Synthesis and Structure of a New Reduced Isopolyvanadate, $[V_{17}O_{42}]^{4-}$

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Reduced heptadecavanadate $[V_{17}O_{42}]^{4-}$ has been synthesized from $[H_3V_{10}O_{28}]^{3-}$ by the reaction using palladium 1,5-COD complex, and characterized by a single crystal X-ray structure analysis. The structure can be regarded as a fused decavanadate and consists of an arrangement of thirteen edge shared VO_6 octahedra and four VO_5 square pyramids.

The structural growth of polyoxometalate by a self-assembled reaction[1] is a current interest due to their potential application as catalysts as well as nanosized molecular systems.[2] We describe here the synthesis and structure of a novel heptadecavanadate which includes a highly condensed V–O octuple-cubane core.[3]

The synthesis of reduced polyoxovanadates is a relatively recent development in polyoxometalates chemistry. While readily available V^V isopolyvanadates are mainly limited to have decavanadate structures,[4] mixed valent species exhibit unique structures, such as cage-like spherical clusters. The spherical vanadate clusters have been observed with encapsulating negative charged ions.[5,6] In this communication, we examined a polymerization growth of decavanadate in acetonitrile by using an organometallic complex as reducing reagent toward vanadium(V) atoms.

The reduced heptadecavanadate $(n\text{-}Bu_4N)_4[V_{17}O_{42}]$ (**1**), was isolated by the reductive coupling reaction of decavanadate $(n\text{-}Bu_4N)_3[H_3V_{10}O_{28}]$ with $[Pd(1,5\text{-}COD)Cl_2]$ in refluxing acetonitrile under nitrogen (Yield: 80%).[7] The reaction without using $[Pd(1,5\text{-}COD)Cl_2]$ was unsuccessful. The control experiments with other reducing agent such as sodium borohydride gave no isolable product. The decavanadate(V^V) in these reaction mixture is partly reduced to V^{IV} in the formation of **1,** and thus exposure of the reaction mixture to the atmosphere must be avoided to suppress air oxidation of reduced vanadate and organometallic fragment.[8] It should be noted that the refluxing of $[V_{10}O_{28}]^{n-}$ without $[Pd(1,5\text{-}COD)Cl_2]$ in acetonitrile produces $[CH_3CN\cdot(V_{10}O_{32}{}^{4-})]$ or $(n\text{-}Bu_4N)_3[H_3V_{13}O_{34}]$ depending on the reaction conditions.[4b,d] Complex **1** shows a characteristic IR band of $\nu(V{=}O_{terminal})$ centered at 993 cm^{-1}. The IR bands in the region 723–812 cm^{-1} were assigned to the $\nu(V–O)$ bonds.

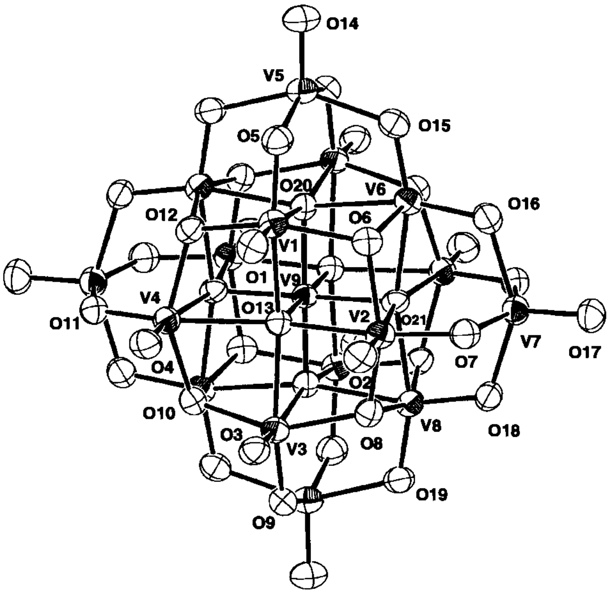

Figure 1. Structure of the $[V_{17}O_{42}]^{4-}$ anion showing the pseudo-supercubane framework. Selected distances (Å) are as follows: V–Ot, 1.574(4)-1.594(4); V–μ^2-O, 1.661(4)-2.011(4); V–μ^3-O, 1.920(4)-1.954(4); V–μ^5-O, 1.892(4)-2.366(4); V····V, 3.0736(9)-3.1196(13).

The X-ray structure determination reveals[9] two crystallographically independent anions of **1** in the asymmetric unit showing the same geometry. The structure provides a rare example of polyoxometalate framework that possesses an inversion center at the vanadium atom on the center of a core.[6] The anion shown in Figure 1 reveals that the cluster is actually regarded as an O–V–O (3 × 3 × 3) cubic closest packed distorted-supercubane (octuple cubane) core, $V_{13}O_{14}$, capped by four V=O groups. Each V=O group is bounded to the four faces of supercubane core with approximate D_{4h} symmetry. The super cubane core is distorted from the positions of an idealized cubic closest lattice. The structure of cluster anion consists of an arrangement of thirteen edge-shared VO_6 octahedra and four VO_5 square pyramids (V5 and V7). The V–O interatomic distances at V5–O20 (2.514(4)) and V7–O21 (2.479(4)) are too large to form bonds to fulfill the bond valence sum. The close structural relationship between the heptadecavanadate and decavanadate can be easily understood from the polyhedral representation in Figure 2. The heptadecavanadate may be regarded as the edge-sharing condensation of two decavanadates. The related *hetero*-tetradecavanadate, $K_7[AsV_{14}O_{40}]$ has been reported.[10] The cluster **1** has two additional V=O capping group and *iso*-polyanion framework instead of *hetero*-polyanion framework of $[AsV_{14}O_{40}]^{7-}$ which As^{5+} sits on the center.

