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Hybrid Polyoxovanadates: Anion-Influenced Formation of Nanoscopic Cages and Supramolecular Assemblies of Asymmetric Clusters

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S *Supporting Information*

ABSTRACT: Two novel hybrid polyoxovanadates that are functionalized by (4-aminophenyl)arsonic acid ligands form upon the reduction of vanadates(V) in aqueous systems, whereby the underlying condensation reactions are influenced by the nature of the employed acid. In the presence of Cl^- ions that derive from hydrochloric acid, a tetradecanuclear cage structure $[V^{IV}{}_{14}O_{16}(OH)_8(O_3AsC_6H_4\text{-}4\text{-}NH_2)_{10}]^{4-}$, whose cavity contains stabilizing halide ions and water molecules, is obtained. When nitric acid is used, a decanuclear $[V_{10}O_{18}(O_3AsC_6H_4\text{-}4\text{-}NH_2)_7(DMF)_2]^{5-}$ cluster can be isolated. The latter organizes into a hexagonal packing arrangement in the solid state.

Self-assembled molecular capsules provide a fascinating subclass of metallosupramolecular systems.[1] Their syntheses have received considerable scientific interest over the last decades, whereby facile and modular coordination chemistry approaches have produced a series of molecular entities of varying composition, size, and topology.[2] The resulting restricted inner cavities in these species often provide unique chemical environments to promote molecular recognition or catalysis processes. Envisaged applications extend to areas such as enzyme mimetics, artificial photosynthesis, sensors, and drug-delivery systems.[3]

Polyoxometalates are highly applicable materials, and their chemical, electronic, and geometrical characteristics enable them to form stable molecular clusters with nanoscopic dimensions and cavities.[4] The stability of the observed molecular species and their convex subunits can partly be attributed to short terminal M═O bonds, which protect the cluster to the outside and limit further condensation reactions to form the parent 3D oxide materials. However, these bonds with d−π character that generally point radially to the outside of the cluster core debilitate functionalization of the clusters by organic ligands and may hamper some advanced applications. Much work has been done in the understanding of the self-assembly of polyoxovanadates in the presence of aromatic organophosphonate and arsonate ligands producing cage-type molecules, for instance, $[2CH_3OH{\subset}V_{12}O_{14}(OH)_4(PhAsO_3)_{10}]^{4-}$, $[2H_2O{\subset}V_{12}O_{12}(OH)_2(H_2O)_2(PhAsO_3)_{10}(PhAsO_3H)_4]^{2-}$, $[Cl_4{\subset}V_{18}O_{25}(H_2O)_2(PhPO_3)_{20}]^{4-}$, $[(H_2O)_2N_3{}^-{\subset}V_{14}O_{22}(OH)_4(PhPO_3)_8]^{7-}$, and $[Cl_2{\subset}(V_{12}O_{20})(H_2O)_{12}(Ph_2CHPO_3)_8]^{2-}$.[5] These and related compounds clearly underline that the condensation of $\{OVO_4\}$ square pyramids favors the formation of hollow structures in which tetra- and pentanuclear subunits provide binding sites for neutral nucleophiles or anionic species (e.g., halides).[6] It has previously been demonstrated by Müller, Zubieta, and others that these guests may influence or template the condensation of subunits into larger capsular entities, whereby the shape and interaction strength between the guest and the host cavity determine the architecture and topology of the cluster.[5−7] We are interested in the concept of hybrid organic−inorganic materials leading to compounds that combine advantageous properties of organic and inorganic moieties,[8] and previously we demonstrated that rigid bifunctional ligands can be used to link preorganized pentanuclear mixed-valent vanadium complexes intramolecularly to generate a new class of hybrid organic−inorganic capsules.[9] Here we describe an intriguing extension of this reaction system.

