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A Cagelike Polyanion with a Ag^+ Enwrapped, $[AgAs_2Mo_{15}O_{54}]^{11-}$

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S Supporting Information

ABSTRACT: The polyanion $[AgAs_2Mo_{15}O_{54}]^{11-}$ has an unusual cage-like structure composed of $[AsMo_6O_{27}]^{15-}$ and $[AsMo_6O_{24}]^{9-}$ subunits connected by three MoO_4 tetrahedra, and a Ag^+ cation is inclosed at the center of the cage and coordinated by two As atoms with a As—Ag—As bond angle of 180° along with three μ_3-oxo groups from MoO_4 tetrahedra to lead to a trigonal-pyramidal coordination geometry. The compound was also characterized by IR, X-ray photoelectron spectroscopy, fluorescent spectroscopy, and thermogravimetry-differential scanning calorimetry. The stability of $[AgAs_2Mo_{15}O_{54}]^{11-}$ in aqueous solution was investigated by using electronic absorbance spectroscopy and electrospray ionization mass spectrometry.

INTRODUCTION

Polyoxometalates (POMs) are a fascinating class of metal—oxygen cluster compounds, which exhibit compositional diversity and structural versatility as well as potential applications in a variety of fields, including catalysis, analytic chemistry, medicine, and materials science.[1,2] One of the key characteristics of POMs is a strong affinity for metallic cations. Certain POMs can selectively trap metal cations, and these water-soluble anions can be potentially useful for applications, such as detergents, artificial enzymes, and antibiotics, and possible uses for sequestration and immobilization of nuclear wastes.[3−8] The cage-like and cryptate compounds in POMs are especially important, some kinds of POMs can capture metallic cations in their cavities upon formation owing to template effects, or by substitution, the cations can either be trapped in a cluster cavity with closed or open pores. The first cryptate in polyoxometalate, $[NaSb_9W_{21}O_{86}]^{18-}$,[9] was reported in 1976. Up to now, there have been a few, and their derivatives reported, such as, $[NaAs_4W_{40}O_{140}]^{27-}$[10] and its derivatives: $[NH_4Co_2As_4W_{40}O_{140}]^{23-}$,[11] $[M^nAs_4W_{40}O_{140}]^{(28-n)-}$ (M^{n+} = K^+, Ba^{2+}, Ce^{3+}),[12] $[Ln_3As_4W_{40}O_{140}]^{20-}$ (Ln^{III} = Ce, Nd, Sm, Gd), $[M^mLn_2As_4W_{40}O_{140}]^{(18-m)-}$ (M = Ba^{II}, K^+, none, and Ln^{III} = La, Ce, Gd),[13] $[LnNi_2As_4W_{40}O_{140}]^{21-}$ (Ln^{III} = Y, Ce, Pr, Nd, Sm, Eu, Gd),[14] $[(UO_2)_3V^{IV}As_4W_{40}O_{140}]^{19-}$,[15] $[Na_2Ni_3As_4W_{40}O_{140}]^{20-}$;[16] and $[NaSb_9W_{21}O_{86}]^{18-}$ derivatives: $[M^nSb_9W_{21}O_{86}]^{(19-n)}$ (M^{n+} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+},[17] most Ln^{3+});[18] $[NaP_5W_{30}O_{110}]^{14-}$[19] and its derivatives: $[M^nP_5W_{30}O_{110}]^{(15-n)-}$ (M^{n+} = Ca^{2+}, most Ln^{3+}, U^{4+}),[20−22] and $[P_8W_{48}O_{184}]^{40-}$[23] and its derivatives.[24] Recently, a supramolecular POM based on $[AsW_9O_{33}]^{9-}$ and $[Mo_3S_4]^{4+}$ selectively encapsulates Cu^+ and Ag^+,[25] and a cage-like disilicoicosatungstate, $[H_n(\gamma\text{-}SiW_{10}O_{32})_2(\mu\text{-}O)_4]^{(8-n)-}$ (n = 1, 2), encapsulating dicationic Pb^{2+} and Sr^{2+} ions and monocationic Ag^+, Na^+, K^+, and Rb^+ ions have been reported.[26] The mechanism of formation of these POMs is not well-known, and structurally they may be seen as larger polyoxoanion assemblies by transition metals or inorganic groups connecting several basic building blocks, such as $SbW_7O_{24}{}^{3-}$, $AsW_9O_{33}{}^{9-}$, $PW_5O_{26}{}^{14-}$, $P_2W_{12}O_{48}{}^{14-}$, etc. All of the above-mentioned POMs embedded metallic cations in their cavities are polyoxotungstates; in contrast cage-like or cryptate polymolybdates remains far less developed. So far the reports on the polymolybdates enclosed with a metal cation in their cavity or circle have been mainly concentrated on several well-known structural polyanions and their derivatives in which the metal cationic species act as the templates, such as Keggin-type ion, $[M^{II}Mo_{12}O_{40}]^{6-}$ (M = Co, Ni)[27] and its derivative capped with four $Ni(en)(H_2O)$ groups, $[(Ni^{II}O_4)Mo^V{}_8Mo^{VI}{}_4O_{30}(\mu_2{-}OH)_6\{Ni(en)(H_2O)\}_4]$,[28] Silverton-type polyanion with D_{3d} symmetry, $[CeMo_{12}O_{42}]^{8-}$[29] and $[GdMo_{12}O_{42}]^{9-}$;[30] Waugh heteropolymolybdate with D_3 symmetry, $[XMo_9O_{32}]^{6-}$ (X = Ni^{4+}, Mn^{4+});[31] and Anderson-type polyanion $M^{x+}Mo_6O_{24}{}^{(12-x)-}$ (M = Al, Cr, Fe, Co, Rh, Ga)[32] and its derivatives capped with two cyclic As_3O_6 trimers on opposite faces, $[(M^{II}O_6)(As_3O_3)_2Mo_6O_{18}]^{6-}$ (M = Co, Zn, Ni).[33] Recently, a chelated cobalt(III) center as structural components of polyoxomolybdates has been reported by Pope and his co-workers, $[\{Co^{II}(H_2O)_2\}\{Co(en)\}_8\{Mo_{20}O_{76}\}]^{6-}$.[34] In addition, Müller et al. reported a mixed-valent molybdenum blue-type polyoxomolybdate $[Mo_{120}O_{366}(H_2O)_{48}H_{12}\{Pr(H_2O)_5\}_6]^{6-}$, where the six nine-fold-coordinated Pr^{3+} centers are linked to the inner (cavity) surface of the cluster.[35] However, the exact meaningful cage-like heteropolymolybdate anion inclosed a metal ion has not been reported.

