A Stepwise Growth of Polyoxovanadate by Reductive Coupling Reaction with Organometallic Palladium Complex: Formation of $[\{(\eta^3\text{-}C_4H_7)Pd\}_2V_4O_{12}]^{2-}$, $[V_{10}O_{26}]^{4-}$ and $[V_{15}O_{36}(Cl)]^{4-}$

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The three step synthesis of pentadecavanadate, $(n\text{-}Bu_4N)_4[V_{15}O_{36}(Cl)]$ has been achieved by a stepwise growth process. The reaction of $(n\text{-}Bu_4N)VO_3$ with $[(\eta^3\text{-}C_4H_7)PdCl]_2$ gives a tetravanadate supported organometallic compound $[\{(\eta^3\text{-}C_4H_7)Pd\}_2V_4O_{12}]^{2-}$. The thermal decomposition of $[\{(\eta^3\text{-}C_4H_7)Pd\}_2V_4O_{12}]^{2-}$ leads to the formation of reduced species $[V_{10}O_{26}]^{4-}$, which is then converted into a larger cluster $[V_{15}O_{36}(Cl)]^{4-}$.

The chemistry of reduced polyoxovanadates which exhibit non-carbon cage structures like fullerenes has developed in the last decade.[1] A series of spherical vanadium oxides formed by linking of VO_n polyhedra allows an inclusion of anionic guest in the cage.[2] These condensed VO_n polyhedra have been prepared based on self-assemble process by control of pH values in aqueous media by one step reaction. The syntheses of reduced vanadate in organic media have been undeveloped due to the lack of synthetic methodology. In this communication, we describe the three step synthesis of pentadecavanadate in acetonitrile, which constructs the vanadium oxide cage structures without a pH control.

The first step is the supporting reaction to the organometallic palladium species. The tetravanadate supported organometallic palladium complex $[\{(\eta^3\text{-}C_4H_7)Pd\}_2V_4O_{12}]^{2-}$ (**1**) was obtained by the reaction of $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ (236 mg, 0.6 mmol) with $(n\text{-}Bu_4N)VO_3$ (410 mg, 1.2 mmol) in 5 cm^3 of acetonitrile (Yield: 313 mg, 43%).[3] The crystal structure of PPh_4 salts of **1**[4] reveals the tetravanadate supported organopalladium complex.[5] The cyclic tetravanadate structure was supported by two $(\eta^3\text{-}C_4H_7)Pd$ groups on both side of the tetravanadate ring with an inversion center on the center of the molecule. The geometrical data are in agreement with the available structures of tetravanadate supported compounds of Rh or Ir.[5]

The four vanadium atoms and the bridging oxygens O(4) and O(4') are found to be planar (deviation is 0.080(5) Å for O(4)) which is a part of the V_4O_4 eight membered ring. The square plane around Pd(1) is defined by the C(1), C(3), O(1'), and O(6) atoms (largest deviation from the mean plane is 0.067(4) Å for C(3) and the palladium atom is 0.092(3) Å out of this plane). The planes defined by the V(1)-V(2)-V(1')-V(2') and C(1)-C(3)-O(1')-O(6) sets of atoms form a dihedral angle of 43.8(1)°.

The second step is the thermal decomposition of **1**. 10 cm^3 of the pale yellow acetonitrile solution of **1** (241 mg, 0.20 mmol) was refluxed for 2 h under N_2 atmosphere to give a condensed cluster $(n\text{-}Bu_4N)_4[V_{10}O_{26}]\cdot H_2O$ (**2**) (Yield: 50 mg, 33%).[6] The X-ray structure determination reveals the spherical structure which has a cyclic octavanadate capped by the two V(IV) tetragonal pyramids (Figure 2).[7] The average bond parameters for **2** are seen to be similar to those previously

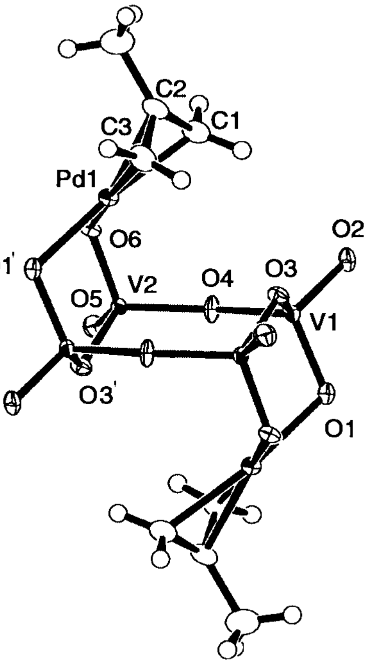

Figure 1. Structure of the $[\{(\eta^3\text{-}C_4H_7)Pd\}_2V_4O_{12}]^{2-}$ anion. Selected distances (Å) are as follows: Pd(1)–O(1'), 2.126(4); Pd(1)–O(6), 2.119(3); Pd(1)–C(1), 2.126(5); Pd(1)–C(2), 2.130(5); Pd(1)–C(3), 2.104(5); V(1)–O(1), 1.676(3); V(1)–O(2), 1.623(3); V(1)–O(3), 1.805(3); V(1)–O(4), 1.790(3); V(2)–O(3'), 1.807(3); V(2)–O(4), 1.785(3); V(2)–O(5), 1.614(3); V(2)–O(6), 1.685(3).

