Vanadium Oxide Clusters as Building Blocks for the Synthesis of Metal Oxide Surfaces and Framework Materials: Synthesis and X-ray Crystal Structure of [H$_6$Mn$_3$V$^{IV}_{15}$V$^{V}_4$O$_{46}$(H$_2$O)$_{12}$]·30H$_2$O

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While a large number of important industrial chemical transformations take place on the catalytic transition metal oxide surfaces, the mechanism of their interaction with substrate molecules is less understood due mainly to the complex nature of these poorly characterized surfaces that are inaccessible to many physicochemical techniques.[1] The suitability of currently employed catalytic surfaces is determined empirically with practically little or no possibility of improvements in their performance. The idea of rational synthesis of well characterizable metal oxide surfaces with desired features to meet the environmental and technological challenges of modern times[1a,g,2] is, therefore, considerably appealing.[1e,g,3]

Transition metal oxide clusters or polyoxometalates and their derivatives, which are perceived to represent structure and bonding in infinite metal oxide surfaces,[1d,4] provide remarkably diverse and well-defined building blocks suitable for generating nanosized molecular systems.[4a,5] However, assembling of the well-characterizable metal oxide clusters, without using conventional organic ligands, to prepare desired 3-D framework materials and true solid surfaces composed purely of well-defined transition metal oxide building blocks remains a rewarding challenge. By adopting a simple synthetic approach we have now been able to prepare novel framework materials based 100% on well-defined metal oxide building blocks without incorporating any conventional organic or inorganic (e.g. PO$_4^{3-}$, AsO$_4^{3-}$, SO$_4^{2-}$, etc.) ligands. This report describes the synthesis and characterization of the new solid- [H$_6$Mn$_3$V$^{IV}_{15}$V$^{V}_4$O$_{46}$(H$_2$O)$_{12}$]·30H$_2$O (**1**) by complete single-crystal X-ray structure analysis, elemental analysis, manganometric titration, TGA, and FT-IR spectroscopy.

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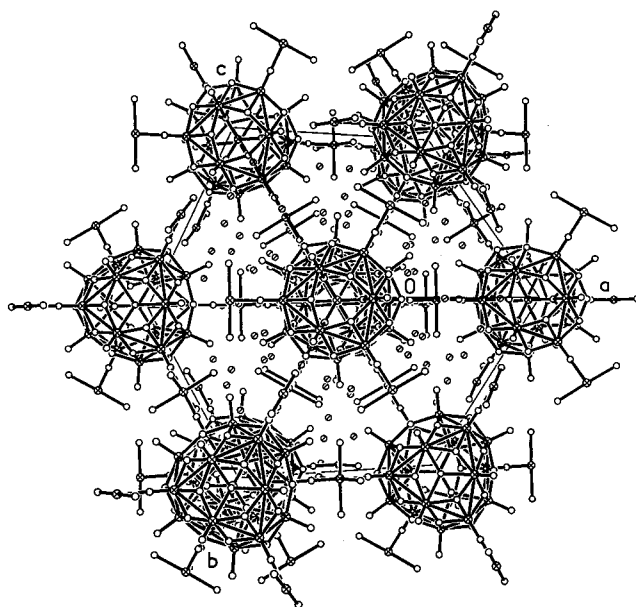
Figure 1. A view of the structure of [H$_6$Mn$_3$V$^{IV}_{15}$V$^{V}_4$O$_{46}$(H$_2$O)$_{12}$]·30H$_2$O along the *a* axis showing arrays of {V$_{19}$O$_{46}$} clusters interconnected through {Mn(H$_2$O)$_4$} bridging groups and channels occupied by the water molecules (striped circles) of crystallization. Hydrogen atoms have been omitted.

