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$Cs_5Mo_8O_{24}(OH)_2AsO_4·2H_2O$ and $Cs_7Mo_8O_{26}AsO_4$: Two Novel Molybdenum(VI) Arsenates Containing Heteropolyanions $[AsMo_8O_{30}H_2]^{5-}$ and $[AsMo_8O_{30}]^{7-}$

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Two novel molybdenum(VI) arsenates, $Cs_5Mo_8O_{24}(OH)_2AsO_4·2H_2O$ and $Cs_7Mo_8O_{26}AsO_4$, have been prepared and their structures determined. $Cs_5Mo_8O_{24}(OH)_2AsO_4·2H_2O$ was synthesized by a high-temperature, high-pressure hydrothermal method and characterized by single-crystal X-ray diffraction, IR spectroscopy, and thermogravimetric analysis. Diffraction measurements were performed on a CCD area detector system. It crystallizes in the orthorhombic space group *Cmcm* with $a = 8.8048(3)$ Å, $b = 23.4314(9)$ Å, $c = 16.0499(6)$ Å, and $Z = 4$. The structure consists of $[AsMo_8O_{30}H_2]^{5-}$ cluster anions which are made up of two tetranuclear $\{Mo_4O_{15}H\}$ cores linked by an arsenic(V) atom. Upon heating, half of the structural unit first transforms to $Cs_7Mo_8O_{26}AsO_4$, and the other half decomposes to Cs_3AsO_4 and MoO_3 at higher temperature. $Cs_7Mo_8O_{26}AsO_4$ crystallizes in the orthorhombic space group *Ibca* with $a = 12.1247(4)$ Å, $b = 22.9153(7)$ Å, $c = 24.3777(7)$ Å, and $Z = 8$. It possesses $[AsMo_8O_{30}]^{7-}$ cluster anions resembling to those found in the original structure. $Cs_7Mo_8O_{26}AsO_4$ may be viewed as a dehydrated form of $Cs_5Mo_8O_{24}(OH)_2AsO_4·2H_2O$ from which the lability of $[AsMo_8O_{30}H_2]^{5-}$ with respect to dissociation of AsO_4^{3-} is first shown in the solid state. Structural differences between $[AsMo_8O_{30}H_2]^{5-}$ and $[AsMo_8O_{30}]^{7-}$ are closely correlated with the cesium cations and water molecules present in the crystals. The title compounds are also the first structurally characterized examples in the Cs−Mo−As−O system.

