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Hydrothermal Synthesis of the First Vanadomolybdenum Polyoxocation with a “Metal-Bonded” Spherical Framework

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The heteropoly compound $[(V^{V}O_4)Mo^{VI}_{12}O_{36}(V^{IV}O)_6][(OH)_9]\cdot 11H_2O$ (**1**), synthesized by hydrothermal method under weak basic conditions, represents the first mixed Mo/V six-capped Keggin structural derivative with a spherical skeleton, and the first transition metal polyoxocation. The successful synthesis of **1** demonstrates that basic hydrothermal synthesis might be a power synthetic route to the isolation of more new polycationic metal-oxo clusters.

Transition metals, especially molybdenum and vanadium, are flexible, able to form various coordination geometries (from regular and distorted octahedra and square pyramids to tetrahedra), and have a strong tendency to offer mixed-valence states. These features have led to the formation of numerous polyoxometalates (e.g., Keggin isomers and gigantic polyoxomolybdates reported by Professor Müller and co-workers) with potentially useful catalytic, electrical, optical, and magnetic properties.$^{1-2}$ However, all of these polyoxometalates are anionic or neutral and are usually prepared under acidic or neutral conditions.

It has been recently demonstrated that polyoxoaluminum cations are prepared under basic conditions.$^{3-5}$ It will be of great interest to investigate whether other transition metal polyoxometalate cations can be obtained under similar basic conditions or not. We have been attempting to carry out the hydrothermal syntheses for new Mo/V heteropoly compounds under weak basic conditions, and we have successfully isolated a novel mixed Mo/V six-capped Keggin derivative formulated as $[(V^{V}O_4)Mo^{VI}_{12}O_{36}(V^{IV}O)_6][(OH)_9]\cdot 11H_2O$ (**1**), which represents the first structurally characterized cationic polyoxometalate. Although containing six V^{IV} metals, the six-capped Keggin cation in **1** is diamagnetic because of the delocalization of the d electrons of the reduced vanadium centers over the spherical shell.

Hydrothermal treatment of the mixture of $(NH_4)_2MoS_4$,^{6} NH_4VO_3, NaOH, $NH_2OH\cdot HCl$, and H_2O in the molar ratio 3.75:1.0:10.0:15.0:1650 at 190 °C for 25 h gave rise to a large amount of colloid precipitate and a deep violet solution.^{7} Dark violet crystals of **1** were precipitated in about 25% yield from the mother liquor stored under nitrogen atmosphere. Our attempts to increase the yield of **1** by changing the hydrothermal reaction conditions (stoichiometry, reaction temperature, heating cycles, etc.) have met with limited success. Various parallel reactions using $Na_2MoO_4\cdot 2H_2O$ instead of $(NH_4)_2MoS_4$ gave no product under similar basic conditions. However, when appropriate $(NH_4)_2MoS_4$ was added into a weakly acidified aqueous mixture of $Na_2MoO_4\cdot 2H_2O$, NH_4VO_3, and $NH_2OH\cdot HCl$; crystals of $\{Mo_{57}V_{12}\}$^{8} were obtained. These facts indicate that $(NH_4)_2MoS_4$ plays a key role in the formation of **1** and $\{Mo_{57}V_{12}\}$, which might be functioned as reactive intermediate or reductive by releasing sulfur. The reduced heteropolymolybdovanadate **1** is mildly air-sensitive. When the aqueous solution of **1** was exposed in air, the color of the solution changed from deep violet to orange-yellow within an hour. Therefore, the reaction mixture must not be exposed to air to avoid oxidation of reduced V^{IV} during the crystallization of **1**. The IR spectrum exhibits two strong bands at 958 and 903 cm^{-1}, ascribed to $\nu(M{=}O)$, and at 694 and 606 cm^{-1},

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(7) $(NH_4)_2MoS_4$ was prepared according to the literature,^{6} and other chemicals were used as purchased. A mixture of $(NH_4)_2MoS_4$, NH_4VO_3, NaOH, $NH_2OH\cdot HCl$, and H_2O in a molar ratio of 3.75:1.0:10.0:15.0:1650 was fully stirred at room temperature, sealed in a Teflon-lined stainless steel reactor, and heated at 190° for 25 h, giving rise to a large amount of colloid precipitate and a deep violet solution. After filtering off the colloid precipitate, the deep violet filtrate was allowed to be stored in a Schlenk flask under nitrogen atmosphere at 0 °C, resulting in dark violet crystals of **1** in about 25% yield (based on Mo) within two weeks. Anal. Calcd: Mo, 44.36; V, 13.74; H, 1.20%. Found: Mo, 44.32; V, 13.77; H, 1.18%.