Herein we report a novel cage-like polyoxoanion $[AgAs_2Mo_{15}O_{54}]^{11-}$, in which a silver cation is enwrapped at the center of the cage. As far as we know, this is the first polyoxometalate capturing a Ag^+ cation in its cavity.

EXPERIMENTAL SECTION

General Methods and Materials. All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer; Ag, As, and Mo were analyzed on a IRIS

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Advantage ICP atomic emission spectrometer. The powder X-ray diffraction (PXRD) data were collected on a Bruker D8 diffractometer with Cu Kα radiation. IR spectra were recorded in the range of 400−4000 cm^{-1} on an EQUINOX55 FT/IR spectrophotometer using KBr pellets. thermogravimetry-differential scanning calorimetry (TG-DSC) analyses were performed on a NETZSCH STA 449C TGA instrument in flowing N_2 with a heating rate of 10 $°C \cdot min^{-1}$. X-ray photoelectron spectroscopy (XPS) measurement was performed an ESCALab220i-XL electron spectrometer from VG Scientific with 300W Mg Kα radiation. The base pressure was about 3×10^{-9} mbar. The binding energy was referenced to the C_{1s} line at 284.8 eV from adventitious carbon. All spectra were collected at an electron takeoff angle of 90° from the surface. Excitation and emission spectra were obtained on a Hitachi F4500 spectrofluorometer equipped with a 450W xenon lamp as the excitation source. UV spectra were performed on a Shimazu UV-2550 spectrophotometer. MicroTOF-QII mass spectrometer with an electrospray ionization (ESI) source (Bruker, Germany) was used. The desolvation temperature was to set to 180 °C. A capillary voltage of 2.6 kV was used in the negative scan mode, collision energy −10.0 eV. Time-of-flight mass spectra were acquired at a resolution of ca. 17 500 (full width at half-maximum) at m/z 2000. Mass calibration was performed using a solution of tunemix from m/z 322 to 1522. Acetonitrile sample solutions were infused via a syringe pump directly connected to the ESI-MS source at a flow rate of 3 μL/min. The observed isotopic pattern of each compound perfectly matched the theoretical isotopic pattern calculated from their elemental composition using the microTOF control program.