An aqueous solution (3 mL) of LiOH·H$_2$O (5 mmol) was added to a slurry of V$_2$O$_5$ (2.5 mmol) in water (10 mL) maintained at 95 °C. After treating the resulting solution with solid hydrazinium sulfate (2.5 mmol), the reaction mixture was heated for another 5−10 min. The dark solution was diluted to 25 mL and subsequently treated with KMnO$_4$ (1.25 mmol) and heated for 1.5 h. The resultant solution was filtered and allowed to stay at room temperature for 12 h. Dark black prism-shaped crystals were filtered from the mother liquor, washed with water, and dried in air at room temperature to give 0.25 g (60% yield based on vanadium) of [H$_6$Mn$_3$V$^{IV}_{15}$V$^{V}_4$O$_{46}$(H$_2$O)$_{12}$]·30H$_2$O.[6]

The X-ray structural[7] analysis of a single crystal of **1** revealed a three-dimensional framework structure (Figure 1) composed of the transition metal oxide building-block units shown in Figure 2. The extended structure consists of "spheres" of {V$_{19}$O$_{46}$} clusters, each one linked to six others by six μ$_2$-{Mn(H$_2$O)$_4$}

(6) Anal. Calcd for H$_{90}$O$_{88}$Mn$_3$V$_{19}$: C, 0.00; H, 3.45; N, 0.00; Mn, 6.26. Found: C, 0.04; H, 2.56; N, 0.04; Mn, 6.33.

(7) Crystal data for **1**: Cubic space group *Pn*$\bar{3}$ (No. 201), *a* = 15.5623 (2), *Z* = 2, *D*$_{calcd}$ = 2.319 mg·m^{-3}, μ(Mo Kα) = 2.854 mm^{-1}. The data were collected at 133 K using a Siemens P4/CCD diffractometer (graphite monochromatized Mo Kα radiation; λ = 0.71073 Å) and ϕ scan frames. Of the 16508 reflections (2.62° ≤ θ ≤ 29.08°), 1634 unique reflections were used to solve the structure by direct methods (SHELXTL Version 5) and refine it on *F*^{2} by full-matrix least-squares techniques. At convergence, *R*1 equals to 0.0407 and the goodness-of-fit on *F*^{2} is 1.147. One region of the water solvent was disordered and was modeled in two orientations with refined occupancies of 0.249(9) and 0.251(9) for O(3S) and O(4S), respectively.
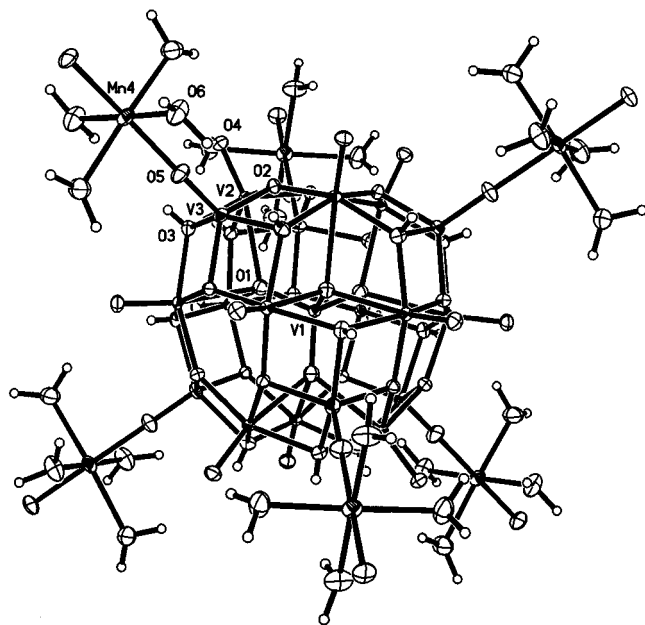
Figure 2. The building block unit in the crystal structure of [H$_6$Mn$_3$-V$^{IV}_{15}$V$^V_4$O$_{46}$(H$_2$O)$_{12}$]·30H$_2$O showing the atom labeling scheme in the asymmetric unit. Small open circles represent hydrogen atoms. Displacement ellipsoids are drawn at the 50% probability level.

bridges. This generates a network of [−{V$_{19}$O$_{46}$}−μ_2-Mn(H$_2$O)$_4$−{V$_{19}$O$_{46}$}−]$_\infty$ arrays running along three mutually perpendicular directions.

