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An Unusual Metallic Oxygen Cluster Consisting of a $\{AlMo_{12}O_{40}(MoO_2)\}$

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Ⓢ *Supporting Information*

ABSTRACT: A novel aluminum-containing, bimolybdenum-capped Keggin-type polyoxomolybate cluster of the $\{AlMo_{12}O_{40}(MoO_2)_2\}$ anion has been synthesized and characterized. This is the first experimentally determined Keggin-type $\{AlMo_{12}O_{40}\}$ polyoxoanion. The polyoxometalate crystal exhibits high selectivity toward the heterogeneous catalytic oxidation of cyclohexanol to cyclohexanone.

Polyoxometalates (POMs) have been extensively studied because of their diverse structural characteristics as well as wide applications in fields of materials, medicine, and catalysis.[1] POM study has been one of the rapidly growing areas in inorganic chemistry.[2,3] In 1826, the first POM phosphomolybdate, $[PMo_{12}O_{40}]^{3-}$, was reported by Berzelius[4] and features 12 distorted octahedral $\{MO_6\}$ (M = Mo or W) surrounding a central $\{XO_4\}$ tetrahedron (X = a main group or a transition-metal ion). Since then, Keggin-type clusters have been thoroughly studied in structures and applications and are the most widely recognized and stable POM anion. Theoretical studies based on density functional theory (DFT) and discrete variational methods have shown that the electronic structures of the central atoms play a significant role in the stability, oxidizing ability, and acidity of Keggin-type cores.[5] Compared to widely studied Keggin clusters using group 14 (Si^{IV} and Ge^{IV}) and 15 (P^{V} and As^{V}) elements as central atoms, because of their higher surface charge density, Keggin anions having group 13 (B^{III} and Al^{III}) elements as central-deficient atoms are relatively limited.[6]

Aluminum compounds with structurally well-defined, accessible aluminum sites are of particular interest for the development of novel aluminum-based POM materials.[7] In this sense, introducing Al^{3+} into the center of a Keggin core represents a promising and straightforward approach. However, only a few Al-centered Keggin-type polyoxotungstate $[AlW_{12}O_{40}]^{5-}$ anions have been reported and their structures determined by X-ray crystallographic analysis,[6c,8] largely because of the higher charge density of the anionic cluster and difficulties in synthesis. Thus far, the design and synthesis of aluminum-containing POMs remains a challenge. Herein, we reported a supramolecular hybrid compound, $(H_2bpp)_{1/2}(H_2bpp)_2[AlMo_{12}O_{40}(MoO_2)_2]\cdot 2H_2O$ [**1**; bpp = 1,3-di(4-pyridyl)propane], which consists of a novel bimolybdenum-capped Keggin-type cluster. For the first time, the crystal structure for pure metallic oxygen Keggin-type $\{AlMo_{12}O_{40}\}$ has been experimentally determined.

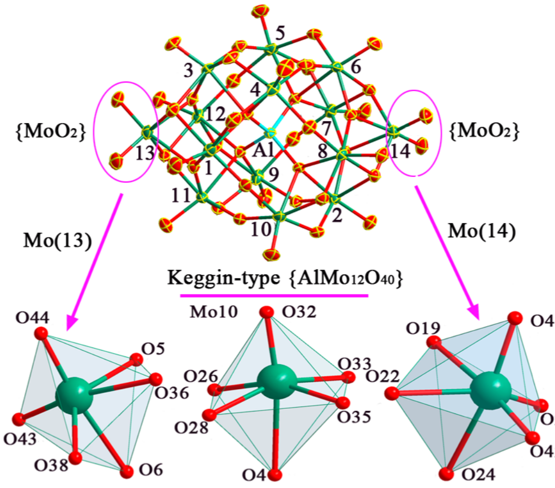

Figure 1. ORTEP and polyhedral views of anionic $\{AlMo_{14}O_{44}\}$ in compound **1**.