Synthesis. $(NH_4)_{11}[AgAs_2Mo_{15}O_{54}] \cdot 6H_2O \cdot 2CH_3CN$ (**1**): The synthesis of compound **1** was accomplished by adding a solution of As_2O_3 (0.08 g, 0.4 mmol) dissolving in 4 M aqueous ammonia (2 mL) to a solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.99 g, 0.8 mmol) dissolving in H_2O (10 mL) with vigorous stirring, and the pH value was adjusted to 6.5 by adding nitric acid. Then 0.07 g of $AgNO_3$ (0.4 mmol) dissolved in 5 mL of water was added, and the solution was heated to 90 °C for 30 min. After then 2 mL of 1:1 CH_3CN and $NH_2CH_2CH(NH_2)CH_3$ mixture solution was added, and the mixture was stirred for another 15 min, filtered, and allowed to cool to ambient temperature. After 1−2 days colorless crystals were isolated (yield: 0.76 g, 65%, based on Ag). IR for **1**: 3421(s), 3160 (s), 1621(m), 1404 (s), 1036 (s), 935 (sh), 899 (s), 820 (sh), 850 (sh),760 (s), 674 (m), 638 (m), 556 (w), and 447 (w) cm^{-1}. Anal. calcd (found) for $C_4H_{62}N_{13}AgAs_2Mo_{15}O_{60}$: Mo, 48.8(49.2); As, 5.1(5.0); Ag, 3.7(3.6); C, 1.63(1.66); N, 6.17(6.14); and H, 2.12(2.22).

$(NH_4)_{11}[AgAs_2Mo_{15}O_{54}] \cdot 8H_2O$ (**2**): The synthesis of compound **2** was accomplished by adding a solution of As_2O_3 (0.08 g, 0.4 mmol) dissolving in 4 M aqueous ammonia (2 mL) to a solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.99 g, 0.8 mmol) dissolving in H_2O (10 mL) with vigorous stirring, and the pH value was adjusted to 7.0 by adding nitric acid. Then 0.07 g of $AgNO_3$ (0.4 mmol) dissolved in 5 mL of water was added, and the solution was heated to 90 °C for 30 min. After then 2 mL of 1:1 CH_3OH solution was added, and the mixture was stirred for another 15 min, filtered, and allowed to cool to ambient temperature. After 1−2 days colorless crystals were isolated (yield: 0.49 g, 44%, based on Ag). IR for **2**: 3426 (s), 3165 (s), 1620 (s), 1404 (s), 935 (sh), 897 (s), 850 (sh), 820 (sh),760 (s), 674 (m), 638 (m), 515 (w), and 446 cm^{-1}. Anal. calcd (found) for $H_{60}AgAs_2Mo_{15}N_{11}O_{62}$: Mo, 49.6(50.1); As, 5.2(4.9); Ag, 3.7(3.8); N, 5.31(5.25); and H, 2.08(2.10).

These crystals are stable in the mother liquid but easily lose solvent molecules and effloresce into microcrystals in air.

X-ray Crystallography. The selected crystal of **1** or **2** was sealed in a capillary with mother liquid for diffraction measurement on a BRUKER SMART APEX II CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) radiation at 293(2) K. The structures were solved by direct methods and refined on F^2 by full matrix least-squares using the SHELXTL-97 program package.[36] Heavy atoms (Mo, As, and Ag) and the framwork oxygen atoms of the polyanion were refined with anisotropic displacement parameters except O10 and O25 of **2**, the other atoms were refined isotropically. Hydrogen atoms were not included but were included in the structure factor calculations. For the hydrated ammonium salt, the data did not support discrimination between oxygen and nitrogen atoms, and the ammonium ions were modeled as oxygen atoms. As usual for polyoxometalates, the crystal shows large disorder in the range of counterions and water molecules. Accordingly, the exact formula was determined by elemental analyses. A summary of the crystallographic date and structure refinement for compounds **1**-**2** is given in Table 1. The selected bond lengths and angles of the two compounds are listed in the Supporting Information. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC number 781799 for **1** and Inorganic Crystal Structure Database with CSD number 422183 for **2**, respectively.

