Inorg. Chem. **2008**, *47*, 3492−3494

Inorganic Chemistry
Communication

Mixed-Valent Dodecanuclear Vanadium Cluster Encapsulating Chloride Anions and Its Reaction To Form a “Bowl”-Shaped Cluster

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Received January 3, 2008

Two oxovanadium phosphonate cage compounds have been synthesized in an organic solvent, and their characterization has been done by single-crystal X-ray analysis, IR spectroscopy, and bond valence sum calculations. The simple reaction of a mixed-valent closed V_{12} cage system produced another quasi-closed system composed of two V_6 bowl-type cages.

The synthesis of designed inorganic materials of specific size, conformation, and properties is a key aspect in various fields as modern materials, such as electronics, catalysis, or medicine.[1−4] Special efforts are being made on the synthesis of spherical and bowl-shaped discrete molecular metal−oxo clusters displaying very interesting host−guest and encapsulation properties, as reported mainly by Müller and co-workers[5] and Zubieta and co-workers.[6] In addition to their intrinsic properties, such species could self-assemble to nanoscale and are potential building blocks for molecular nanodevices, and this approach is called the “bottom-up” route[7] for nanomaterial synthesis. New synthetic routes, especially those in organic media with soluble vanadium precursors, are worth exploring because they may lead to the assembly and construction of new sophisticated vanadium organophosphonate clusters containing different compositions and frameworks. In this Communication, we report the synthesis and characterization of two such clusters and the reaction of one to form another one.

The mixed-valent vanadium host−guest compound $(HNEt_3)_2[(V_{12}O_{20})(H_2O)_{12}(Ph_2CHPO_3)_8](H_2O)_7(CH_3CN)_4Cl_2$ (**1**) has been first synthesized hydrothermally and later produced in a one-pot reaction between VCl_3 and $Ph_2CHPO_3H_2$[8] in CH_3CN at 80 °C.[9a] The X-ray crystallographic study[10] of complex **1** reveals that the structure consists of a pair of $HNEt_3$ cations and a neutral mixed-valent vanadium [V^V and V^{IV}; see the bond valence sum (BVS) calculations[11] and the magnetic measurement results in the Supporting Information] cluster $[(V_{12}O_{20})(H_2O)_{12}(Ph_2CHPO_3)_8]$ encapsulating two chloride anions. The structure of the cluster could be described as consisting of two cationic $[V_4{}^VO_8]^{4+}$ caps, bridged symmetrically through four $Ph_2CHPO_3{}^{2-}$ tetrahedra to a central grid of four $[V^{IV}O(H_2O)_3]^{2+}$ groups (Figure 1). Each tetranuclear cap exhibits an eight-membered ring of V^V square pyramids (Figure 2), sharing corners through bridging oxo

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(8) A mixture of biphenylmethyl bromide (2.47 g, 10 mol) and triethylphosphite (22.6 g, 0.135 mol) was heated for 6 h at 165 °C under a gentle stream of nitrogen. After cooling, excess triethylphosphite and ethyl bromide (generated as the byproduct) were distilled off. Then the crude product was refluxed with 6 M HCl to hydrolyze the final product biphenylmethylphosphonic acid. The acid was recrystallized from aqueous MeOH. The phosphonate ester as well as the acid was characterized by ^1H NMR and electrospray ionization mass spectra. Final yield: 2.1 g, 90%.