Single-crystal X-ray diffraction analysis revealed that compound **1** consists of a novel bimolybdenum-capped Keggin-type anion, $\{AlMo_{12}O_{40}(MoO_2)_2\}$, presenting an unusual $\{Mo_{14}\}$ cluster (Figures 1 and S1 in the Supporting Information, SI). It is remarkable in POM chemistry that two $\{Mo^{VI}O_2\}$ subunits cap onto two oppositely disposed tetragonal faces of the Keggin-type framework (Tables S1−S4 in the SI). The parent core presents a classical α-Keggin-type $\{AlMo_{12}O_{40}\}$ structure. It is composed of four $\{Mo_3O_{13}\}$ groups and one $\{AlO_4\}$ tetrahedron by sharing edges and vertices. The bond lengths of Al−O were 1.764(5)−1.783(5) Å (average value 1.770 Å). These values are significantly shorter than the theoretical 1.81 Å calculated by a fragment-interaction study[9] but in good agreement with the value of 1.765 Å calculated by using DFT (see Table S5 in the SI).[10] The bond angles of O−Al−O were in the range of 106.5(2)−115.4(2)°. These results showed that there is a slight distortion for the $\{AlO_4\}$ tetrahedron. However, 12 Mo centers provide highly distorted octahedral coordination environments. The bond distances of Mo−O can be grouped into three sets: one short $Mo-O_t$ (terminal O atom), 1.687(5)−1.701(5) Å (theoretical value 1.748 Å); four middle $Mo-O_b$ (bridge O

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atom), 1.814(5)−2.175(5) Å; one long Mo−O_c (central O atom), 2.208(5)−2.278(4) Å (theoretical value 2.27 Å). The former two sets are almost consistent with that in $\{XMo_{12}O_{40}\}$ (X = P or Si), while the Mo−O_c bond lengths are shorter because of the bigger ionic radius of Al^{3+}. In the two capping $\{Mo^{VI}O_2\}$ subunits, the Mo−O bond distances of Mo13 and Mo14 fall into a relatively narrow range: two short Mo−O_t bonds, 1.709(6)−1.716(6) Å; four remaining longer Mo−O_b bridging bonds, 1.976(5)−2.184(5) Å. A comparison of the Mo···Mo distances in the edge-sharing octahedra of the $\{Mo_3O_{13}\}$ unit of the Keggin core shows an expansion involved in bonding with the capping $\{Mo^{VI}O_2\}$. The Mo···Mo distances between the Mo atoms of the Keggin core and the Mo atoms of the extra capping $\{Mo^{VI}O_2\}$ subunits are in the same range [3.2470(9)−3.3176(9) Å], except that the distances of Mo6···Mo7 [3.4996(12) Å], Mo2···Mo8 [3.4962(12) Å], Mo11···Mo12 [3.4980(12) Å], and Mo1···Mo3 [3.5259(12) Å] are significantly longer than the other Mo···Mo separations.

Successful synthesis of the anionic cluster is dependent on many factors including the temperature, solvent, ionic strength, and nature of the counteraction.[10] In the $[AlW_{12}O_{40}]^{5-}$ polyanion, competition may exist between the Al and W atoms for the heteroatom site in the Keggin-type structure because of their similar size.[6,8,11] However, the very similar structure $[AlMo_{12}O_{40}]^{5-}$ has never been verified by experiment, in spite of its similar ionic radius (pm, octahedral environment): Mo^{VI}, 79; Mo^V, 75; W^{VI}, 74; W^V, 76.[12] Pope hypothesized[13] that a fully oxidized Keggin anion can be viewed as a neutral $M_{12}O_{36}$ cage encapsulating the internal $\{XO_4\}^{n-}$ subunit, which is in agreement with theoretical calculations carried out on the Keggin anions.[6,14] Poblet and co-workers carried out a DFT study of the $[XM_{12}O_{40}]^{n-}$ relative stability (M = W or Mo and X = P, Si, Al, As, Ge, or Ga) and showed that the Mulliken charge of the $\{XO_4\}^{n-}$ subunit is −3.53 for α-$[AlMo_{12}O_{40}]^{5-}$ and −3.80 for α-$[GaMo_{12}O_{40}]^{5-}$.[9] These values are much higher than those obtained for Keggin-type anions with X = P, Si, As, or Ge. Herein, the anions $[AlW_{12}O_{40}]^{5-}$, $[AlMo_{12}O_{40}]^{5-}$, and $[AlMo_{14}O_{44}]^{5-}$ were chosen, and all of the calculations in this work were carried out by using the *GAUSSIAN 09W* program package (see the SI). Through the calculated energy comparison between $[AlW_{12}O_{40}]^{5-}$ and $[AlMo_{12}O_{40}]^{5-}$, we find that $[AlW_{12}O_{40}]^{5-}$ is lower in energy than $[AlMo_{12}O_{40}]^{5-}$ for about 2768 kcal mol^{-1}, suggesting that $[AlMo_{12}O_{40}]^{5-}$ is less stable than $[AlW_{12}O_{40}]^{5-}$. On the basis of the above analysis, we deduce that the difficulty in synthesizing Keggin-type $[AlMo_{12}O_{40}]^{5-}$ is due to the poor stability of the highly charged $\{AlO_4\}$. It has been reported that some reduced, highly charged Keggin species could be stabilized by introducing capped groups such as {V═O}, {Sb}, and {M-ligand} (M = Cu, Ni, Co, Ag, etc.).[15] Through inspiration of this strategy, a Keggin-type $\{AlMo_{12}O_{40}\}$ anion capped by two $\{MoO_2\}$ groups has been obtained successfully. The experimental results show that the presence of $NiCl_2$ or $Cu(Ac)_2$ in the system is necessary for successful preparation because no crystals are formed otherwise.