Table 1. Summary of Crystallographic Data for the Structures of $(NH_4)_{11}[AgAs_2Mo_{15}O_{54}] \cdot 6H_2O \cdot 2CH_3CN$ (1) and $(NH_4)_{11}[AgAs_2Mo_{15}O_{54}] \cdot 8H_2O$ (2)

	1	2
empirical formula	$C_4H_{62}N_{13}AgAs_2Mo_{15}O_{60}$	$H_{60}AgAs_2Mo_{15}N_{11}O_{62}$
M, g mol^{-1}	2949.48	2903.40
cryst syst	orthorhombic	orthorhombic
space group	*Pnma*	*Pnma*
a (Å)	25.144(8)	25.556(8)
b (Å)	19.410(6)	19.643(6)
c (Å)	13.355(5)	13.527(4)
V, $Å^3$	6518(4)	6791(4)
Z	4	4
temp (K)	293(2)	293(2)
d_{calcd}, g cm^{-3}	3.006	2.840
GOF	0.995	1.009
$R1^a$ [$I > 2\sigma(I)$]	0.0606	0.0734
$wR2^b$ [($I > 2\sigma(I)$]	0.1583	0.1696
$R1^a$ (all data)	0.1043	0.1235
$wR2^b$ (all data)	0.1692	0.1696
$\Delta\rho_{min/max}$ ($e/Å^3$)	2.355/ −1.297	2.342/ −1.290

[a] $R1 = [\Sigma|F_o| - |F_c|]/[\Sigma|F_c|]$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

RESULTS AND DISCUSSION

Structures of $[AgAs_2Mo_{15}O_{54}]^{11-}$. X-ray structural analysis reveals that the structure of the polyanion $[AgAs_2Mo_{15}O_{54}]^{11-}$ (**1a**) has a C_{3v} molecular symmetry and exhibits a cage-like structure which is composed of one $[AsMo_6O_{27}]^{15-}$ subunit (subunit A) and one $[AsMo_6O_{24}]^{9-}$ subunit (subunit B) connected by three MoO_4 tetrahedra, and a silver(I) ion is inclosed at the center of the cage (Figures 1−2 and S1, Supporting Information). Both subunits A and B consist of a heteroatom As(III) surrounded by a ring of six MoO_6 octahedra. However, the connection fashion of six MoO_6 octahedra in subunits A and B is different from that of the well-known Anderson-type polyanion in which six MoO_6 octahedra are connected to each other by sharing edges. The six MoO_6 octahedra alternately share edges and corners in subunit A and alternately share faces and corners in subunit B, respectively. The Mo−Mo distances of $\{Mo_2O_9\}$ of the face-sharing octahedral of MoO_6 in subunit B are in the range of 3.128−3.141(2) Å, which is much shorter than 3.290−3.297(2) Å of $\{Mo_2O_{10}\}$ of the edge-sharing octahedra in subunit A. Each MoO_4 tetrahedron connects subunit A via two μ_2-oxoygen and subunit B via one μ_3-oxoygen. The central heteroatom As(III) both in subunits A and B, located slightly above the plane of six molybdenum atoms with the lone pair of As(III) on the side of the central Ag(I) ion, is coordinated to Ag(I) ion with the Ag−As distances of 2.500(2) Å and 2.575(2) Å, respectively, which falls within the range of 2.47−2.87 Å observed for other Ag(I)−As complexes.[37] In addition, there are three μ_3-oxo groups from MoO_4 tetrahedra close to Ag(I) ion with the Ag−O distances in the range of 2.752(2)−2.849(2), which fall within the range of 2.13−3.03 Å observed for other Ag(I)−O complexes.[38] Thus, two shorter axial Ag(I)−As bonds with the As(1)−Ag(1)−As(2) bond angle of 179.92(11)° and three longer equatorial Ag(I)−O bonds lead to a trigonal-pyramidal coordination geometry. The Ag(I) ion is typically characterized as "soft" in coordination chemistry. It can adopt a variety of coordination environments, and the coordination number of Ag(I) ion varies from two to seven according to ligand conformation and counterion; the most common one being a four-coordinate tetrahedral geometry. Searches of the Cambridge Crystallographic (http://www.ccdc.cam.ac.uk) and Inorganic Crystal (http://icsdweb.fiz-karlsruhe.de) Structure Databases show that the angle of As−Ag−As varies from 51.6 to 168.8°.[37e,f] Therefore, this is the first example of bonding mode with a As−Ag−As bond angle of 180° in coordination chemistry.