The methyl groups of two acetonitrile molecules were found to be weakly interacted with the four terminal oxygen atoms bounded to the vanadium center at the corner of supercubane core (C_{methyl}–O1 = 3.397(8), C_{methyl}–O2 = 3.341(8), C_{methyl}–O3 = 3.298(8), C_{methyl}–O4 = 3.310(8) Å). This orientation of methyl groups of acetonitrile molecules heading toward the oxide-mimic surfaces is very interesting and has been observed in inorganic–organic hybrid type polyoxoanion supported organometallic compounds.[11] The mean bond valences for the remaining oxygen atoms of the cluster show no sign of protonation.

The redox titration[12] and bond valence sum of vanadium and oxygen suggested that the cluster is $V(V)_{12}V(IV)_5$ mixed

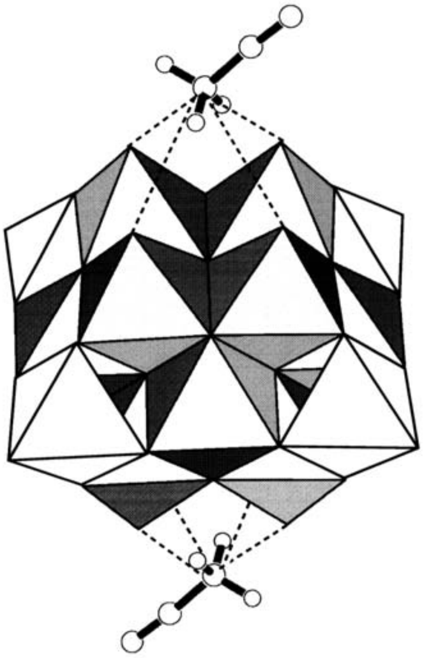

Figure 2. The polyhedral representation of **1**•2CH_3CN showing the weak interaction with acetonitrile molecules. The heptadecavanadate anion **1** is shown with VO6 units (shaded) and VO5 units(unshaded).

valence anion. The vanadium atoms at V5, V5', V7, V7' and V9 are formally regarded as V(IV) site. The deep blue-green color of **1** with a broad absorption maximum (820 nm) is characteristic of reduced polyoxovanadate. The magnetic moment at room temperature shows the value of 3.41 B.M.(per molecule), supporting the antiferromagnetic interaction between vanadium centers.[6]

In conclusion, the first example of the heptadecavanadate has been synthesized from decavanadate by the reductive coupling reaction with organometallic palladium complexes. The assembling of polyoxovanadates into larger reduced polyoxovanadates by utilizing organometallic palladates has proved to be useful, and we will continue our efforts to explore such reductive coupling synthetic strategies as well as detailed reaction pathway.

References and Notes

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6 See, for example: M. T. Pope and A. Müller *Angew. Chem., Int. Ed. Engl.*, **30**, 41 (1991) and references therein.

7 The reaction of decavanadate (n-$Bu_4N)_3[H_3V_{10}O_{28}]$ (500 mg, 0.296 mmol) with [Pd(COD)Cl_2] (124 mg, 0.436 mmol) and *p*-toluenesulfonic acid (10 mg, 0.058 mmol) in 10 cm^3 of acetonitrile at 82 °C for 24 h under nitrogen atmosphere yields an deep blue-green solution. After addition of 80 cm^3 of ether to the solution, trace amount of undissolved material was removed by filtration. Deep blue-green crystals having the composition of (n-$Bu_4N)_4[V_{17}O_{42}]$·2CH_3CN were isolated in high yield (345 mg, 80% based on V) by recrystallization from the mixture of acetonitrile and ether. The crystals were soluble in common organic solvents. Upon exposure to air the deep blue-green solution slowly decomposes to green unidentified products. Anal. Found: C, 30.92; H, 5.80; N, 2.92%. Calcd for (n-$Bu_4N)_4V_{17}O_{42}$·2CH_3CN: C, 31.54; H, 5.84; N, 3.24%. UV-vis (acetonitrile): 818 nm (ε, 3250).

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9 Crystal data for **1**·2CH_3CN: M = 2589.0, monoclinic, space group $P2/a$, a = 18.337(1), b = 23.363(1), c = 24.172(1) Å, β = 91.02(1)°, V = 10354(1) Å^3, Z = 4, Mo Kα radiation (λ = 0.71073 Å), T = –120 °C. Data were collected using the Rigaku RAXIS IV imaging plate system, and the structure was solved by direct methods. Full-matrix least-squares refinement on F^2 using SHELXL97 converged with final R_1 = 0.069 and R_w = 0.177 for 19453 independent reflections with I > 2σ(I) and 1218 parameters. Highest residual electron density 0.88 e Å^{-3}. All hydrogen atoms were included. n-Bu_4N^+ cations exhibited considerable disorder, and the part of bond lengths were constrained.

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12 The aqueous solution was titrated with permanganate under nitrogen to give 5.0 V(IV) per V_{17} core.