We report the structure of a tetradecanuclear vanadate cage, $[V^{IV}{}_{14}O_{16}(OH)_8(O_3AsC_6H_4\text{-}4\text{-}NH_2)_{10}]^{4-}$ (**1**; Figures 1 and 2), which forms upon the reduction of sodium vanadate using hydrazine hydrate in the presence of (*p*-aminophenyl)arsonic acid. Slight modifications of the preparation conditions and exchange of Cl^- ions by $NO_3{}^-$ ions during the synthetic procedure direct the condensation reaction to produce a condensed, rather unsymmetrical, decanuclear, mixed-valent V^V/V^{IV} cluster, $[V_{10}O_{18}(O_3AsC_6H_4\text{-}4\text{-}NH_2)_7(DMF)_2]^{5-}$ (**2**; DMF = *N*,*N*-dimethylformamide), which self-organizes in the solid state into a hydrogen-bonded supramolecular assembly with hexagonal topology.[10]

Cluster anion **1** is stabilized by 10 fully deprotonated (*p*-aminophenyl)arsonic acid ligands (L). It can be visualized as the linkage of two tetranuclear $\{LV^{IV}{}_4O_{12}\}$ subunits through two trinuclear, hydroxy-bridged $\{O_4V^{IV}(OH)_2V^{IV}(OH)_2V^{IV}O_4\}$ inorganic moieties. Within the tetranuclear $\{LV^{IV}{}_4O_{12}\}$ subunit, a central arsonic acid functionality of the organic ligand is surrounded by four V^{IV} units. These ions form square-pyramidal coordination polyhedra whose V centers occupy the corners of a square. The As atom of the organic ligand is situated in the center of the square arrangement and is surrounded by O-atom donors that also form the base of a square-pyramidal coordination arrangement. The base of this central $\{AsO_4\}$ pyramid shares common edges with its four surrounding $\{V^{IV}O_5\}$ polyhedra to give a convex unit. All V^{IV} ions contain short V−O bonds (tips of the pyramids) with

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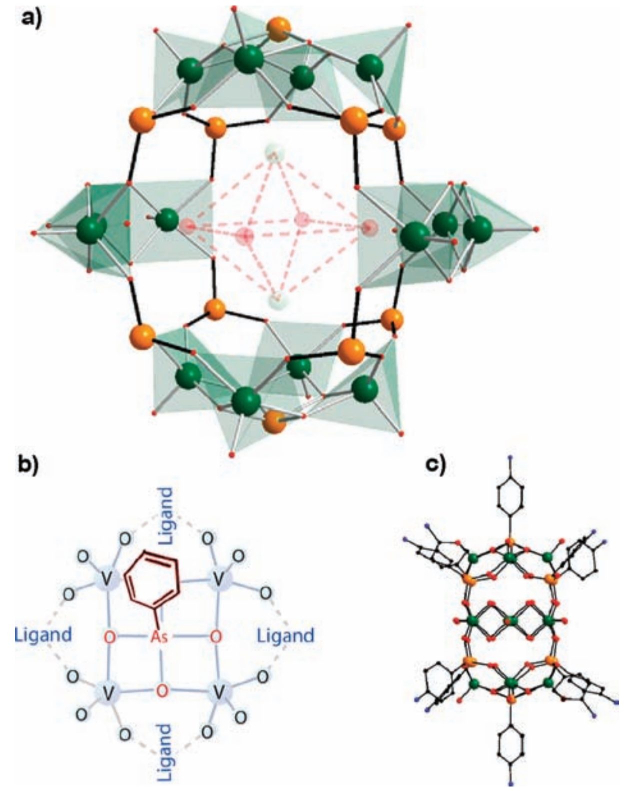

Figure 1. (a) Capsular entity in **1** (V centers in a polyhedral representation). (b) Schematic of the capping motif of **1**. (c) Side-on perspective of the anionic cage **1**. H atoms have been omitted for clarity. Color code: V, green; As, orange; O, red; N, blue; C, dark gray.

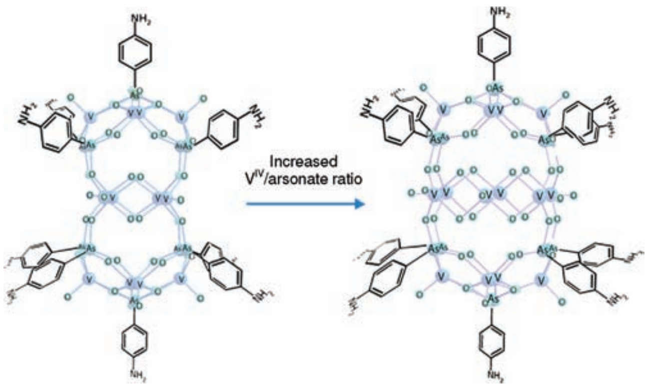

Figure 2. Rationalization of the formation of **1** by a comparison of its structure with that of $[V_{12}O_{14}(OH)_4(O_3AsC_6H_4\text{-}4\text{-}NH_2)_{10}]^{4-}$.[9]