Introduction

A large number of new compounds have been synthesized and structurally characterized in the A−Mo−P−O system, where A is an organic or inorganic cation.[1] They exhibit varieties of novel frameworks and are of much interest as catalysts or as ionic exchangers.[2] In contrast to the rich structural chemistry of molybdenum phosphates, the Mo/As/O system remains relatively undeveloped. In an effort to obtain new materials with novel structures and interesting properties, we recently employed hydrothermal methods for the synthesis of molybdenum arsenates. Molybdenum is well-known for its ability to adopt different oxidation states. Many reported phosphates have Mo in oxidation states below VI, where polyanion clusters with Mo−Mo bonds often occur.[3] On the other hand, the chemistry of $Mo^{VI}/X^{V}/O$ in aqueous solution has been dominated by the so-called Keggin ions[4] $[Mo_{12}O_{40}X]^{3-}$, and Dawson polyanions[5] $[Mo_{18}O_{62}X_2]^{6-}$, where X = P, As. These cluster anions are formed of edge- and corner-shared MoO_6 octahedra. By employing hydrothermal reactions under mild conditions, we had obtained the Mo(VI) compound, $(C_5H_5NH)_2(Mo_2O_5)(HAsO_4)_2·H_2O$,[6] which contained the cluster anions $[(Mo_4O_{10})(HAsO_4)_4]^{4-}$ made up of two pairs of binuclear $[Mo_2O_{10}]^{2-}$ cores without Mo−Mo bonds. In an attempt to prepare structures containing larger metal−oxygen clusters, a new molybdenum(VI) arsenate, $Cs_5Mo_8O_{24}(OH)_2AsO_4·2H_2O$, has been obtained under more rigorous hydrothermal conditions. The structure consists of $[AsMo_8O_{30}H_2]^{5-}$ cluster anions which are formed of two $\{Mo_4O_{15}H\}$ cores linked by an arsenic(V) atom. The tetranuclear core was first characterized in the well-known anion $[R_2AsMo_4O_{14}(OH)]^{2-}$.[7] Interestingly, the dialkyl tetramolybdoarsinate anion consists of one $\{Mo_4O_{15}H\}$ core whereas the $[AsMo_8O_{30}H_2]^{5-}$ cluster anion has two. Such a dimer structure is unprecedented in the heteropolyoxometalates. Furthermore, $\{Mo_4O_{15}H\}$ cores lose protons in the solid state[8] to form the higher negatively charged $[AsMo_8O_{30}]^{7-}$ anion as observed in the dehydrate $Cs_7Mo_8O_{30}AsO_4$. Structural differences between $[AsMo_8O_{30}H_2]^{5-}$ and $[AsMo_8O_{30}]^{7-}$ are closely correlated with the number of cesium cations and water molecules in their crystals. Being the first structurally characterized examples in the Cs−Mo−As−O system, $Cs_5Mo_8O_{24}(OH)_2AsO_4·2H_2O$ and $Cs_7Mo_8O_{26}AsO_4$ belong to a new class of anion clusters distinctly different from those of Keggin and Dawson types. In this paper, we present the hydrothermal synthesis, structure, and IR data of $Cs_5Mo_8O_{24}(OH)_2$ $AsO_4·2H_2O$. The thermal decomposition scheme of $Cs_5Mo_8O_{24}(OH)_2$ $AsO_4·2H_2O$ to $Cs_7Mo_8O_{26}AsO_4$ and their structural relationship are discussed as well.

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Experimental Section

Synthesis. Hydrothermal reactions were performed in gold ampules contained in a Leco Tem-Pres autoclave where pressure was provided by water. Chemicals of reagent grade or better were used as received. CsH_2AsO_4 was prepared from a solution of As_2O_3 dissolved in H_2O_2 with cesium hydroxide. Colorless chunk crystals of $Cs_5Mo_8O_{24}(OH)_2AsO_4{\cdot}2H_2O$ were obtained by reacting CsH_2AsO_4 (0.2728 g, 1.0 mmol), MoO_2 (0.0512 g, 0.4 mmol), 3 M H_3AsO_4 (0.334 mL, 1.0 mmol), and H_2O (0.084 mL) in sealed gold ampules (0.234 cm inside diameter) with 65% filling and heated at 550 °C and an estimated pressure of 33 000 psi for 8 h. The autoclave was first cooled at 5 °C/h to 250 °C and then cooled to room temperature by turning off the power of the furnace. The product was filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. The reaction product obtained was a pure phase of $Cs_5Mo_8O_{24}(OH)_2AsO_4{\cdot}2H_2O$. The X-ray powder diffraction pattern of the product compared well with that calculated from the single-crystal data. Energy-dispersive X-ray fluorescence analysis on several crystals showed that the Cs:Mo:As mole ratio was close to 5:8:1, which is in accord with the structural analysis results (see below).

Thermal Analysis. Thermogravimetric (TG) and differential thermal (DT) analysis (a DuPont thermal analyzer) were performed on a powder sample of $Cs_5Mo_8O_{24}(OH)_2AsO_4{\cdot}2H_2O$ in flowing N_2. The weight loss occurs in two steps between ~110 and ~450 °C. Two endothermic peaks occurred at ca. 385 and 520 °C in the DTA curve. The latter one has no counterpart in the TGA curve. In order to characterize the decomposition products, two experiments were performed in which crystals of $Cs_5Mo_8O_{24}(OH)_2AsO_4{\cdot}2H_2O$ were separately heated in flowing N_2 at 450 and 550 °C for 12 h followed by furnace cooling to room temperature. Both reactions yielded polycrystalline products. One pale-green crystal was obtained from the product of the thermal treatment at 550 °C. Single-crystal structural analysis revealed that the crystal was $Cs_7Mo_8O_{26}AsO_4$ (*vide infra*). Powder X-ray diffraction measurements identified the bulk product as a mixture of three phases, i.e., MoO_3[9] and Cs_3AsO_4[10] together with $Cs_7Mo_8O_{26}AsO_4$. FT-IR absorption spectra for the samples of $Cs_5Mo_8O_{24}$ (OH)]$_2AsO_4{\cdot}2H_2O$ and its thermal treatments in KBr pellets were recorded in the range 500−4000 cm^{-1} with a resolution of 4 cm^{-1} (BOMEM Michelson spectrophotometer).