The Keggin-type $[PMo_{14}O_{44}]^{4-}$ anion with capping Mo groups was first mentioned by Zubieta et al. but never published.[16] Then another two Mo-capping Keggin structures as tetramethylammonium (TMA) salts, $(TMA)_4[SiMo_{14}O_{44}]$ ($SiMo_{14}$) and $(TMA)_6[Si_2Mo_{28}O_{84}(H_2O)_2]$ (Si_2Mo_{28}), had been reported by reaction of the oxothio precursor $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]^{4-}$ with hydrochloric acid, silicate anions, and tetramethylammonium hydroxide under hydrothermal conditions.[17] The third compound, $[Fe(C_8H_7N_3)_3]_2[SiMo_{14}O_{44}]$, was reported in 2010.[18] It should be noted that, among the reported ($SiMo_{14}$), the two Mo−O_t bonds of the capping Mo coordination sphere are one short (ca. 1.62 Å) and one long (ca. 1.80 Å), which differ from the compound reported in this study with average values of 1.764(5)−1.783(5) Å. The aggregation of capping units to the Keggin-type polyanion can be described as a Lewis-type interaction between the four-electron-reduced $[AlMo^V_4Mo^{VI}_8O_{40}]^{9-}$ species, acting as a base, and the $\{Mo^{VI}O_2\}$ Lewis acid, producing a structure-stabilizing effect.

As shown in Table S7 in the SI, the bond valence sums (BVSs)[19] calculated from the observed bond lengths for **1** are in the range of 5.703−5.907 (average 5.847) for the 14 Mo atoms in the Keggin unit, indicating that the Mo centers consist of mixed-valence states of Mo^V and Mo^{VI}. The dark-blue color is due to intervalence charge-transfer transitions and is characteristic of molybdenum blue species. In compound **1**, there are five protons located on the pyridine N atoms based on the crystal data of intermolecular hydrogen-bonding interactions. In agreement with the acid−base equilibrium of this compound, the four-electron-reduced species of $[AlMo_{14}O_{44}]^{5-}$ is present. The four lower BVS values of 5.734 (Mo4), 5.705 (Mo5), 5.726 (Mo9), and 5.703 (Mo10) probably exist mainly as Mo^V forms. The Mulliken charges analysis on Mo atoms in $[AlMo_{14}O_{44}]^{5-}$ also supported their values (see the SI). The four Mo atoms occupied a central belt of the anion, which is often observed for compounds consisting of Keggin structures.[20] As mentioned above, the polyanion formula can be described as $[AlMo^V_4Mo^{VI}_8O_{40}(Mo^{VI}O_2)]^{5-}$. The BVS calculations are 2.899 for the Al atom in the central Al−O diamond core and 1.676−2.198 (average 1.927) for the 44 O atoms in the Keggin cluster. The BVS values of the O atoms around the capped Mo13/Mo14 centers are 1.676 (O41), 1.698 (O42), 1.680 (O43), and 1.708 (O44), suggesting that these O atoms coordinate to the Mo centers with a double-bond length of Mo═O. The X-ray photoelectron spectroscopy spectrum for Mo in **1** (see Figure S2 in the SI for other elements) gives two peaks at 232.3 and 235.5 eV, attributable to $Mo^{6+}{}_{3d5/2}$ and $Mo^{6+}{}_{3d3/2}$, respectively. However, the deconvoluted spectrum gives peaks at 231.4 and 234.7 eV, corresponding to the Mo^V oxidation state. These results further confirm the existence of Mo with different oxidation states.