Each {V$_{19}$O$_{46}$} unit may be viewed as constructed from the {V$_{18}$O$_{42}$} shell[8] encapsulating a tetrahedral {VO$_4$}$^{3-}$ group which interacts with the 12 V-centers of the shell, each oxygen (O1) of the {VO$_4$}$^{3-}$ unit (V1−O = 1.661 Å) interacting in μ_4-mode with three V(2)-centers, forming V(1)−O(1)−V(2)$_{shell}$ bonds (O1−V$_{shell}$ = 2.440 Å) and forcing the local idealized tetrahedral symmetry upon the {V$_{19}$O$_{46}$} unit. The 12{VO$_6$} units of {V$_{19}$O$_{46}$}core are fused with 6{VO$_5$} groups through common edges and linked with the central {VO$_4$} unit via corner sharing. The octahedral geometry around each vanadium (V2) in the 12{VO$_6$} units is defined by a terminal oxo group (O4) (V2−O4 = 1.609 Å), four μ_3-oxygens (O2, O3) of the shell (V2−O = 1.949−1.981 Å), and one μ_4-oxygen (O1) (O1−V2 = 2.440 Å) from the central {VO$_4$} unit. The square-pyramidal geometry around each vanadium (V3) in 6{VO$_5$} is defined by four basal μ_3-oxo groups (O2, O3) (V3−O = 1.889−2.019 Å) from the shell and an apical μ_2-oxygen (O5) (V3−O5 = 1.640 Å) which in turn is linearly bonded to the manganese(II) center of one of the six {Mn(H$_2$O)$_4$} bridges that link {V$_{19}$O$_{46}$} cluster with six others. The octahedral geometry around each manganese(II) is completed by four oxygen atoms (O6) from the aqua ligands (Mn−O(H$_2$) = 2.200 Å), each one disordered over three positions, and two *trans*-oxo groups (O5) (Mn−O = 2.136 Å).

The bond valence sum (BVS) calculations[9] and metal−oxygen bond lengths identify twelve O3 groups having attached hydrogen, which refines with occupancy of 0.5, and O6 to be H$_2$O. The charge balance requires **1** to be a mixed-valence species which

is supported by the result of manganometric titration of V^{IV} sites (15 V^{IV} per formula unit).

The structure of **1** contains tunnels and cavities, defined by {V$_{19}$O$_{46}$} and {Mn(H$_2$O)$_4$} units, occupied by lattice water molecules (Figure 1). The thermogravimetric analysis[10] shows initial weight loss of 20.5%, corresponding to the total removal of the lattice water, at 70 °C followed by the weight loss due to the removal of coordinated water at 257 °C. Further heating up to 500 °C yielded an incompletely characterized metal oxide phase. A sample of **1** heated at 70 °C for 4 h shows no apparent skeletal changes in the structure and the dehydrated sample exhibits reversible water absorption as evidenced by IR spectral studies.[10]

This report constitutes a step toward demonstrating the application of transition metal oxide clusters in the synthesis of metal oxide surfaces and framework materials with predictable features. Given the proven role of polyoxometalates in catalysis[11] and in the development of new oxide-supported transition metal catalysts,[12] their application in preparing new surfaces is valuable. The synthetic method, described here, employs polyoxometalate building blocks, generated in solution, for preparing stable framework structures composed essentially of transition metal oxide units linked through additional metal oxide units without incorporating any conventional ligand in the framework. Given a plethora of well-characterized metal oxide clusters and compounds, this may potentially provide access to a variety of transition metal oxide based solids. Well-characterizable solid surfaces may provide additional opportunities for theoretical studies of specific metal oxide surfaces to gain insight of their reactivities and surface dynamics.[1d]

The chemistry associated with {V$_{19}$O$_{46}$} and {V$_{18}$O$_{42}$} cores is further exploitable for understanding the property of **1** and for synthesizing new surfaces, for example, functionalized derivatives of **1**, for which these clusters will provide good models. The replacement of H$_2$O from {Mn(H$_2$O)$_4$} by other organic and inorganic groups may offer possibility of anchoring groups (e.g. metal ions, clusters, asymmetric units) deemed suitable for enhancing the reactivity of the surface. Also, the bridging Mn(II) centers may be substituted by other metal ions (Cu(II), Cd(II), Mg(II), etc.) and organometallic groups as evidenced by the ongoing work in our research laboratories.

Supporting Information Available: Tables listing crystal data and structure refinement details, atomic coordinates, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for the structure of **1** (10 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The thermogravimetric analysis was performed on a Universal V1.9D Instrument by heating (2.5 °C/min) 18.720 mg of the sample under nitrogen atmosphere in the temperature range 25−500 °C. IR spectra (4000−400 cm^{-1}) were recorded on a Paragon 1000 FT-IR spectrophotometer.
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