Single-Crystal X-ray Structure Analysis. Two crystals of dimensions 0.20 × 0.20 × 0.33 mm for $Cs_5Mo_8O_{24}$ (OH)]$_2AsO_4{\cdot}2H_2O$ and 0.13 × 0.18 × 0.23 for $Cs_7Mo_8O_{26}AsO_4$ were selected for indexing and intensity data collection on a Siemens Smart-CCD diffractometer system equipped with a normal focus, 3 kW sealed tube X-ray source ($\lambda = 0.710\ 73$ Å). Intensity data were collected in 1271 frames with increasing ω (width of 0.3°/frame). The intensity data for the two crystals were corrected for *Lp* and absorption effects. Corrections for absorption effects were based on symmetry-equivalent reflections using the program SAINT.[11] On the basis of the systematic absences and statistics of intensity distribution, the space group was determined to be *Cmcm* for $Cs_5Mo_8O_{24}(OH)_2AsO_4{\cdot}2H_2O$ and *Ibca* for $Cs_7Mo_8O_{26}AsO_4$. Direct methods were used to locate the Mo, the As, and a few oxygen atoms with the remaining non-hydrogen atoms being found from successive difference maps. Bond-valence calculations[12] were used to identify hydroxo and water oxygen atoms. All of the hydrogen atoms could be located from difference maps calculated at the final stage of structure refinements. Both structures were refined by full-matrix least-squares refinement based on *F* values. All of the non-hydrogen atoms were refined with anisotropic temperature factors. The atomic coordinates and isotropic thermal parameters for the hydrogen atoms were fixed. Corrections for secondary extinction and anomalous dispersion were applied. Neutral-atom scattering factors for all atoms were taken from standard sources. Calculations were performed on a DEC VAX 4000/90 workstation using the SHELXTL-Plus programs.[13] The summary of crystallographic data is listed in Table 1, and atomic coordinates and thermal parameters are listed in Table 2 and selected bond lengths and bond valence sums in Table 3.

Table 1. Crystallographic Data for $Cs_5Mo_8O_{24}(OH)_2AsO_4{\cdot}2H_2O$ (**1**) and $Cs_7Mo_8O_{26}AsO_4$ (**2**)

	1	2
empirical formula	$H_6AsCs_5Mo_8O_{32}$	$AsCs_7Mo_8O_{30}$
a, Å	8.8048(3)	12.1247(4)
b, Å	23.4314(9)	22.9153(7)
c, Å	16.0499(6)	24.3777(7)
V, Å^3	3311.2(9)	6773.1(14)
Z	4	8
fw	2025.0	2252.9
space group	*Cmcm*	*Ibca*
T, °C	23	23
λ, Å	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	4.058	4.418
μ, cm−1	94.42	113.45
$R(F_o)^a$	0.0237	0.0554
$R_w(F_o)^b$	0.0294	0.080

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o) + gF_o{}^2]^{-1}$, $g = 0.0005$ for **1** and 0.0024 for **2**.