10.1021/ic800013f CCC: $40.75

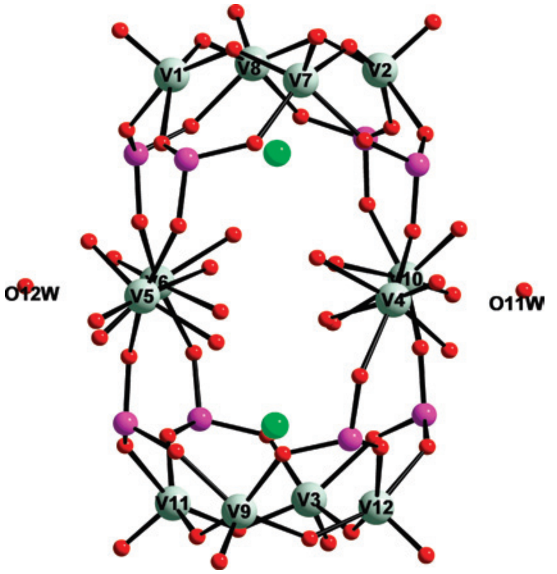

Figure 1. Core structure of **1**. Color code: red, oxygen; pink, phosphorus; light gray, vanadium; green, chloride. Hydrogen and carbon atoms are removed for clarity. Bond length ranges [Å]: V═O(oxo) 1.573(9)−1.609(7), V−O(μ_2-O) 1.740(5)−1.927(11), V−O(phosphonate) 1.952(12)−2.010(14), V−O(H_2O) 1.967(7)−2.319(2).

groups and with each V^V site further linked by a bridging bidentate phosphonate ligand of which the third oxygen is donated to a central V^{IV} octahedron. The octahedral coordination of the central V^{IV} sites is fulfilled by an oxo group, two phosphonate oxygens from each side, and three water molecules of which one is directed toward the center of the molecule. Four such waters virtually divide the interior of the molecule into two compartments. The compound could also be described as a combination of two positively charged $V_4O_8^{4+}$ units bridged by four hypothetical negatively charged complex anions, $[VO(H_2O)_3(Ph_2CHPO_3)_2]^{2-}$. The encapsulated chloride anions are located inside the cluster at 3.046 Å apart from the center and balance the charge of the two triethylammonium cations. There are a few disordered uncoordinated water molecules present in the crystal, but the exact number is undetermined. Interestingly, two of those water molecules (O11w and O12w; Figure 1) are located at the same distance from a pair of V^{IV} ions [O11w is located at 4.023(11) and 4.046(10) Å distances from V4 and V10, respectively; O12w is located at 4.080(12) and 4.025(12) Å distances from V5 and V6, respectively]. Both water molecules are encased by the four phenyl groups of the phosphonate ligands and are strongly hydrogen-bonded with two of the coordinated water molecules of the nearby vanadiums of the central grid. Two similar encapsulation compounds have been reported elsewhere.[2b,12]

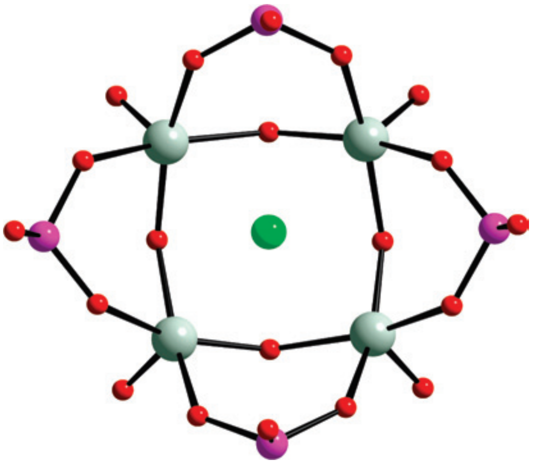

Figure 2. View of one of the $[V_4O_8(-PO_3)]$ caps in **1**, illustrating the location of the chloride template.

Compound **1** on refluxing with VCl_3 and Py in acetonitrile produced compound **2**, $(PyH)_5[V_{12}O_{24}(Ph_2CHPO_3)_6]$-$Cl_5(H_2O)_{10}(Py)_6(CH_3CN)_3$[9b] along with an unidentified green sticky compound. Later **2** was also synthesized on reaction between VCl_3, biphenylmethylphosphonic acid, and pyridine in acetonitrile, with better yield. All of the vanadiums in **2** are in the 5+ oxidation state, as revealed from BVS calculations and confirmed by the diamagnetic nature of the compound. Single-crystal X-ray analysis[10] revealed that compound **2** is composed of 2 open "bowl"-shaped neutral $[V^V_6O_{12}(H_2O)_3(Ph_2CHPO_3)_3]$ cages, 5 chloride anions, and 11 Py molecules, of which 5 should be protonated to balance the overall charge. These could not be identified from structural analysis, and in the text, we mentioned all of the pyridines as pyridine molecules not cations. In the cage, the vanadium atoms are all five-coordinated with the VO_5 square-pyramidal coordination geometry and are divided into two groups to form two triangles according to their coordination