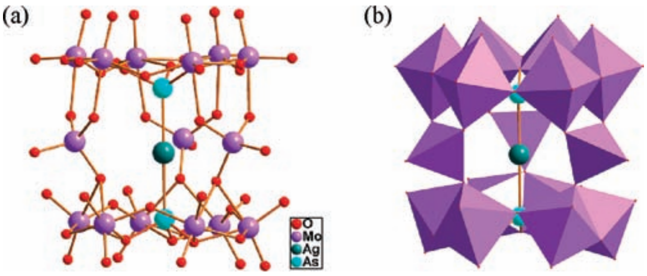

Figure 1. (a) Ball-and-stick representation of polyanion **1a**. (b) Combined polyhedral/ball-and-stick representation of polyanion **1a**.

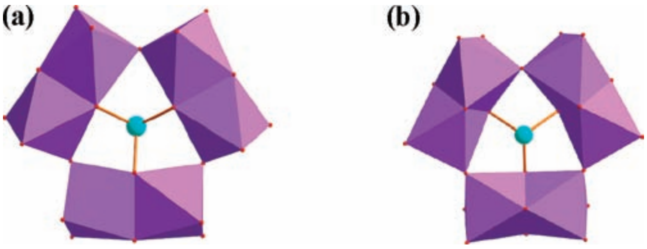

Figure 2. Combined polyhedral/ball-and-stick representation of subunits A (left) and B (right).

The molybdenum-oxo framework of subunit A has been observed before in the functionalized heteropolymolybdates, $[XMo_6O_{21}(O_2CRNH_3)_3]^{n-}$ (n = 2, X = Se^{IV}, Te^{IV}; n = 3, X = As^{III}, Sb^{III}, Bi^{III}; R = CH_2, C_2H_4, C_3H_6,$CHCH_3$, $CH(CH_2)_4NH_2$), $HMo_6VO_{22}(NH_3CH_2COO)_3{}^{2-}$,[39] $CH_3AsO_3Mo_6O_{18}(H_2O)^{2-}$,[40] $(O_3PCH_2OPO_3)Mo_6O_{18}(H_2O)^{4-}$[41] and $(O_3POPO_3)Mo_6O_{18}(H_2O)^{4-}$.[42] The molybdenum-oxo framework of subunit B has never been observed and should be specially noted owing to the presence of the face-sharing