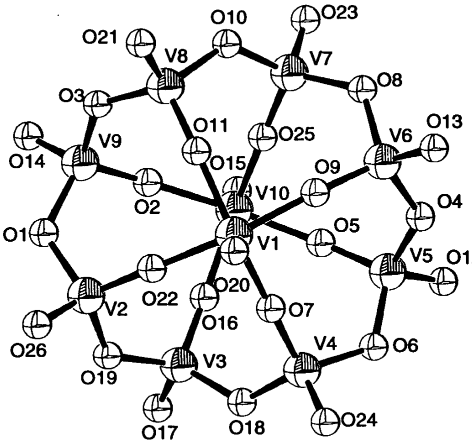

Figure 2. Structure of the $[V_{10}O_{26}]^{4-}$ anion. Selected distances (Å) are as follows: V(V)–Ot, 1.58(1)–1.63(1); V(V)–Ob, 1.64(1)–1.82(1); V(IV)–Ot, 1.59(1)–1.58(1); V(IV)–Ob, 1.90(1)–1.96(1); V(IV)···V(IV), 4.500(4); V(V)···V(V), 3.208(5)–3.310(4);V(IV)···V(V), 3.556(4)–3.609(4).

observed in tetraethylammonium salt of $[V_{10}O_{26}]^{4-}$ core.[8] In the case of **2**, absence of hydrogen bonds from the packing water molecule elongates the V^{IV}–V^{IV} bonds 0.6 Å compared to the tetraethylammonium salt (V^{IV}–V^{IV} 4.44 Å).

The last step is the reaction with organometallic palladium without the isolation of supported species. The mixture of **2** (382 mg, 0.20 mmol) and [Pd(cod)Cl$_2$] (114 mg, 0.40 mmol) in 10 cm^3 acetonitrile was refluxed overnight. After addition of 30 cm^3 of ether, the black precipitate was washed with ether three times and recrystallized from acetonitrile/ether to give deep blue crystal of $(n\text{-}Bu_4N)_4[V_{15}O_{36}(Cl)]$ (**3**) (Yield 270 mg, 86%).[9] The ORTEP[10] drawing is shown in Figure 3. The $[V^{IV}{}_6V^{V}{}_9O_{36}(Cl)]^{4-}$ anion is a spherical cluster (D_{3h}) by linkage of fifteen tetragonal VO$_5$ pyramids encapsulating chloride anion and formally contains six V^{IV} and nine V^{V} centers. The V–V distances (2.83–3.03 Å) are significantly shorter than the values of reported V$_{15}$ clusters (3.2–3.6 Å) which have higher negative charges of 6– to 7–.[11] This is due to the lower negative charge of cluster **3** which decreases the cluster shell size and shortens the metal-metal distances.

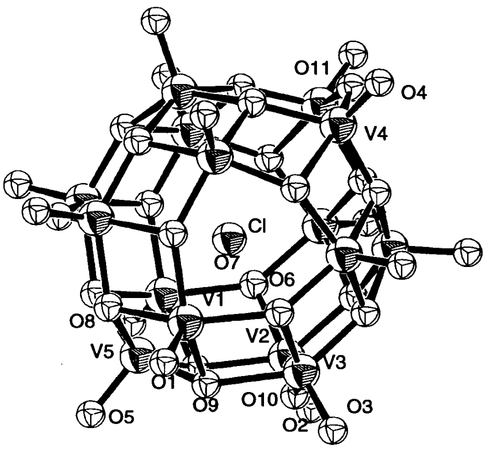

Figure 3. Structure of the $[V_{15}O_{36}(Cl)]^{4-}$ anion. Selected distances (Å) are as follows: V–Ot, 1.46(9)–1.59(2); V–Ob, 1.78(1)–2.15(2); V···V, 2.821(7)–3.033(6); V···Cl, 3.070(6)–3.704(6).

The mean bond valences for the remaining oxygen atoms of the cluster show no sign of protonation. The intense purple color of **3** with a broad absorption maximum (898 nm) is characteristic of reduced polyoxovanadate. The magnetic moment at room temperature shows the value of 2.35 B.M. (spin only value is 4.24 B.M.) supporting the strong antiferromagnetic interaction between vanadium centers compared to the highly negative charged species.[11] The observation is consistent with the web of short V−V distances around the spherical cluster.

In conclusion, the synthesis of pentadecavanadate has been achieved by the following three reaction steps: 1) supporting reaction of tetravanadate to π-allyl palladium complex **1**, 2) formation of spherical cluster **2** by the thermal decomposition of **1**, and 3) reductive coupling of decavanadate with [Pd(cod)Cl$_2$] which leads to a chloride included cluster **3**. The reductive coupling reaction of polyoxovanadate by the use of organometallic compound is attractive in that it provides an easy access to a larger polyoxovanadate core.

