A Novel Decavanadium(V) Cluster with a Chiral Framework: $[(O{=}V)_{10}(\mu_2\text{-}O)_9(\mu_3\text{-}O)_3(C_5H_7O_2)_6]$ Having an Approximate C_3 Symmetry

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Herein we report the preparation, isolation, and structural determination of a remarkable high-nuclearity vanadium(V) cluster, $[(O{=}V)_{10}(\mu_2\text{-}O)_9(\mu_3\text{-}O)_3(C_5H_7O_2)_6]$, (**1**). This investigation has particular significance in that vanadium cluster has become especially important in a wide variety of heterogeneous oxidation chemistry including commercial reactions such as oxidation of butane to maleic anhydride,[1] and its possible utilization as a cathode material for lithium batteries has been extensively studied.[2] Furthermore, the V−O−V core was recently shown by the authors to possess marked catalytic activities not only in the 4-electron electroreduction of O_2 to H_2O[3] but also in the O_2 oxidative polymerization of organosulfur molecules such as diphenyl disulfide and thioanisole to produce poly(*p*-phenylene sulfide), an important engineering plastic.[4]

The chemistry of high-nuclearity oxovanadium(V) clusters incorporating oxygen donor ligands has been dominated by a decavanadate ion $V_{10}O_{28}^{6-}$ which has been isolated as alkali metal salts.[5] Structural investigations of the $V_{10}O_{28}^{6-}$ ion have been performed on the three compounds $K_2Zn_2V_{10}O_{28}\cdot 16H_2O$, $Ca_3V_{10}O_{28}\cdot 16H_2O$, and $Na_6V_{10}O_{28}\cdot 18H_2O$, which revealed that in each case the anion is a discrete unit of VO_6 octahedra and the complex ion has D_2 symmetry.[6]

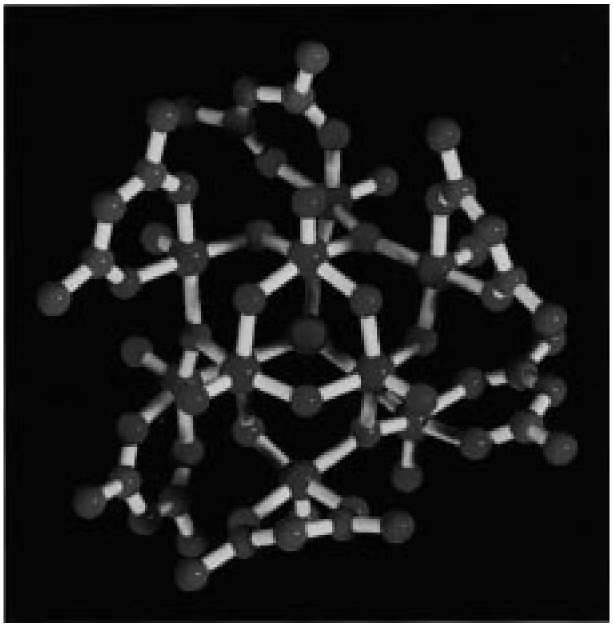

Figure 1. A perspective view of the crystal structure of **1** projected along the approximate C_3 axis passing through the vanadium and oxygen atoms in the central V=O group: V (green), O (red), C (gray). Hydrogen atoms are omitted for clarity.

The $V_{10}O_{22}$ cluster (**1**) was isolated as the 2,4-pentanedionate complex from the reaction of $NaVO_3$ and 2,4-pentanedione.[7] The entire crystal structure of $[(O{=}V)_{10}(\mu_2\text{-}O)_9(\mu_3\text{-}O)_3(C_5H_7O_2)_6]\cdot 2CH_2Cl_2$ was determined from an X-ray crystallographic analysis.[8] The X-ray structure (Figure 1) shows a molecular framework formed by nine square-pyramidal VO_5 polyhedra surrounding one VO_4 tetrahedron linked through the corners. It is known that the average V=O bond length of oxovanadium is approximately 1.6 Å, while the equatorial V−O bond length is in the range of 1.8−2.1 Å.[9] In the VO_5 polyhedra of **1**, the vanadium atom lying as far as 0.338−0.442 Å above the equatorial O_4 least-squares plane and the one terminal oxygen atom being 1.561(5)−1.583(5) Å beyond the vanadium represent a typical square-pyramidal arrangement; in the central VO_4 group, the vanadium atom is