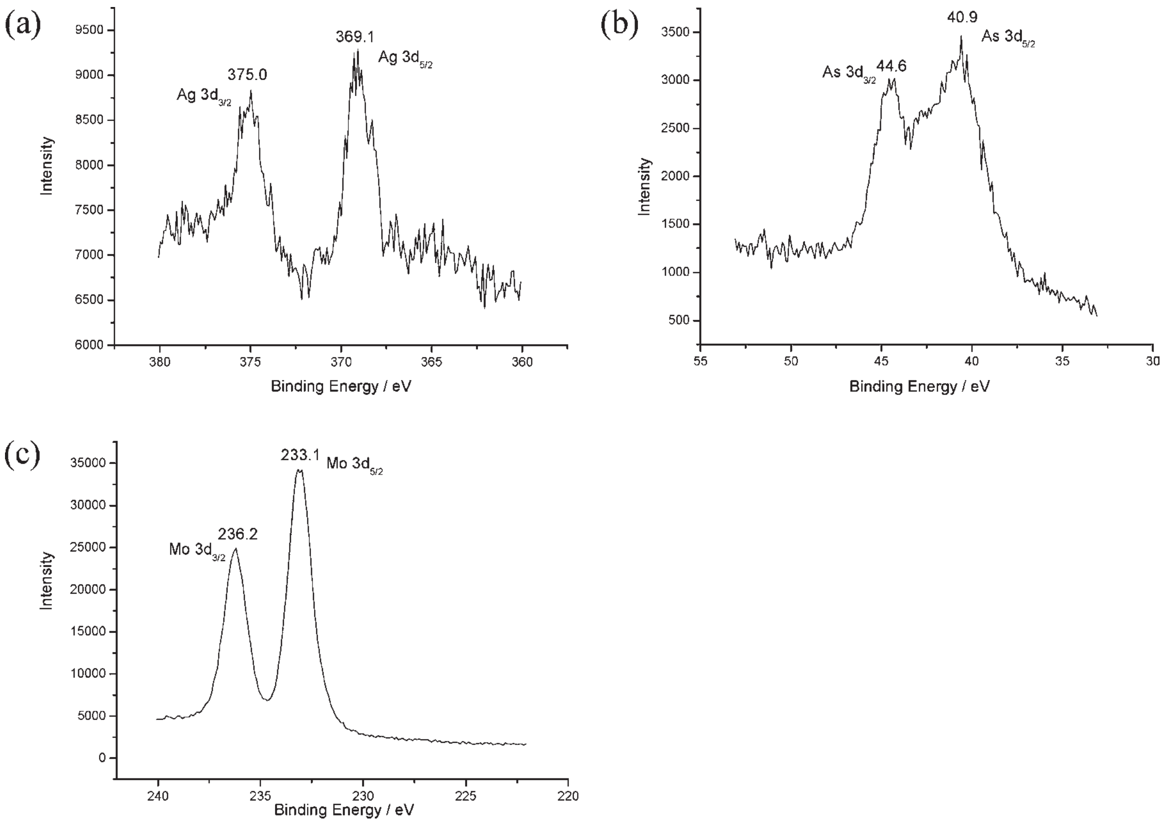

Figure 3. (a) XPS spectra of **1** for Ag $3d_{5/2}$ and Ag $3d_{3/2}$. (b) XPS spectra of **1** for As $3d_{5/2}$ and As $3d_{3/2}$. (c) XPS spectra of **1** for Mo $3d_{5/2}$ and Mo $3d_{3/2}$.

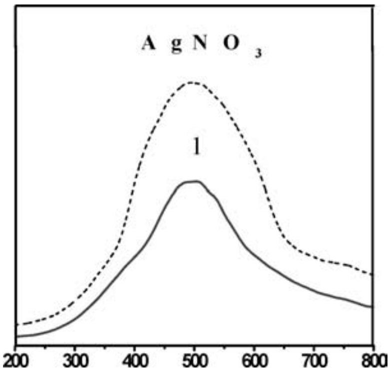

Figure 4. Fluorescence spectra of compound **1** and $AgNO_3$. The line code is as follows: $AgNO_3$(• • •) and compound **1**(---).

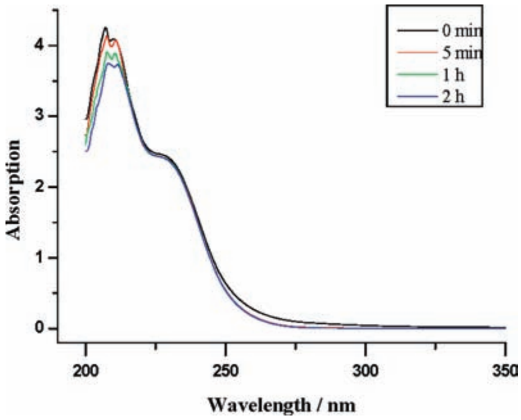

Figure 5. Time profile of the electronic absorption spectra of a 0.01 mM aqueous solution (pH = 6.5) of **1**.

octahedra of MoO_6. The molybdenum dinuclear fragments of edge- and angle-sharing octahedral are well-known as the fundamental building units in the polyoxomolybdate anions. But the face-sharing octahedral of MoO_6 is rare. The tetranuclear complex $[(H_2CO_2)Mo_4O_{12}(OH)]^{3-}$[43] and the hexanuclear complex $[(PhAs)_2Mo_6O_{24}(H_2O)]^{4-}$[44] are examples which have been reported owning the face-sharing octahedra of MoO_6.

The oxidation states for the As and Mo atoms are consistent with their coordination geometries and are also confirmed by bond valence sum (BVS) calculations. The BVS values for the As and Mo atoms are from 3.18 to 3.35 with the average of 3.27 and from 5.84 to 6.10 with the average of 5.94, respectively.

Figure S2, Supporting Information shows the packing arrangement of **1** along *c*- and *b*-axis, respectively. The adjacent polyanions are aligned in *a* direction and alternatively anti-aligned in *b* direction. The ammonium cations, lattice water, and solvent molecules fill the interspace of polyanions and interact each other through electrostatic interactions and hydrogen bonds.