Here bpp with a flexible $-(CH_2)_3-$ subunit can present abundant structural configurations (TT, TG, GG, and GG′). There are a number of significant noncovalent contacts between the oxo groups of the anions (Figure S3 in the SI), protonated bpp cations (Figure S4 in the SI), and water molecules (see Table S8 in the SI), including multipoint N−H···O and C−H···O interactions. A pseudo "core−shell" structure with a size of ca. 24.0 × 20.0 $Å^2$ was constructed (Figure S5 in the SI). This kind of complex hydrogen-bonding network (see Figure S6 in the SI) makes crystal **1** very stable in aqueous solution as well as some common organic solvents, which is important for heterogeneous catalysis.[21]

As shown in Figure 2, cyclic voltammetry of **1**-CPE (CPE = carbon paste electrode) shows five oxidation waves at +0.868, +0.462, −0.003, −0.183, and −0.300 V and three reduction waves at +0.423, +0162, and −0.364 V. When the potential is scanned from 0.25 V, where no Faradaic current flows, to 1.20 V, two oxidation waves can be observed.

The heterogeneous catalytic activity of compound **1** was evaluated for the oxidation of cyclohexanol to cyclohexanone using 30% aqueous H_2O_2 as the oxidant. Under optimal reaction

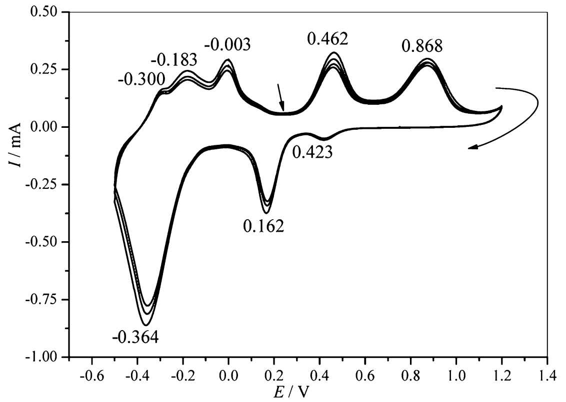

Figure 2. Cyclic voltammogram obtained with **1**-CPE in a 1 M H_2SO_4 aqueous solution (conditions: CPE working electrode, platinum counter electrode, SCE reference electrode, scan rate 10 mV s^{-1}).

parameters, 20 mg of catalyst **1** was added into a solution of 10 mL of cyclohexanol in 30 mL of *tert*-butyl alcohol and heated to 80 °C under stirring. Cautiously, 10 mL of 30% H_2O_2 was added dropwise into the solution in 20 min. The reaction was kept at 80 °C for 8 h. A 26.7% conversion with a high selectivity of 98.5% to cyclohexanone was obtained. The catalysts also can be easily isolated by centrifugal separation. The IR spectra obtained for the crystals before and after reaction show that compound **1** is very stable in this catalytic reaction (see Figure S7 in the SI). A blank reaction without the presence crystal **1** was also carried out under the same conditions, and only 4.2% conversion was observed.

In summary, an unusual aluminum-containing bimolybdenum-capped Keggin-type polyoxomolybate cluster of $\{AlMo_{12}O_{40}(MoO_2)_2\}$ has been synthesized and characterized. The polyoxoanion presents a pure metallic oxygen Keggin-type $\{AlMo_{14}\}$ framework. The cluster represents the first experimentally verified single crystal of an α-Keggin-type $\{AlMo_{12}\}$ polyanion. The catalytic activity of this crystal was evaluated in the oxidation of cyclohexanol to cyclohexanone with significantly improved conversion yield and selectivity. Our study shows that there is vast space to prepare and employ aluminum-containing POMs for potential applications in heterogeneous catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, computational details, CIF file of **1**, Tables S1−S8, and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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