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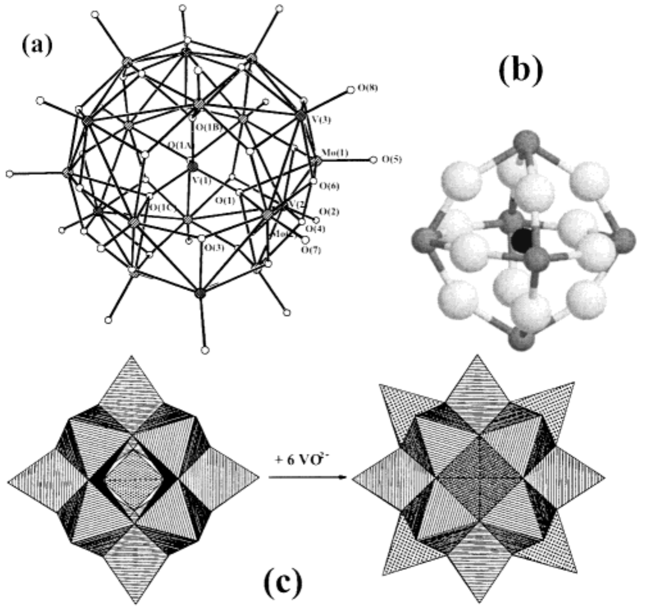

Figure 1. (a) Ball-and-stick representation of **1a** with atom labeling for an asymmetric unit. The central V(1) atom at (0, 0, 0) is surrounded by eight oxygen atoms with partial occupancy of 0.5 (four of the eight O atoms bonded to V(1) are omitted for clarity). Selected M−O bond lengths (Å): Mo(1)−O(5), 1.650(7); Mo(1)−O(6), 1.846(8); Mo(1)−O(4), 1.985(7); Mo(1)−O(1), 2.467(10); Mo(2)−O(7), 1.642(10); Mo(2)−O(6), 1.914(8); Mo(2)−O(3), 1.921(8); Mo(2)−O(1), 2.467(11); V(1)−O(1), 1.567(11); V(2)−O(2), 1.624(18); V(2)−O(4), 1.976(8); V(3)−O(8), 1.680(17); V(3)−O(6), 1.993(12). (b) "Metal-bonded" sphere observed in **1a** (Mo, white; capping V, gray; central V, black). Selected V−Mo distances (Å): V(2)−Mo(1), 3.030(3); V(3)−Mo(1), 2.842(5); V(3)−Mo(2), 2.887(11). (c) Polyhedral representation of the α-Keggin anion (left) and the six-capping Keggin structure (right) of **1a**.

ascribed to μ(M−O−M) (M = Mo or V). The title compound was characterized by single-crystal X-ray diffraction.[9]

The structure of **1** contains a discrete six-capped Keggin structural polyoxocation $[(V^{V}O_4)Mo^{VI}_{12}O_{36}(V^{IV}O)_6]^{9+}$ (**1a**) (Figure 1), which is based on the well-known α-Keggin structure of $[XM_{12}O_{40}]^{n-}$ with six additional square-pyramidal terminal VO^{2+} units. The polyoxocation lies on a crystallographic 4-fold axis, which passes through V(1) and V(2) and contains a central V^{5+} at (0, 0, 0). The number of Mo sites revealed by X-ray analysis is consistent with the result from elemental analysis, which gives a ratio Mo/V = 1.71:1. Twelve Mo atoms lie on a sphere with the most distribution possible, and each has a distorted octahedral environment with Mo−(t-O), 1.642−1.650 Å; Mo−(μ_3-O), 1.846−1.985 Å; and Mo−(μ_4-O), 2.467−2.468 Å. Three crystallographically distinct vanadium sites display two different coordination environments. The central vanadium V(1), residing in a tetrahedral coordination environment, is coordinated by four oxygen atoms with V−O distances 1.567(11) Å and bond angles in the range 109.0(4)−110.4(8)°. It should be pointed out that the four oxygens are distributed on eight symmetrical positions with occupancy of 0.5. V(2) and V(3) atoms possess a square-pyramidal coordination geometry with one terminal oxygen and four bridging oxygens. The V−O distances for capping VO_5 square pyramids are in the range 1.624−2.082 Å, comparable to those found in capped Keggin structures.[10]

