# Synthesis of a Reduced Tridecavanadate Dimer Linked by Eight Hydrogen Bonds

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The reaction of highly condensed heptadecavanadate with labile metal compound gave the first reduced tridecavanadate with hydrogen bonds to make a novel dimeric structure: the protonated and reduced sites were unambiguously determined by X-ray analysis. The reduced tridecavanadate was not directly converted chemically or electrochemically into the oxidized form.

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Polyoxometalates have been attracting much attention in the fields of catalysis,[1] magnetism,[2] and pharmaceutical chemistry.[3] Polyoxovanadates have a unique structural chemistry due to the availability of various coordination environments such as tetrahedral $\{VO_4\}$, square-pyramidal $\{VO_5\}$, and octahedral $\{VO_6\}$ building units. Recently, new inorganic host–guest and supramolecular chemistries have been developed using the "reduced forms" of polyoxovanadates containing V(IV) atoms. These are composed of the square-pyramidal $\{VO_5\}$ units, as seen in $[V_{15}O_{36}(Cl)]^{5-}$,[4] $[V_{18}O_{42}(X)]^{n-}$,[5] ($X = H_2O$, $Cl^-$, $Br^-$, $I^-$), $[V_{22}O_{54}(ClO_4)]^{7-}$,[6] and $[V_{34}O_{82}]^{10-}$.[7] On the other hand, the corresponding chemistry based on the reduced forms with the octahedral $\{VO_6\}$ units has not been explored. In an effort to establish the synthetic method of such polyoxovanadates, we utilized the recently prepared $[V^V{}_{12}V^{IV}{}_5O_{42}]^{4-}$ anion[8] as a starting material consisting of the octahedral $\{VO_6\}$ units with V(V) and V(IV) atoms to generate a reduced polyoxovanadates by simple fragmentation of the $V_{17}$ framework induced by Lewis acids. Here, we report the synthesis of the reduced $[H_4V^V{}_9V^{IV}{}_4O_{34}]^{3-}$ which can not be prepared directly from the corresponding oxidized form of $[V^V{}_{13}O_{34}]^{3-}$.[9]

In acetonitrile, the treatment of $[(n\text{-}C_4H_9)_4N]_4[V^V{}_{12}V^{IV}{}_5O_{42}]$ with the Lewis acid, $[Cu(CH_3CN)_4]BF_4$ gave deep blue crystals of $[(n\text{-}C_4H_9)_4N]_4[H_4V^V{}_9V^{IV}{}_4O_{34}]$.[10] The compounds, $AgBF_4$, $Pd(PhCN)_2Cl_2$, and $VOCl_2$ also work as the Lewis acid, but *p*-TsOH and $CCl_3COOH$ do not give the product and give unknown insoluble greenish yellow precipitate. The reduced $[(n\text{-}C_4H_9)_4N]_4[H_4V^V{}_9V^{IV}{}_4O_{34}]$ is stable in both solid and solution: The deep blue color of the acetonitrile solution is maintained over a week. The color is characteristic of reduced polyoxovanadates. The electronic spectra show a broad absorption band at 680 nm ($\varepsilon = 2300$) which is attributed to the charge transfer between V(IV) and V(V). The IR spectra show distinct bands assignable to $\nu(V{=}O_{terminal})$ at 993, 979, and 952 $cm^{-1}$ and $\nu(V\text{–}O_{bridge})$ within the range of 574–821 $cm^{-1}$.

The X-ray structure[11] of the polyoxoanion is shown in Figure 1. The anion is composed of thirteen $\{VO_6\}$ units sharing the edge of the octahedra forming sodium chloride type close-packed cluster. Comparison of the bond lengths between $[H_4V^V{}_9V^{IV}{}_4O_{34}]^{3-}$ and $[V^V{}_{13}O_{34}]^{3-}$ reveals the volume expansion of the cluster framework due to the four electron reduction. The average distances of V=O, V–$\mu^2$-O, V–$\mu^3$-O, and V–$\mu^6$-O in the reduced form are 1.597, 1.859, 1.984, and 2.243 Å, respectively. Those of the oxidized form are 1.581, 1.828, 1.960, and 2.233 Å, respectively.

Redox titration also indicates that there are four V(IV) centers in the cluster. The bond-valence sum calculations based on the X-ray data[12] display that the reduced sites are V(3), V(5), V(7), and V(13) with the bond-valence values, 4.26, 4.28, 4.14, and 4.29, respectively. The rest of vanadiums fall in the range between 4.72–5.02. The reduced sites occupy the farthest positions from one another in the vanadate framework to minimize the inhomogeneity in the charge, occupying the vertices of pseudotetrahedral geometry.