partial double-bond character. Two O-atom donors in the base of each $\{V^{IV}O_5\}$ square pyramid are provided by four (4-aminophenyl)arsonate ligands, each bridging between two V atoms in an O,O′-syn,syn coordination mode. Two of these convex units further bind through their remaining O-atom donors of the organic ligands to two $\{O_4V^{IV}(OH)_2V^{IV}(OH)_2V^{IV}O_4\}$ moieties to give a tetradecanuclear V^{IV} cage. Within the $\{O_4V^{IV}(OH)_2V^{IV}(OH)_2V^{IV}O_4\}$ unit, square-pyramidal coordination polyhedra share common edges through four OH^- bridges to form a trinuclear strand whose four terminal O atoms are provided by the organic ligands. Bond valence sum (BVS) analyses are in agreement with the assigned IV+ oxidation states of all V centers in **1** (see the Supporting Information).

The inner cavity of the cage structure is characterized by an almost ideal cubic arrangement of the As atoms, resulting in a cross-sectional vertex–vertex diagonal of ca. 10 Å; the dimensions as given by the As–As distances along the cubic edges are 5.8 × 5.9 × 5.9 Å. **1** encloses four water molecules and two Cl^- ions in its electrophilic intramolecular cavity. The two Cl^- atoms are situated in the focal points of the convex capping units occupying the apical positions of an octahedron. The four water molecules are located in the equatorial plane of the octahedron, and two molecules appear to stabilize the two trinuclear vanadium moieties (see the Supporting Information). Previously, we observed similar octahedral assemblies in hybrid vanadate cages that form in MeCN solutions and used these as templates to control the topologies of cluster cages.[11]

The isolated cage structure **1** represents a higher homologue of dodecanuclear vanadates [e.g., $[V_{12}O_{14}(OH)_4(O_3AsC_6H_4\text{-}4\text{-}NH_2)_{10}]^{4-}$] in which structurally related capping units are linked through dinuclear hydroxo-bridged $\{O_4V^{IV}(OH)V^{IV}O_4\}$ moieties.[5a,9] In agreement with the composition, **1** forms at higher vanadium/organoarsonate ratios than its dodecanuclear homologue.[9] The fact that we find Cl^- ions in the hollow cavity of **1** prompted us to exclude chlorides during the synthesis and to use $HNO_3(aq)$ in place of HCl(aq) to acidify the reaction system. This approach resulted in a fundamentally new, mixed-valent, decanuclear polyoxovanadate anion, $[V_{10}O_{18}(O_3AsC_6H_4\text{-}4\text{-}NH_2)_7(DMF)_2]^{5-}$ (**2**; Figure 3).