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(9) (a) Synthesis of **1**: Anhydrous VCl_3 (0.126 g, 0.8 mmol) was taken with biphenylmethylphosphonic acid (0.08 g, 0.3 mmol) and NEt_3 (0.05 g, 0.5 mmol) in acetontrile in an Erlenmeyer flask and refluxed at 80 °C for 30 min. The resultant clear green solution was filtered, and the filtrate was kept at room temperature. After 2 days, X-ray-quality green single crystals had grown. The initial and final pH values of the reaction were 2.5 and 3.0, respectively. The yield of the reaction was ~20% (on the basis of vanadium). Elem anal. Calcd (%): C, 43.54; H, 4.60; N, 2.46. Found: C, 44.36; H, 4.12; N, 2.88. Selected IR data (KBr pellet): 3110(s), 2927(m), 2820(m) 1573(w), 1442(w), 1350(w), 1055(s), 787(m), 755(m), 549(m), 506(m) cm^{-1}. (b) Synthesis of **2**: **1** was taken with VCl_3 (1:1) in Py and CH_3CN (1:1) in an Erlenmeyer flask and refluxed at 80 °C for 4 h. The resultant clear green solution was filtered, and the filtrate was kept at room temperature. After a few days, X-ray-quality orange single crystals were obtained along with some unidentified amorphous green compound. The yield of the reaction was ~10% (on the basis of vanadium, nonoptimized). The initial and final pH values of the reaction were 3.0 3.0, respectively. Elem anal. Calcd (%): C, 45.37; H, 4.29; N, 5.40. Found: C, 46.18; H, 4.89; N, 5.27. Selected IR data (KBr pellet): 3230(s), 3021(m), 2835(m), 1589(w), 1475(m), 1357(w), 1067(s), 782(w), 548(m), 517(m) cm^{-1}. **2** has also been synthesized following the same procedure as that for **1**, except that the same equivalent of pyridine was taken instead of triethylamine. Large orange crystals were grown up from the solution, and an unidentified green oil separated out. The yield of the reaction was ~20% (on the basis of vanadium).

(10) Crystallographic data for **1** (at 110 K): $M = 3653.37$, triclinic, $P\bar{1}$, $a = 17.528(11)$ Å, $b = 19.255(12)$ Å, $c = 25.444(15)$ Å, $\alpha = 86.430(11)°$, $\beta = 81.083(10)°$, $\gamma = 78.355(11)°$, $V = 4641(2)$ Å^3, $Z = 2$, R1 = 0.1453, wR2 = 0.4024. The *R* factor of the compound is very high because of the presence of highly disordered triethylaammonium cations. Crystallographic data for **2**: $M = 3371.18$, hexagonal, $P\bar{6}2c$, $a = 16.8442(16)$ Å, $b = 16.8442(16)$ Å, $c = 34.778(7)$ Å, $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 120.00°$, $V = 8546(2)$ Å^3, $Z = 2$, R1 = 0.0632, wR2 = 0.1809. One phenyl ring of the phosphonate ligand is disordered over two positions and was not assigned to hydrogen atoms. Three atoms of the pyridine near sandwiched chlorides were symmetry-generated from the other three. So, the nitrogen atom could not be assigned. This is due to the fact that those pyridines are in different orientations in the packing and the X-ray data gave us an averaged diffraction pattern.