Results and Discussion

The structure of $Cs_5Mo_8O_{24}(OH)_2$ $AsO_4{\cdot}2H_2O$ (**1**) consists of $[AsMo_8O_{30}H_2]^{5-}$ cluster anions, cesium cations, and water molecules, while $Cs_7Mo_8O_{26}AsO_4$ (**2**) consists of cesium cations and the more negatively charged $[AsMo_8O_{30}]^{7-}$ cluster anions with atomic connectivities nearly identical with those of $[AsMo_8O_{30}H_2]^{5-}$. Perspective views of the two structures along the *a* axis are shown in Figure 1, and ORTEP drawings of cluster anions are shown in Figure 2. In structure **1**, the $[AsMo_8O_{30}H_2]^{5-}$ anion is formed of two crystallographically independent $\{Mo_4O_{15}H\}$ cores linked by an arsenic(V) atom. The anion possesses *m*2*m* symmetry in that all four molybdenum atoms in the $\{Mo_4O_{15}H\}$ core are coplanar. On the other hand, the $[AsMo_8O_{30}]^{7-}$ anion in structure **2** contains symmetry-related $\{Mo_4O_{15}\}$ cores linked by the atom As residing on a 2-fold axis. The $\{Mo_4O_{15}\}$ core possesses no symmetry, but the four Mo atoms are nearly coplanar. As depicted in Figure 2, both the $\{Mo_4O_{15}H\}$ and $\{Mo_4O_{15}\}$ cores are composed of two pairs of confacial bioctahedral $\{Mo_2O_9\}$ units with the μ_4-O atoms out of the Mo_4 least-squares planes by ~0.56−0.75 Å. Face-sharing bioctahedra are uncommon structural motifs in molybdenum chemistry. Other than the salts of $[R_2AsMo_4O_{15}H]^{2-}$[7,14] and $[(C_6H_5As)_2Mo_6O_{25}H_2]^{4-}$,[15] the two molybdenum(III) silicophosphates $Mo_3P_5SiO_{19}$[16] and $Mo_4P_6Si_2O_{25}$[17] are the only known examples in which isolated face-sharing binuclear $\{Mo_2O_9\}$ units exist.

In both structures, connections between cluster anions are primarily provided by the O−Cs−O bonds. In structure **1**, three crystallographically distinct Cs sites are all in 10-fold coordination.[18] The $[AsMo_8O_{30}H_2]^{5-}$ cluster anions are bridged together by Cs(1) into one-dimensional strings running parallel to [100] (Figure 3). The anion−cation interactions are further extended into a three-dimensional architecture by cations Cs(2) and Cs(3) with each linking four cluster anions and one water molecule. In turn, the water molecules also connect cluster anions by forming hydrogen bonds with the hydroxo groups of [AsMo$_8$-