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(7) To a solution of $NaVO_3$ (1.6 g; 0.04 mol) in 80 mL of H_2O was added a solution of 2,4-pentanedione (4 g, 0.04 mol) in 40 mL of methanol at room temperature. Addition of HCl to the resultant solution to pH 2 gave rise to a brown precipitate. After the methanol was removed by evaporation, the precipitate was filtered, washed with H_2O, and dried under vacuum (5 g). Recrystallization from CH_2Cl_2/Et_2O produced dark brown prismatic crystals. Yield: 4.7 g (73%). Anal. Calcd for $C_{32}H_{46}O_{34}V_{10}Cl_4$: C, 24.75; H, 2.907. Found: C, 24.13; H, 2.80. IR (KBr, cm^{-1}): 999 ($\nu_{V=O}$). FABMS (*m/z*): 1456. ^1H NMR (500 MHz, CD_3CN at 20 °C): 5.50, 2.05 ppm.

(8) Crystal data for $[(O{=}V)_{10}(\mu_2{-}O)_9(\mu_3{-}O)_3(C_5H_7O_2)_6]\cdot 2CH_2Cl_2$: monoclinic space group $P2_1/n$ (No. 14), $a = 13.35(4)$ Å, $b = 26.57(4)$ Å, $c = 16.25(5)$ Å, $\beta = 92.9(3)°$, $V = 5755(24)$ Å,^{3} $Z = 4$, $D_{calcd} = 1.876$ g/cm^3, μ (Mo Kα) = 18.21 cm^{-1}. The data were collected at 23 °C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 55°. Scan rate = 16°/min (in ω). All measurements were made on a Rigaku AFC5R diffractometer with a 7.5 kW rotating anode generator and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. Of the 14 149 reflections, 13 585 were unique ($R_{int} = 0.027$). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement (function minimized: $\sum w(|F_o| - |F_c|),^2$ where $w = (\sigma(F_o)^2 + (0.0015(F_o))^2)^{-1}$) was based on 7460 observed reflections ($I > 3\sigma(I)$) and 890 variable parameters and converged with $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.051$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^{\,2})^{1/2} = 0.054$. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (teXsan; Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992).

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tetrahedrally coordinated to four oxygen atoms, one of which is terminal (at 1.663(4) Å)[10] and three of which are bridging (at 1.717(5)−1.730(4) Å), and deviated from the equatorial O_3 plane by 0.533 Å.

Four cluster molecules are involved in a monoclinic cell.[8] The molecule occupies a general equivalent position with no crystallographic site symmetry. Nevertheless the molecule appears to consist of 3-fold rotational symmetry (Figure 1). Its unique chiral metal core geometry may be characterized by the approximate 3-fold axis which passes through the V═O group in the central tetrahedron, and its propellerlike shape is clearly apparent when the molecule is viewed along this axis. The bond distances and angles in the $V_{10}O_{22}$ core adhere reasonably closely to the C_3 symmetry. A divergence form the symmetry is still small in the distal 2,4-pentanedionate ligands (Figure 1).

The $V_{10}O_{22}$ assembly exhibits a domed structure, providing a chiral interior cavity for accommodation of a guest molecule. Indeed, a recurrent theme of the chemistry of polyvanadate is the formation of cagelike "hollow spheres" capable of encapsulating a variety of templates.[11] On the other hand, the influence of central templates is also pronounced in organizing the closed cluster framework.[12] The topology of the molecular framework of **1** is, to our knowledge, unprecedented for vanadium clusters. It can be reasoned that the central VO_4 core takes a role as an intrinsic template in organizing the molecular structure with the C_3 symmetry.

Another curious feature of the structure is the geometry of the triply bridging μ_3-oxo groups which form similar V−O interactions at 1.841(4)−2.008(5) Å to vanadium sites. This structural feature defines the cluster as VO^{3+} decanuclear species rather than as containing VO_2^+ groups, a characteristic presumably associated with the high oxidation state of vanadium.

At this time, we are pursuing the investigations of the X-ray absolute configuration analysis of **1** and of the physicochemical properties including its electrochemical behavior and oxidation reactions of organic substrates with the potential to lead to chiral recognition. This research also inspires extensive studies of related reactions including the formation of vanadium(V) clusters with other β-diketone ligands.

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Supporting Information Available: Anisotropic atomic thermal ellipsoid figure of **1** and tables listing crystallographic data (20 pages). See any current masthead page for ordering and Internet access instructions.

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[10] The terminal oxygen atom in the VO_4 tetrahedron is at considerable distances from the three adjacent vanadium atoms (2.395(4) Å, 2.411(6) Å, and 2.412(5) Å, respectively). Thus, the four central vanadium atoms in the cluster form a hollow cage, rather than a Keggin-type structure.

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