Self-assembled All-inorganic Chiral Polyoxovanadate: Spontaneous Resolution of Nitrate-incorporated Octadecavanadate

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(Received February 13, 2008; CL-080165; E-mail: hayashi@kenroku.kanazawa-u.ac.jp)

A chiral octadecavanadate has been isolated and optically resolved into enantiomers by spontaneous resolution. From the partial oxidation reaction of a reduced decavanadate $[V_{10}O_{26}]^{4-}$ with nitric acid, a chiral octadecavanadate encapsulating a nitrate template was formed. A nitrate anion was incorporated at the center of the spherical polyoxovanadate cage. The structure may be regarded as a double helical V8 ribbon between two square pyramidal $V^{VI}O_5$ units, consisting of half-pitch helix with ca. 11.0 Å diameter and a half pitch length of 8 Å.

For decades, self-assembled inorganic architectures like helicates,[1] an artificial equivalent of double-stranded DNA molecules, have been investigated through the control of ligands and metal systems.[2] Enantiopure polyoxometalates for which the rational synthesis of the metal oxide frameworks are much more difficult, have also been sought for potential applications such as asymmetric catalysts.[3] A key advantage of chiral metal oxide molecules[4] over carbon-based asymmetric compounds is their high thermal stability. Recent work in our laboratory has focused on reductive coupling methods for the controlled synthesis of reduced polyoxovanadates.[5] In this paper, the discovery of a discrete inorganic double helical compound of reduced polyoxovanadate is described, taking advantage of the versatility of vanadate coordination environments.

To design spherical polyoxovanadates, we applied self-condensation methods that are the partial oxidation of reduced species. To prompt the self-condensation reaction, we used a self-coupling method between a nucleophilic reduced species and an electrophilic V^{V} species that are prepared in situ by partial oxidation. The reduced polyoxovanadate prefers VO_5 square-pyramidal coordination, and tends to form a spherical cage-like structure.[6] When an appropriate template anion is added to the condensation reaction, it produces template-incorporated spherical polyoxovanadates. We used the reduced decavanadate, $[V_{10}O_{26}]^{4-}$, which is the smallest spherical polyoxovanadate without template incorporation, as a starting material for the preparation of template encapsulating spherical vanadates.

When an oxidation reaction of the reduced decavanadate with *t*-butylhydroperoxide was performed with the nitrate template anion in nitroethane, the reaction gave a deep green octadecavanadate, $[V^{V}{}_{16}V^{IV}{}_{2}O_{46}(NO_3)]^{5-}$ (**1**).[7] Complex **1** exhibits an intense broad absorption band centered near 911 nm (550–1500 nm, ε 3892 $mol^{-1}\,dm^{3}\,cm^{-1}$), indicative of the inter valence band between V^{V} and V^{VI} centers. The crystal structure[8] shows the two reduced V^{VI} sites localized at V16 and V17 where the vanadiums have a square-pyramidal coordination. The nitrate anion is encapsulated at the center of the cavity as shown in Figure 1.

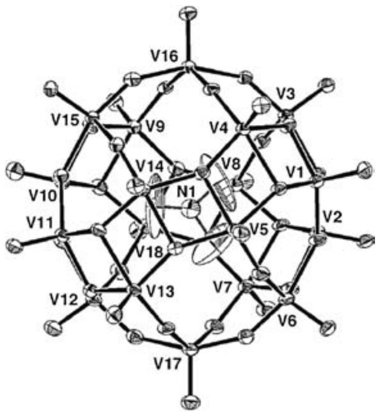

Figure 1. ORTEP representation of cluster anion **1**.

Three N–O stretchings in the IR spectra were observed at 1380, 1359, and 1342 cm^{-1} as expected for its local C_{2v} symmetry.[9] The flat shape of the nitrate anion is reflected in the cluster shape. The polyoxovanadate anion is constructed by the arrangement of two identical V8 ribbon (V3, V1, V4, V5, V14, V13, V11, V12 and V15, V10, V9, V18, V8, V7, V2, V6) which are composed by edge sharing of eight $V^{V}O_5$ pyramids, and the two ribbons were arranged into spiral form around the nitrate. The molecule crystallized in the non-centrosymmetric space group $P2_12_12_1$ and the absolute structure was determined as the right-handed screw arrangement for a given crystal which is optically resolved into an enantiomer by spontaneous resolution. Manual separation of the chiral crystals was impossible due to the quick efflorescence of the crystal.

It is very interesting that Zubieta's group reported the double helical polyoxovanadate, $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$ by hydrothermal technique[10] which has an infinite chain of double helix formed from interpenetrating spirals of vanadium oxo pentamers bonded together by P^{5+}. The B-form DNA like stacking (stacking distance 3.4 Å) of the nucleotide-supported polyoxomolybdate was also reported.[11] Our case may be regarded as a first example of discrete polyoxometalates with helical chirality.