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Table 2. Atomic Coordinates and Thermal Parameters (Å^2) for **1** and **2**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]	atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
		1					**2**		
Cs(1)	0.50000	0.12047(3)	0.75000	0.0330(2)	Cs(1)	0.00000	0.25000	0.12482(8)	0.0378(5)
Cs(2)	0.00000	0.38421(2)	0.53924(3)	0.0287(2)	Cs(2)	0.25000	0.00441(6)	0.00000	0.0447(6)
Cs(3)	0.00000	0.14096(2)	0.47368(3)	0.0298(2)	Cs(3)	0.25000	0.24091(7)	0.00000	0.0455(6)
Mo(1)	0.19016(5)	0.01461(2)	0.65054(3)	0.0192(2)	Cs(4)	0.2409(1)	0.00000	0.25000	0.0452(7)
Mo(2)	0.18102(5)	0.24035(2)	0.64588(3)	0.0204(2)	Cs(5)	0.25000	0.25000	0.25000	0.0484(7)
As(1)	0.00000	0.12728(4)	0.75000	0.0145(3)	Cs(6)	−0.0037(1)	0.0394(1)	0.12437(7)	0.0785(7)
O(1)	0.1560(5)	0.0849(2)	0.7500	0.020(1)	Mo(1)	0.5064(1)	0.12955(7)	0.21785(6)	0.0344(5)
O(2)	0.0000	0.1706(2)	0.6655(3)	0.018(1)	Mo(2)	0.6865(1)	0.12946(6)	0.12686(5)	0.0344(5)
O(3)	0.0000	0.0428(2)	0.6104(3)	0.025(1)	Mo(3)	0.50083(8)	0.12939(7)	0.03385(7)	0.0341(5)
O(4)	0.3032(5)	−0.0052(2)	0.7500	0.025(1)	Mo(4)	0.3190(1)	0.12867(6)	0.12340(5)	0.0341(5)
O(5)	0.3155(4)	0.0570(2)	0.5977(2)	0.033(1)	As(1)	0.50000	0.25000	0.1253(1)	0.0260(6)
O(6)	0.1996(4)	−0.0502(2)	0.6024(2)	0.035(1)	O(1)	0.5832(8)	0.2070(4)	0.1657(4)	0.038(3)
O(7)	0.0000	−0.0162(3)	0.7500	0.020(2)	O(2)	0.4217(8)	0.2068(4)	0.0863(4)	0.035(3)
O(8)	0.0000	0.2724(3)	0.7500	0.022(2)	O(3)	0.3720(8)	0.1582(5)	0.1918(4)	0.047(4)
O(9)	0.0000	0.2581(2)	0.5835(3)	0.024(1)	O(4)	0.6583(9)	0.1131(5)	0.2030(4)	0.047(4)
O(10)	0.2529(6)	0.2114(2)	0.7500	0.024(1)	O(5)	0.4712(10)	0.0638(5)	0.2431(5)	0.058(4)
O(11)	0.2852(4)	0.2006(2)	0.5779(2)	0.036(1)	O(6)	0.5203(9)	0.1702(7)	0.2755(6)	0.059(5)
O(12)	0.2624(5)	0.3067(2)	0.6441(2)	0.038(1)	O(7)	0.5037(7)	0.1046(5)	0.1220(5)	0.040(4)
O(13)	0.0000	0.1322(3)	0.2500	0.038(3)	O(8)	0.8019(9)	0.1709(6)	0.1338(5)	0.054(5)
O(14)	0.0000	0.3950(4)	0.7500	0.040(3)	O(9)	0.736(1)	0.0628(5)	0.1078(4)	0.056(4)
H(7)	0.0000	−0.0653	0.7500	0.050	O(10)	0.6380(8)	0.1599(5)	0.0594(4)	0.047(4)
H(8)	0.0000	0.3123	0.7500	0.050	O(11)	0.5379(10)	0.0628(5)	0.0096(5)	0.062(5)
H(13)	0.1106	0.1284	0.2500	0.050	O(12)	0.4884(8)	0.1735(7)	−0.0214(6)	0.053(5)
H(14)	0.0765	0.4217	0.7500	0.050	O(13)	0.3500(8)	0.1125(5)	0.0477(4)	0.044(4)
					O(14)	0.2056(9)	0.1699(6)	0.1172(4)	0.048(4)
					O(15)	0.2726(11)	0.0618(5)	0.1415(5)	0.062(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) and Bond Valence Sums ($\sum s$) for **1** and **2**