Synthesis. The polyanion can be isolated in the form of $(NH_4)_{11}[AgAs_2Mo_{15}O_{54}]\cdot 6H_2O\cdot 2CH_3CN$ **1** or $(NH_4)_{11}[AgAs_2Mo_{15}O_{54}]\cdot 8H_2O$ **2** in aqueous solution. In the process of synthesis, the pH value is a crucial factor affecting the isolation of the title compounds and should be carefully controlled between 6.0 and 7.0. When pH value is lower than 6.0, $[\beta\text{-}Mo_8O_{26}]^{4-}$ is obtained, and when pH value is higher than 7.0, there is a large number of precipitation, and in addition, the presence of a small amount of organic solvent, such as acetonitrile or methanol, is needed for the isolation of the polyanion.

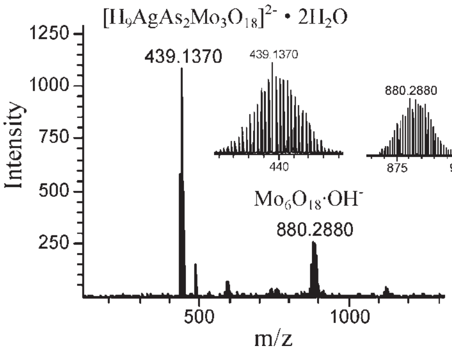

Figure 6. Negative mode electrospray mass spectrum in CH_3CN solution of compound **1** recorded under wide declustering conditions.

FT-IR and XRPD Patterns. The IR spectra (Figure S3, Supporting Information) of compounds **1** and **2** show similar patterns characteristic of the polyanion $[AgAs_2Mo_{15}O_{54}]^{11-}$. These are a strong band in the range of 935−850 cm^{-1} assigned to the characteristic absorption of terminal oxo groups $\upsilon(MoO_t)$, the weak absorption at about 820 cm^{-1} to that of υ(As−O) and the band at 760−674 cm^{-1} to those of υ(Mo−O−Mo), respectively.[45] The band at 3421 and 1404 cm^{-1} is ascribed to water molecules, stretching and bending vibrations of O−H. The band at 3160−3000 cm^{-1} is ascribed to the N−H stretching vibration of ammonium ion. The band at 1040 cm^{-1} for **1** is ascribed to the N−C stretching vibration of acetonitrile. The XRPD patterns for compounds **1** and **2** are presented in Figure S4, Supporting Information. The diffraction peaks of both simulated and experimental patterns match well in key positions, indicating thus the phase purities of compounds **1** and **2**.

XPS Spectra. In the XPS spectra (Figure 3), two peaks at 236.2 and 233.1 eV are attributed to $Mo^{6+}(3d_{5/2})$ and $Mo^{6+}(3d_{3/2})$, respectively; two peaks at 44.6 and 40.9 eV are ascribed to As^{3+}-$(3d_{5/2})$ and As^{3+} $(3d_{3/2})$, respectively; two peaks at 369.1 and 375.0 eV are assigned to $Ag^{+}(3d_{5/2})$ and $Ag^{+}(3d_{3/2})$, respectively.

Fluorescent Spectroscopy. Excitation of solid sample of **1** at λ = 490 nm produces an intense luminescence with a peak maximum at 496 nm (Figure 4) assigned to the emission of the d−d electronic transition of Ag^+ from the excited to ground state. The intensity of **1** is weaker than that of $AgNO_3$ owing to the change of the chemical environment around the Ag^+.

Thermal Analyses. Thermogravimetric analysis of **1** exhibits three weight-loss stages in the range of 20 and 500 °C (Figure S5, Supporting Information). The first weight loss of 5.7% occurs between 30 and 220 °C due to the loss of all water and acetonitrile molecules (calcd 5.9%). The second weight loss is 6.9% from 220 to 328 °C, assigned to the decomposition of 11 ammonia molecules (calcd 6.3%). The DSC curve shows two small endothermic peaks, respectively, at ∼100 and ∼270 °C. The third stage in the temperature range 328−435 °C corresponds to the decomposition of the polyanion framework structure with the sublimation of As_2O_3 according to the reaction $H_{11}[AgAs_2Mo_{15}O_{54}] \rightarrow As_2O_3\uparrow + 5.5H_2O\uparrow + 0.5Ag_2O + 15MoO_3$. The DSC curve shows a small exothermic peak at 420 °C. The observed total weight loss of 21.6% compares well with the calculated value of 22.9%. In general, we take the temperature 420 °C of the exothermic peak in the DSC curve as a sign of its thermostability.