Two types of V18 cages have been reported with the composition, $[V_{18}O_{42}(X)]^{n-}$ ($X = Cl^{-}$, Br^{-}, I^{-}, and $CO_3{}^{-}$) or $[V_{18}O_{44}(X')]^{n-}$ ($X' = N_3{}^{-}$ and $NO_3{}^{-}$) with the incorporation of various types of an anion template.[12] Both compounds have highly symmetrical structure when compared to our case, and have 14th Archimedean solid (T_d) and rhombicuboctahedron (D_{4d}) geometry, respectively. In the precedented nitrate incorporated polyoxovanadate, $[HV_{18}O_{44}(NO_3)]^{10-}$ has no helicity, and shows only one N–O stretching in the IR spectra. The weak interaction between the guest nitrate and the VO cage may be the cause, because of a larger cluster core, with fewer oxygen atoms having higher negative charges and protonations.[13,14] Generally, the use of a small water-soluble cation may produce highly neg-

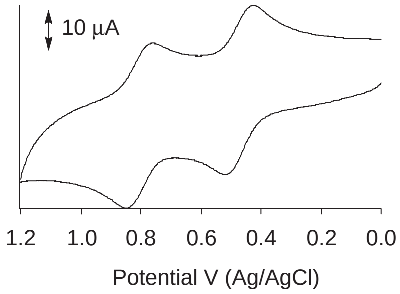

Figure 2. Cyclic voltammogram of 1 mM $[V^V{}_{16}V^{IV}{}_2O_{46}(NO_3)]^{5-}$ in acetonitrile (0.1 M $[(n\text{-}C_4H_9)_4N]ClO_4$ supporting electrolyte, scan rate 100 mV/s) referenced to Ag/AgCl.

ative-charged species. The exploitation of the bulky organic cations in our case restricts the formation of high-negative-charged species, resulting in the isolation of a V18 cage with a large number of oxygen atoms. In contrast to the symmetric predecessor, our molecule has the minimum unit of a double helix capped by two square pyramidal V^{IV} units as molecular entity, prepared from very simple sources, only nitric acid and iso-polyoxovanadates.

Cluster **1** shows two reversible redox waves in cyclic voltammetry in acetonitrile at $E_{1/2} = 0.47$ and $E'_{1/2} = 0.81$ V vs. Ag/AgCl (Figure 2). The results of coulometry at 0.68 and 1.1 V suggest that each reversible step is a one-electron process.

$$\underset{\textit{isolated form}}{[V^{IV}{}_2V^V{}_{16}]^{5-}} \rightleftharpoons [V^{IV}V^V{}_{17}]^{4-} \rightleftharpoons [V^V{}_{18}]^{3-} \qquad (1)$$

The V8 units which constitute a helical ribbon have valence state V^V, therefore the stepwise two-electron oxidation sites that are attributed to the square-pyramidal V^{IV} units sit on top and bottom of the anion.

Magnetic susceptibility measurements of microcrystalline samples of **1** show almost no interaction between the V^{IV} centers. The temperature-dependent susceptibilities were derived from the general isotropic exchange of two $S = 1/2$ centers.[15] Curve fittings over the temperature range 4–200 K gave $g = 1.99$, $J = 0.29\,\text{cm}^{-1}$, TIP (temperature independence paramagnetism) $= 1.39 \times 10^{-3}$ with 0.52% Curie–Weiss-type paramagnetic impurity.

In summary, a polyoxovanadate having an inorganic double helix has been synthesized and its absolute structure has been determined. What makes it remarkable is that the two V8 ribbons form helices themselves with the nitrate anion template and form a chiral molecule without any organic parts: no amino acids, no proteins, not even a C–C bond. Instead, the framework is constructed with the linkages of a VO_5 pyramidal oxide cage. They are the first polyoxovanadate with the framework of a double helix, and further investigations on the interactions with DNA will be interesting.

This work was partly supported by a Grant-in-Aid for Scientific Research, No. 16550051 from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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7 A 0.379 g (0.20 mmol) of $(n\text{-}Bu_4N)_4[V_{10}O_{26}]$ is dissolved in 20 mL of nitroethane, and 20 μL of nitric acid is slowly added to the solution. A 0.06 g of 80% *tert*-BuOOH was then added to the solution. The resulting mixture is stirred for a few days. Any insoluble brown material is removed by filtration, and the filtrate is left to crystallize with the addition of diethyl ether. Isolated yield was 43% based on vanadium. Anal. Calcd for $(n\text{-}Bu_4N)_5[V_{18}O_{46}(NO_3)]\cdot(C_2H_5NO_2)_3$: C, 32.76; H, 6.23; N, 4.00%. Found: C, 32.67; H, 6.24; N, 4.02%. IR (KBr, 500–1500 cm^{-1}): 528(w), 570(m), 632(vs), 784(s), 835 (s), 837(w), 993(vs), 1342(w), 1359(w), 1380(w).

8 The diffraction data were collected with Rigaku/MSC Mercury diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71070$ Å) at −150 °C. Crystal data for **1**: $C_{86}H_{195}N_9O_{55}V_{18}$, 3152.5 g mol^{-1}, orthorhombic $P2_12_12_1$, $a = 19.7196(16)$ Å, $b = 21.0455(17)$, $c = 33.937(3)$, $V = 14084.2(2)$ Å^3, $Z = 4$, $d = 1.556\,\text{g cm}^{-3}$, $T = 123$ K, $\mu = 12.17\,\text{cm}^{-1}$, $F(000) = 6452$, $2\theta_{\max} = 53$, $S = 1.15$, flack parameter $= 0.00(2)$. The structure was solved by direct methods and refined on F^2 to $R_1(wR_2)$ 0.069(0.202) using 28818 reflections with $I > 2\sigma(I)$.

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Published on the web (Advance View) April 26, 2008; doi:10.1246/cl.2008.578