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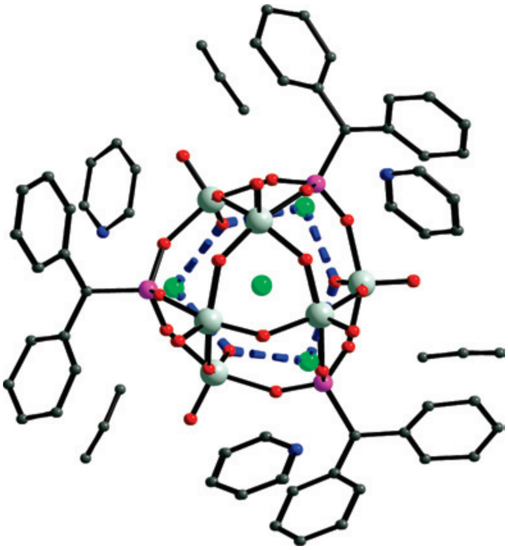

Figure 3. Molecular structure of **2** along the *b* axis. Surrounding pyridine molecules are also shown. Color code: red, oxygen; dark gray, carbon; pink, phosphorus; light gray, vanadium; green, chloride. Hydrogen atoms are removed for clarity. Hydrogen bondings are shown by the blue dotted lines.

environment (Figures 3 and S2 in the Supporting Information). One smaller triangle formed by corner-sharing distorted VO_5 square pyramids, and in the bigger peripheral triangle, phosphonate groups bridged the vanadiums. These two triangles together constitute the novel half-shell configuration (Figure 4). Each of the three V^V sites at the edge are bonded with a water molecule that pointed toward the open face of another cage. There is a mirror plane between the two open bowls, and three chloride anions are positioned on that plane and form a triangle (Cl···Cl distance = 4.535 Å). The most striking feature of the molecule is that each of the chloride anions is strongly hydrogen-bonded with a total of four water molecules, two of them from each side. We believe the hydrogen bonding plays an important role in holding the two cages together "face-to-face" and vice versa. That means strong hydrogen bonding sandwiched the chlorides between two cages. Each cage also encapsulated another chloride anion, which is located almost at the center of the bowl. The arrangement of 9 out of 11 pyridine molecules in the packing is also very interesting. Each cluster is intimately flanked by those pyridine molecules. Three of each are arranged symmetrically near the smaller vanadium triangles of two subunits formed by corner-sharing VO_5 square pyramids (Figure 3). The remainder of the three are located perpendicular to the plane created by the three sandwiched chloride anions. The distance between each pair of pyridine molecules and the chloride anion is 3.452 Å.

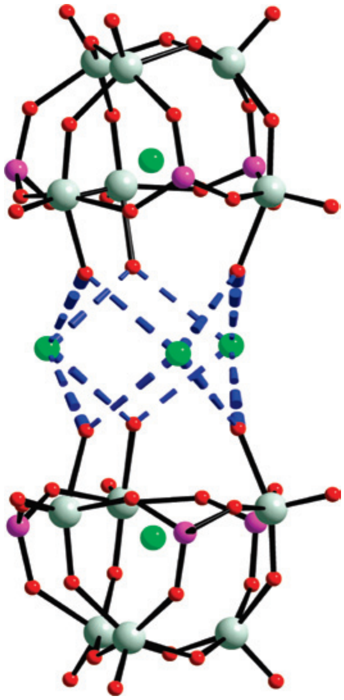

Figure 4. Core structure of **2**. Color code: red, oxygen; pink, phosphorus; light gray, vanadium; green, chloride. Bond length ranges [Å]: V=O(oxo) 1.585(3)−1.586(2), V−O(μ_2-O) 1.744(5)−1.953(4), V− O(phosphonate) 1.929(2)−1.99(2), V−O(H_2O) 2.073(3). Hydrogen bondings are shown by the blue dotted lines.

In conclusion, despite their serendipitous formation, as is typically found in oxovanadium organophosphate systems, it is certainly a fact that intermolecular interactions have an important role in dictating the final product of the reaction. This suggests a selectivity that could be controlled through a judicious choice of solvent, counterions, starting reagents, or reaction conditions. The reaction of one cage to form another one is rare among the cluster compounds.

Acknowledgment. Funding from the National Science Foundation (Grant DMR-0652166) and the Robert A. Welch Foundation (Grant A-0673) is gratefully acknowledged.

Supporting Information Available: Additional drawings of the structures, BVS calculations, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC800013F