				Compound **1**				
Cs(1)−O(10)	3.046(4)	(x2)	Cs(1)−O(1)	3.141(4)	(x2)	Cs(1)−O(5)	3.291(4)	(x4)
Cs(1)−O(4)	3.417(5)	(x2)	$\sum s$[Cs(1)−O] = 1.16					
Cs(2)−O(9)	3.040(5)		Cs(2)−O(5)	3.061(4)	(x2)	Cs(2)−O(6)	3.222(4)	(x2)
Cs(2)−O(11)	3.326(4)	(x2)	Cs(2)−O(12)	3.386(4)	(x2)	Cs(2)−O(14)	3.392(1)	
$\sum s$[Cs(2)−O] = 1.15								
Cs(3)−O(6)	3.017(4)	(x2)	Cs(3)−O(12)	3.075(4)	(x2)	Cs(3)−O(2)	3.156(4)	
Cs(3)−O(3)	3.178(5)		Cs(3)−O(9)	3.261(5)		Cs(3)−O(11)	3.325(4)	(x2)
Cs(3)−O(13)	3.596(1)		$\sum s$[Cs(3)−O] = 1.31					
Mo(1)−O(6)	1.706(4)		Mo(1)−O(3)	1.912(2)		Mo(1)−O(1)	2.314(3)	
Mo(1)−O(5)	1.710(4)		Mo(1)−O(4)	1.938(3)		Mo(1)−O(7)	2.423(2)	
$\sum s$[Mo(1)−O] = 5.91								
Mo(2)−O(11)	1.703(4)		Mo(2)−O(10)	1.911(2)		Mo(2)−O(2)	2.304(3)	
Mo(2)−O(12)	1.712(4)		Mo(2)−O(9)	1.928(4)		Mo(2)−O(8)	2.428(4)	
$\sum s$[Mo(2)−O] = 5.95								
As(1)−O(1)	1.695(5)	(x2)	As(1)−O(2)	1.694(4)	(x2)	$\sum s$[As(1)−O] = 4.97		
O(7)−H(7)	1.150(6)		O(13)−H(13)	0.978(1)	(x2)	H(7)···O(13)	1.569	
O(8)−H(8)	0.935(6)		O(14)−H(14)	0.921(6)	(x2)	H(8)···O(14)	1.935	
O(7)···O(13)	2.719		O(8)···O(14)	2.871				
				Compound **2**				
Cs(1)−O(8)	3.017(13)	(x2)	Cs(1)−O(6)	3.052(15)	(x2)	Cs(1)−O(12)	3.074(14)	(x2)
Cs(1)−O(14)	3.101(12)		$\sum s$[Cs(1)−O] = 1.41					
Cs(2)−O(13)	2.992(11)		Cs(2)−O(11)	3.007(12)	(x2)	Cs(2)−O(9)	3.052(11)	(x2)
$\sum s$[Cs(2)−O] = 1.31								
Cs(3)−O(10)	3.017(11)	(x2)	Cs(3)−O(2)	3.062(10)	(x2)	Cs(3)−O(12)	3.318(11)	(x2)
Cs(3)−O(14)	3.332(12)		Cs(3)−O(13)	3.388(11)	(x2)	$\sum s$[Cs(3)−O] = 1.32		
Cs(4)−O(4)	3.006(11)	(x2)	Cs(4)−O(15)	3.025(13)	(x2)	Cs(4)−O(5)	3.157(12)	(x2)
$\sum s$[Cs(4)−O] = 1.20								
Cs(5)−O(3)	2.937(11)	(x2)	Cs(5)−O(1)	3.047(10)	(x2)	Cs(5)−O(6)	3.390(13)	(x2)
Cs(5)−O(8)	3.421(12)	(x2)	Cs(5)−O(4)	3.519(11)	(x2)	$\sum s$[Cs(5)−O] = 1.33		
Cs(6)−O(9)	3.225(13)		Cs(6)−O(5)	3.293(13)		Cs(6)−O(7)	3.302(11)	
Cs(6)−O(11)	3.335(14)		Cs(6)−O(15)	3.415(14)		$\sum s$[Cs(6)−O] = 0.65		
Mo(1)−O(5)	1.682(12)		Mo(1)−O(3)	1.868(10)		Mo(1)−O(1)	2.374(9)	
Mo(1)−O(6)	1.693(15)		Mo(1)−O(4)	1.915(11)		Mo(1)−O(7)	2.405(12)	
$\sum s$[Mo(1)−O] = 6.25								
Mo(2)−O(8)	1.699(13)		Mo(2)−O(10)	1.880(10)		Mo(2)−O(7)	2.292(9)	
Mo(2)−O(9)	1.705(13)		Mo(2)−O(4)	1.923(10)		Mo(2)−O(1)	2.372(10)	
$\sum s$[Mo(2)−O] = 6.15								
Mo(3)−O(12)	1.690(14)		Mo(3)−O(13)	1.901(10)		Mo(3)−O(7)	2.224(12)	
Mo(3)−O(11)	1.696(13)		Mo(3)−O(10)	1.909(10)		Mo(3)−O(2)	2.388(10)	
$\sum s$[Mo(3)−O] = 6.27								
Mo(4)−O(2)	2.360(10)		Mo(4)−O(3)	1.910(11)		Mo(4)−O(7)	2.308(9)	
Mo(4)−O(13)	1.920(10)		Mo(4)−O(14)	1.674(12)		Mo(4)−O(2)	2.3608(10)	
$\sum s$[Mo(4)−O] = 6.26								
As(1)−O(1)	1.719(10)	(x2)	As(1)−O(2)	1.669(10)	(x2)	$\sum s$[As(1)−O] = 4.88		