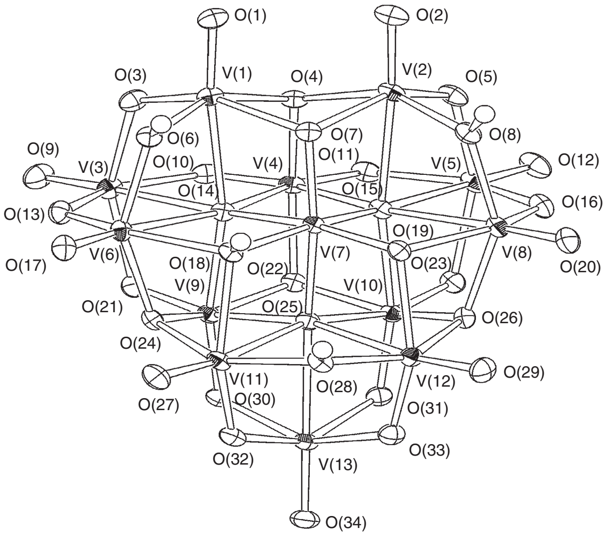

**Figure 1.** ORTEP view of $[H_4V_{13}O_{34}]^{3-}$ anion. Selected distances (Å) are as follows: V(IV)=O, 1.597(2)–1.601(3); V(V)=O, 1.585(3)–1.608(3); V(IV)–$\mu_2$-O, 1.928(2)–2.011(2); V(V)–$\mu_2$-O, 1.675(2)–1.964(2); V(IV)–$\mu_3$-O, 1.809(2)–1.998(2); V(V)–$\mu_3$-O, 1.917(2)–2.163(2); V(IV)–$\mu_6$-O, 1.960(2)–2.456(2); V(V)–$\mu_6$-O, 2.133(2)–2.424(2).

The cluster is dimerized through eight hydrogen bonds, and the protonated sites were also confirmed by bond valence calculations: the bond valence sums of O(6), O(8), O(18), and O(28) are 1.36, 1.31, 1.38, and 1.36, respectively. A similar dimeric structure was reported for $[H_3V_{10}O_{28}]^{3-}$ with six hydrogen bonds.[13]

Electrochemical study shows one irreversible three-electron oxidation wave ($E_a = 0.71$ V) and two reversible one-electron waves. One reversible oxidation wave at −0.31 V ($E_{1/2}$) is attributed to the formation of the $V_8{}^VV_5{}^{IV}$ species and the other reduction wave at +0.21 V ($E_{1/2}$) is attributed to that of $V_{10}{}^VV_3{}^{IV}$. The four electron oxidation of the reduced form resulted in the solution color change from deep blue to brown, and $[V_{12}O_{32}(CH_3CN)]^{4-}$[14] was isolated, which was confirmed by the IR and NMR spectra by comparison of those of the authentic

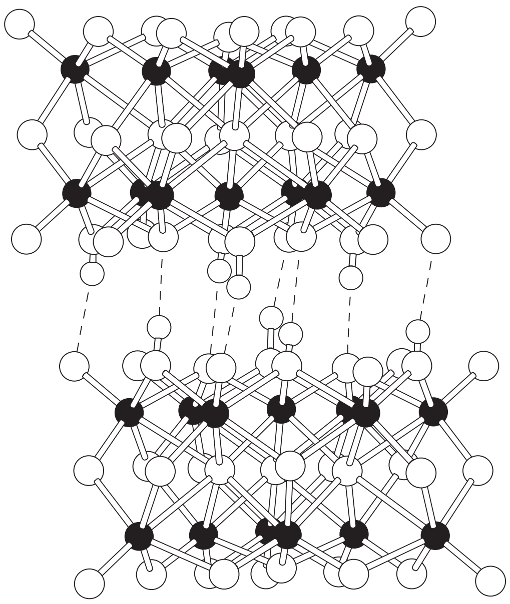

**Figure 2.** Perspective view of the $(H_4V_{13}O_{34})_2{}^{6-}$ dimer. The dotted line indicates the hydrogen bonds. O(6)···O(19) = 2.715, O(8)···O(17) = 2.723, O(18)···O(7) = 2.763, O(28)···O(1) = 2.732 Å.

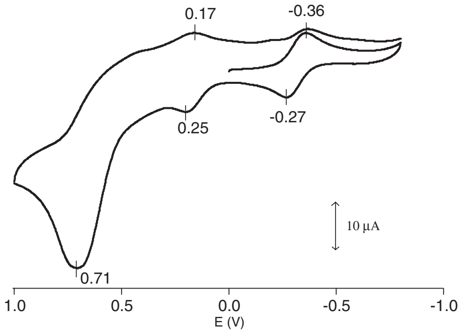

**Figure 3.** Cyclic voltammogram of 1 mM $[H_4V_{13}O_{34}]^{3-}$ in acetonitrile with 1 M $[(n\text{-}C_4H_9)_4N]ClO_4$ supporting electrolyte at scan rate 100 mV/s referenced to Ag/AgCl. The potential for 1 mM ferrocene, $E^\circ = 0.082$ V was observed.

sample. This result indicates the conversion between the oxidized tridecavanadate and reduced one is irreversible. It is also noted that the cyclic voltammogram of the oxidized form shows only two reversible one electron reduction waves.

