *Chem. Sci.* **2013**, *4*, 418−424.

(9) The windmill-shaped Rh−W[10a] and Ru−M (M = Mo, W)[10b−e] oxide cluster complexes structurally related to **1** have been reported. To our knowledge, there is no example of the homometallic oxide cluster complexes (and also heterometallic ones containing vanadium) having the above structure. Although a windmill-shaped homometallic (molybdenum) oxide cluster complex has recently been reported by Gonçalves et al.,[7c] its coordination mode of the metal centers is different from that of **1**.

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(12) Dried chloroform-*d* was used for the NMR measurement. When ^{1}H and ^{51}V NMR analysis were performed using wet chloroform-*d*, several additional signals were observed in the aromatic region of ^{1}H NMR and in the region from δ −557 to −487 of ^{51}V NMR, suggesting partial decomposition of **1** by H_2O.

(13) The ^{51}V NMR spectrum of **1** in methanol-*d* showed mainly four signals in the region from δ −557 to −473, even using a freshly prepared sample solution. We consider that **1** is immediately converted to unidentified oxovanadium(V) species in methanol and only **2** is crystallized. For recent literature concerning the solvent-controlled vanadate assembly, see: Kastner, K.; Streb, C. *CrystEngComm* **2013**, *15*, 4948−4955.

(14) BVS calculations using the bond lengths of **2** were conducted: The valences are 5.07 (V1) and 5.03 (V2) (Table S3 in the SI).

(15) A similar methoxo(oxo)vanadium(V) cluster complex, $[V_4O_8(OMe)_4(5,5'\text{-Mebpy})_2]$, has also been described in the literature by Kabanos et al.[6i]

(16) Although the mechanism for the conversion of **2** to **1** has not been clarified, we consider that **1** is formed through the dehydrative condensation of a hydroxo(oxo)vanadium(V) complex, which is generated by the reaction of **2** and a trace amount of water in a $CHCl_3$−CH_2Cl_2 mixture.