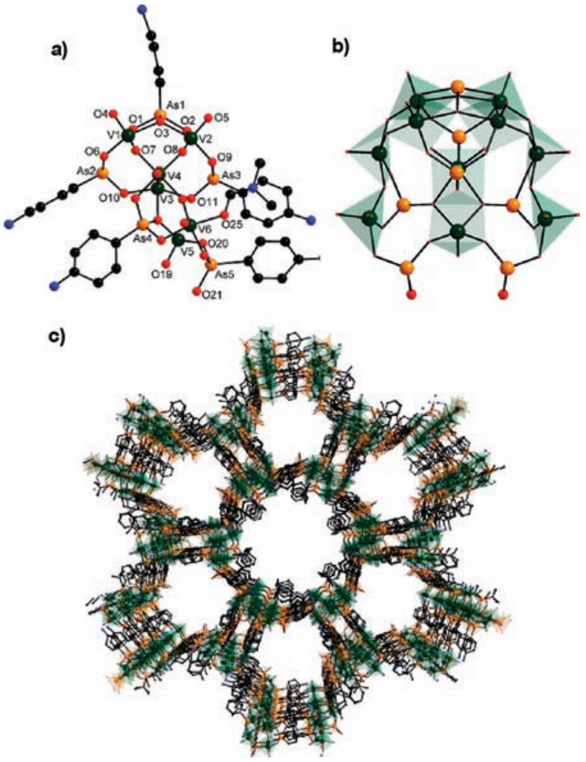

Figure 3. (a) Ball-and-stick representation of the anionic cluster **2**. (b) Polyhedral representation of the core structure of **2**. (c) Hexagonal packing arrangement of the anionic clusters as viewed in the direction of the crystallographic *c* axis. The constitutional solvent molecules, disordered phenyl rings, and H atoms have been removed for clarity. Color code: V, green; As, orange; O, red; C, black; N, blue.

The hybrid polyoxovanadate cluster in **2** can be envisaged as being constructed of distinct structural motifs: a $\{L(\mu_3\text{-}O)_4V^{V}_4O_{12}\}$ capping motif related to the structural unit observed in **1**, in which square-pyramidal vanadium polyhedra are capped by an organoarsonate ligand to form a four-membered ring motif, two corner-sharing square-pyramidal units $\{O_4V^{IV}(\mu_2\text{-}O)V^{IV}O_4\}$, and a central dimeric $\{O_4V^{V}(\mu_2\text{-}O)_2V^{V}O_3\}$ moiety, in which a distorted octahedron and a square pyramid share a common edge. These motifs are interconnected through six further arsonate ligands, which adopt $\mu_4\text{-}\eta^2,\eta^1,\eta^1$ and $\mu_2\text{-}\eta^1,\eta^1$ binding modes. The coordination sphere of the central vanadium ion V(3) is rather unusual for polyoxovanadates and includes two cis-coordinating terminal oxo ligands.[12]

The organoarsonate ligands point in three distinct directions of space. In the solid state, their amine functionalities engage in hydrogen bonds and organize the clusters into a supramolecular assembly with hexagonal topology. The packing arrangement is characterized by two types of tubular channels (larger and smaller channels) that extend in the direction of the crystallographic *c* axis. The channels are filled with disordered solvent molecules and reveal cross-sectional diameters of ca. 12 and 17 Å.

In summary, our applied synthetic approach results in two hybrid polyoxovanadate structures: an unprecedented cage structure and a rather unsymmetrical condensed vanadate that self-organizes in the solid state into a hexagonal supramolecular assembly. We show that condensation reactions in (4-aminophenyl)arsonic acid stabilized reaction mixtures are governed by vanadium/arsonate ratios. Cl^- ions and water molecules stabilize the cavitand cage **1** that accommodates these guests as an octahedral assembly within its capsular entity. The exclusion of chlorides and the use of HNO_3(aq) to acidify the reaction mixture significantly influence the underlying condensation reactions and result in the formation of an unusually asymmetric, condensed cluster **2**. Hydrogen bonds stabilize a remarkable supramolecular packing structure of **2**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format (CCDC 838766 and 838767), experimental procedures and structure details, additional images, BVS analyses, powder X-ray diffraction, thermogravimetric analyses, ORTEP diagrams, and UV−vis and ESI-MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) $H_6[Cl_2\subset\mathbf{1}]\cdot 8DMF\cdot 16H_2O$: $NaVO_3$ (0.19 g, 1.6 mmol), (4-aminophenyl)arsonic acid (0.22 g, 1.0 mmol), H_2O (20 mL), and DMF (20 mL) were stirred at 70 °C for 30 min. HCl(aq) (32%) was then added dropwise to adjust the pH to ca. 5.0. $N_2H_4\cdot H_2O$ (45 μL, 0.93 mmol) was added, and the pH was readjusted with HCl(aq) (32%) to ca. 4.5. Turquoise block crystals were obtained after ca. 3 weeks. Yield: 19%. $H_5[\mathbf{2}]\cdot 7DMF\cdot 5H_2O$: procedure as above, however, concentrated HNO_3(aq) was used instead of HCl(aq) to adjust the pH to ca. pH 4. Green needles formed after ca. 2 weeks. Yield: 35% (for further experimental details, see the Supporting Information).

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■ NOTE ADDED AFTER ASAP PUBLICATION

The version published ASAP December 6, 2011 contained errors in the abstract; the corrected version reposted December 8, 2011.