UV and Electrospray Mass Spectra. The stability of the polyanion **1a** in water has been studied using the time-dependent

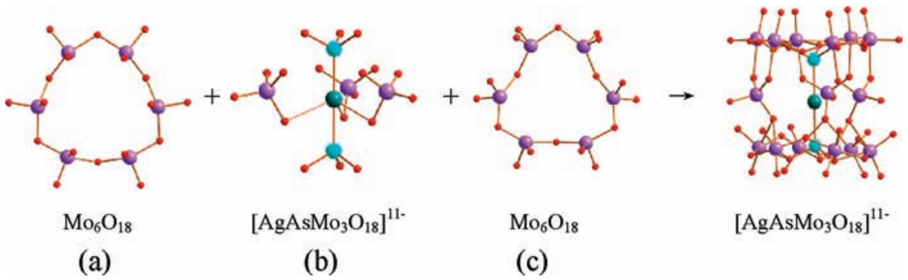

Figure 7. Supposed the three main fragments of the polyanion in the ESI process or the possible mechanism of self-assembly of polyoxometalate clusters in solution.

UV spectra of a 0.01 mM aqueous solution (pH = 6.5). The spectrum of a fresh sample (taken within seconds after dissolving **1** in 0.01 mM aqueous solution, pH = 6.5, aqueous solution) shows two peaks at 207and 210 nm and a broad shoulder at ca. 227 nm (Figure 5). The higher energy bond at ~207 and 210 nm is attributed to the charge transfer of O_t-Mo, and the lower energy bond at about ca. 227 nm is attributed to that of O_b/O_c-Mo. With the extension of time, the profile of the spectra changes with a decrease in intensity. The results may mean that the polyanion **1a** is unstable in the aqueous solution.

ESI-MS has been used to exploit the solution state rearrangement of POM clusters. By employing this approach it is then possible to transmit many of the labile species present in solution into the mass spectrometer and so allow some correlation between the essentially gas-phase measurements with solution and solid-state studies.[46] The negative mode electrospray mass spectrum in CH_3CN solution of compound **1** recorded under wide declustering conditions is shown in Figure 6. The spectrum displays the main fragment peaks of the polyanion, the signal at m/z 439.1 (100%) regularly spaced with $\Delta m/z = 1/2$ which implies a 2− charge could be attributed to $[H_9AgAs_2Mo_3O_{18}]^{2-}\cdot 2H_2O$, which consists of the central fragment $[AgAs_2Mo_3O_{18}]^{11-}$(Figure 7b) attached nine protons and two water molecules, and the signal at m/z 880.3 (14%) paced with $\Delta m/z = 1$ to $Mo_6O_{18}\cdot OH^-$ composed of the basic framework Mo_6O_{18} (Figure 7a and c) of subunits A or B with a OH^-. From the findings we suppose that the polyanion could be decomposed into three main fragments in the ESI process or speculate the possible mechanism of self-assembly of polyoxometalate clusters in solution.

In conclusion, we have successfully synthesized a novel polyoxoanion $[AgAs_2Mo_{15}O_{54}]^{11-}$.The polyanion represents the first example of the exact meaningful cage-like heteropolymolybdate anion enclosed in a silver cation at the center of the cage. The silver cation is coordinated by two As(III) ions with the As−Ag−As bond angle of 180° and three μ_3-oxo groups to lead to a trigonal-pyramidal coordination geometry, and the five-coordinate Ag(I) was also observed in the central fragment $[AgAs_2Mo_3O_{18}]^{11-}$ of the polyanion by using ESI approach. The isostructural species would be expected by substituting Ag^+ with the similar characteristic cations, such as Cu^+, Au^+ or Hg^{2+}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic information files $(NH_4)_{11}[AgAs_2Mo_{15}O_{54}]\cdot 6H_2O\cdot 2CH_3CN$ (**1**) and $(NH_4)_{11}[AgAs_2Mo_{15}O_{54}]\cdot 8H_2O$ (**2**) and TG-DSC curve of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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