As shown in Figure 1, an unusual feature of **1** is that the VO^{2+} groups cap six square windows on the surface of the $[V^{V}Mo^{VI}_{12}O_{40}]^{3-}$ α-Keggin anion so as to give a sphere-shaped heteropoly cation $[(V^{V}O_4)Mo^{VI}_{12}O_{36}(V^{IV}O)_6]^{9+}$ (**1a**), in which there are three coplanar metal rings parallel to each other; one Mo_4V_4 ring is derived from Mo(2) and V(3), and two Mo_4 rings are derived from Mo(1). Two Mo_4 rings are located above or below the equatorial Mo_4V_4 ring. The spherical shell has the symmetry 4/*m* and is similar to those of the $[V_{18}O_{42}]^{12-}$ anion, which can be considered as a derivative of the α-Keggin cluster shell $\{V_{12}O_{36}\}$ with six additional {VO} caps,[11] and $[V_{18}O_{42}(EO_4)]^{n-}$ (E = S, V), which can be regarded as enlarged Keggin ions with characteristic {VO} caps and a different electron population.[12] In this case, four capping V atoms are located in the equatorial plane, while the other two lie on the C_4 axis below or above the equatorial plane. Alternatively, heteropoly cation **1a** can be described as the following: three previously mentioned parallel rings are linked by sharing oxygens into a spherical crown with two square windows; the two open windows are capped by two VO^{2+} groups to form a spherical shell encapsulating a VO_4 tetrahedron in the center of the sphere.

In contrast to the extensive research on Keggin and transition-metal-substituted Keggin species,[1,13] capped Keggin derivatives are relatively limited because of the lack of good quality single crystals. To our best knowledge, only mono-, bi-, and tetracapped Keggin structures have recently been synthesized from hydrothermal reactions and structur-

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(9) Crystal data for **1**: tetragonal, space group *P*4/*mnc*, $a = 12.7305(18)$ Å, $c = 17.788(4)$ Å, $V = 2882.8(8)$ Å^3, $Z = 2$, and $D_c = 2.990$ g cm^{-3}. A dark violet needle crystal was sealed in a glass capillary with a small amount of mother liquid before diffraction data collection. Reflection data for **1** were collected on a Siemens SMART CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. An empirical absorption correction by SADABS was applied to the intensity data. The structure was solved using direct methods by locating molybdenum and vanadium atoms, and the remaining non-hydrogen atoms were located from Fourier syntheses afterward. All refinements were carried out using full-matrix least-squares on F^2 with anisotropic thermal parameters for all Mo and V atoms and partial oxygen atoms. Structure solution and refinement based on 1475 reflections with $I > 2\sigma(I)$ and 101 parameters gave R (R_w) = 0.0686 (0.2182) and GOF = 1.087.

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ally characterized.[10,14] Compound **1a** represents the first mixed Mo/V six-capped Keggin derivative that has not been previously observed in other heteropoly compounds.

Another important structural feature is that all capping vanadium atoms are in a reduced oxidation (V^{IV}) state, while other metals in the parent Keggin part ($[V^{V}Mo^{VI}_{12}O_{40}]^{3-}$) remain in their highest oxidation states. The assignments of oxidation states for the molybdenum and vanadium atoms are in agreement with their coordination geometries and confirmed by valence bond sum (BVS) calculations.[15] Surely, the central V(1) with tetrahedral coordination is of the type V^{V}; BVS calculations give values of 6.208, 6.155, 4.130, 3.53 for Mo(1), Mo(2), V(2), V(3), respectively. Another remarkable structural feature of **1a** is that each square-pyramidal vanadium atom forms four $Mo^{VI}-V^{IV}$ pairs with short Mo−V distances (2.842−3.030 Å, mean value = 2.961 Å), resulting in a “metal-bonded” sphere (Figure 1b). The V−Mo distances are comparable with Mo−V separations found in many complexes and polyoxometalates, for example, $Na_{0.5}K_{6.5}[(V^{V}O_4)Mo^{VI}_8 V^{IV}_4O_{36}(V^{IV}O)_2]\cdot 12.5H_2O$[10f] and $(Et_3NH)_5[PMo^{V}_6Mo^{IV}_6 O_{40}(V^{IV}O)_2]$.[10i] Although **1a** contains six V^{4+} sites, no EPR signal was evident at room temperature. This might be due to the delocalization of the d electrons of the reduced vanadium centers. The cluster cation charge is balanced by OH^- anion, and the remaining lattic volume is occupied by water.

In conclusion, we have synthesized a novel mixed Mo/V six-capped Keggin derivative with a spherical skeleton, which represents the first structurally characterized cationic polyoxometalate. The successful preparation of **1** demonstrates that basic hydrothermal synthesis may be a powerful synthetic route to the isolation for new polyocationic metal-oxo clusters. Relevant investigations are presently ongoing.

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Supporting Information Available: Tables of crystal data and refinement, atomic coordinates, thermal parameters, bond distances, bond angles, as well as IR spectra of **1** (PDF). Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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