References and Notes

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3 Anal. Found: C, 39.70; H, 7.90; N, 2.26%. Calcd for $(n\text{-}Bu_4N)_2[\{Pd(\eta^3\text{-}C_4H_7)\}_2V_4O_{12}]$: C, 39.91; H, 7.20; N, 2.33%. IR (Nujol, 500–1100 cm^{-1}): 955 (vs), 920 (w), 897 (w), 868 (m), 831 (m), 798 (s), 733 (vs). ^{1}H NMR (400 Mz, CD$_3$CN, 26 °C): δ (ppm) = 0.97 (t, 24H, Bu-CH$_3$), 1.37 (m, 16H, Bu-CH$_2$), 1.62 (q, 16H, Bu-CH$_2$), 2.15 (s, 6H, allyl-CH$_3$), 3.10 (s, 4H, allyl-CH$_2$), 3.12 (t, 16H, Bu-CH$_2$), 3.58 (s, 4H, allyl-CH$_2$). ^{13}C{^{1}H} NMR (400 Mz, CD$_3$CN, 28 °C): δ (ppm) = 13.85 (s, Bu-CH$_3$), 20.39 (s, Bu-CH$_2$), 23.24 (s, allyl-CH$_3$), 24.41 (s, Bu-CH$_2$), 57.54 (s, allyl-CH$_2$), 59.39 (s, Bu-CH$_2$), 129.73 (s, allyl-CH$_2$) ^{51}V NMR (400 Mz, CD$_3$CN, 28 °C, VOCl$_3$): δ(ppm) = –504 (s).

4 The PPh$_4$ salts of **1** which is suitable for crystal structure determination was prepared by mixing PPh$_4$BF$_4$ and **1** in acetonitrile. Anal. Found: C, 48.04; H, 3.83%. Calcd for $(PPh_4)_2[\{Pd(\eta^3\text{-}C_4H_7)\}_2V_4O_{12}]$: C, 48.13; H, 3.89%. Crystal data for (PPh$_4$)$_2$·**1**: M = 1396.9, triclinic, space group $P\bar{1}$, a = 10.1853(4), b = 11.1980(10), c = 13.2760(8) Å, α = 86.219(4)°, β = 71.471(4)°, γ = 77.186(2)°, V = 1399.9(1) Å^3, Z = 1, Mo Kα radiation (λ = 0.71073 Å), T = –120 °C. R_1 = 0.0632 (wR_2 = 0.118) for 6005 independent reflections with $I > 2\sigma(I)$ and 343 parameters. Highest residual electron density 0.495 e·Å^{-3}.

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6 Anal. Found: C, 40.29; H, 7.24; N, 3.01%. Calcd for $(n\text{-}Bu_4N)_4V_{10}O_{26}\cdot H_2O$ ($C_{64}H_{146}N_4O_{27}V_{10}$): C, 40.18; H, 7.69; N, 2.93%. IR (Nujol, 500–1100 cm^{-1}): 997 (m), 970 (s), 957 (s), 926 (s), 891 (vs), 843 (s), 659 (s).

7 Crystal data for **2**·H$_2$O: M = 1912.5, orthorhombic, space group $P2_12_12_1$, a = 17.0517(9), b = 33.777(2), c = 16.7948(8) Å, V = 9673.0(9) Å^3, Z = 4, Mo Kα radiation (λ = 0.71070 Å), T = –120 °C. R_1 = 0.084 (wR_2 = 0.207) for 6114 independent reflections with $I > 2\sigma(I)$ and 1015 parameters. Highest residual electron density 0.782 e·Å^{-3}. All hydrogen atoms were included. n-Bu$_4$N$^+$ cations exhibited considerable disorder, and the parts of bond lengths were constrained.

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9 Anal. Found: C, 32.76; H, 6.28; N, 2.35; Cl, 1.50%. Calcd for $(n\text{-}Bu_4N)_4[V_{15}O_{36}(Cl)]$ ($C_{64}H_{144}ClN_4O_{36}V_{15}$): C, 32.77; H, 6.19; N, 2.39; Cl, 1.51%. IR (Nujol, 500–1100 cm^{-1}): 997 (s, br), 980 (s, sh), 887 (m), 874 (m), 798 (m).

10 Crystal data for **3**: M = 2344.1, tetragonal, space group $P4_22_12$, a = 16.482(1), c = 17.860(1) Å, V = 4851.5(6) Å^3, Z = 2, Mo Kα radiation (λ = 0.71070 Å), T = 20 °C. R_1 = 0.072 (w_2 = 0.178) for 2036 independent reflections with $I > 2\sigma(I)$ and 285 parameters. Highest residual electron density 0.301 e·Å^{-3}. The anion is on a four-fold rotary inversion axis through O(11), Cl, V(5) and O(5) with an inversion point at the position of Cl. Thus, the anion occupying each site in two orientations resulting in the disorder between [V(4)=O(4)–O(11)–V(4')=O(4')] group and V(5)=O(5) group(1:1).

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