In summary, the reaction of $[V_{17}O_{42}]^{4-}$ in acetonitrile gives the reduced $[H_4V_{13}O_{34}]^{3-}$ anion which has the dimeric structure through eight hydrogen bonds. The interconversion of tridecavanadate between oxidized form and reduced form is irreversible electrochemically.

## References and Notes

1 a) R. Neumann and M. Gara, *J. Am. Chem. Soc.*, **117**, 5066 (1995). b) X. Zhang, T. M. Anderson, Q. Chen, and C. L. Hill, *Inorg. Chem.*, **40**, 418 (2001). c) O. A. Kholodeeva, G. M. Maksimov, R. I. Moksimovskaya, L. A. Kovaleva, M. A. Fedotov, V. A. Grigoriev, and C. L. Hill, *Inorg. Chem.*, **39**, 3828 (2000). d) X. Zhang, Q. Chen, D. C. Duncan, C. F. Campana, and C. L. Hill, *Inorg. Chem.*, **36**, 4208 (1997).

2 a) J. M. Clemente-Juan, E. Coronado, J. R. Galan-Mascaros, and C. J. Gomez-Garicia, *Inorg. Chem.*, **38**, 55 (1999). b) C. J. Gomez-Garicia, J. J. Borras-Almenar, E. Coronado, and L. Ouahab, *Inorg. Chem.*, **33**, 4016 (1994).

3 D. A. Judd, J. H. Nettles, N. Nevins, J. P. Snyder, D. C. Liotta, J. Tang, J. Ermolieff, R. F. Schinazi, and C. L. Hill, *J. Am. Chem. Soc.*, **123**, 886 (2001).

4 A. Müller, E. Krickemeyer, M. Penk, H.-J. Walberg, and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, **26**, 1045 (1987).

5 A. Müller, R. Sessoli, E. Krickemeyer, H. Bögge, J. Meyer, D. Gatteschi, L. Pardi, J. Westphal, K. Hovemeier, R. Rohlfing, J. Döring, F. Hellweg, C. Beugholt, and M. Schmidtmann, *Inorg. Chem.*, **36**, 5239 (1997).

6 A. Müller, E. Krickemeyer, M. Penk, R. Rohlfing, A. Armatage, and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, **30**, 1674 (1991).

7 A. Müller, R. Rohlfing, J. Döring, and M. Penk, *Angew. Chem., Int. Ed. Engl.*, **30**, 588 (1991).

8 Y. Hayashi, K. Fukuyama, T. Takatera, and A. Uehara, *Chem. Lett.*, **2000**, 770.

9 D. Hou, K. S. Hagen, and C. L. Hill, *J. Am. Chem. Soc.*, **114**, 5864 (1992).

10 A mixture of 300 mg (0.12 mmol) of $[(n\text{-}C_4H_9)_4N]_4[V_{17}O_{42}]$ and 40 mg (0.12 mmol) of $[Cu(CH_3CN)_4](BF_4)$ in 10 $cm^3$ of acetonitrile was stirred for one day at room temperature under nitrogen atmosphere. To the resulting deep blue solution was added 10 $cm^3$ of ether and the mixture was allowed to stand for one day. Deep blue crystals of $[(n\text{-}C_4H_9)_4N]_3$-$[H_4V_{13}O_{34}]$ were collected and washed with ether. Yield: 130 mg (43% based on V). Found: C, 29.39; H, 5.74; N, 2.23%. Calcd for $C_{48}H_{112}N_3O_{34}V_{13}$: C, 29.75; H, 5.82; N, 2.17%. IR (Nujol, 1000–500 $cm^{-1}$): 993, 979, 952, 887, 821, 734, 574. UV–vis (acetonitrile): 680 nm ($\varepsilon$, 2300).

11 Crystal data for $[(n\text{-}C_4H_9)_4N]_3[H_4V_{13}O_{34}]\cdot CH_3CN$: $M_r = 2061.62$, triclinic, space group $P\bar{1}$, $a = 15.315(1)$, $b = 15.501(4)$, $c = 18.424(9)$ Å, $\alpha = 107.632(1)$, $\beta = 99.236(2)$, $\gamma = 104.248(7)^\circ$, $V = 3907.282(3)$ Å$^3$, $Z = 2$, Mo K$\alpha$ radiation $\lambda = 0.71073$ Å $T = -150$ °C. Data were collected using the Rigaku Mercury CCD system, and the structure was solved by direct methods. Full-matrix least-squares refinement on $F^2$ using SHELXL97 converged with final $R_1 = 0.055$ and $R_w = 0.146$ for 15759 independent reflections with $I > 2\sigma(I)$ and 931 parameters. The positions of the hydrogen atoms were located by the difference Fourier map considering with the bond valence information.

12 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect B*, **B41**, 244 (1985).

13 V. W. Day, W. G. Klemperer, and D. J. Maltbie, *J. Am. Chem. Soc.*, **109**, 2991 (1987).

14 V. W. Day, W. G. Klemperer, and O. M. Yaghi, *J. Am. Chem. Soc.*, **111**, 5959 (1989).

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