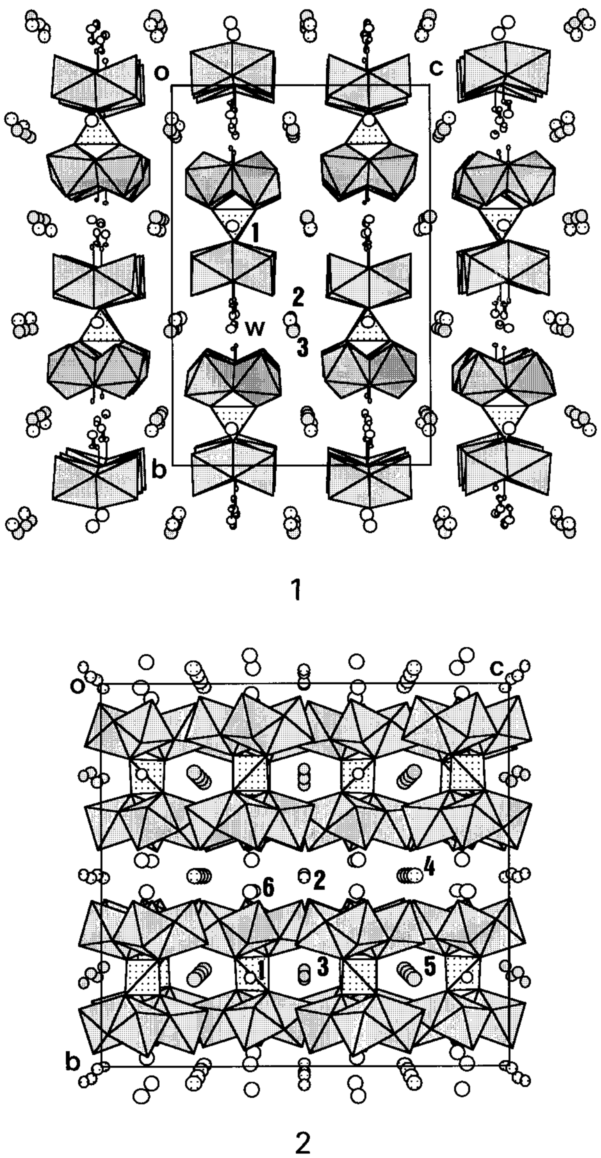

Figure 1. Perspective views of $Cs_5Mo_8O_{24}(OH)_2AsO_4{\cdot}2H_2O$ (**1**) and $Cs_7Mo_8O_{26}AsO_4$ (**2**) along the *a* axis. In these representations the corners of polyhedra are O atoms and the Mo and As atoms are at the center of each octahedron and tetrahedron, respectively. The dark stippled polyhedra represent MoO_6; the dotted tetrahedra AsO_4; the letter "W" H_2O; the large open, dotted, and stippled circles Cs; the smallest open circles H.

$O_{30}H_2]^{5-}$. The hydroxo oxygen O(7) is a stronger hydrogen-bond donor than O(8) as indicated by less saturation in its bond valence [$\sum s = 1.47$ for O(7) vs 1.84 v.u. for O(8)] and the shorter O···H (1.569 vs 1.935 Å) and O···O distances (2.719 vs 2.871 Å). The H-bonding interactions are also evidenced by IR data. Three broad bands centered at 3072, 3288, and 3440 cm^{-1} are due to the O−H stretchings for two water molecules and one hydroxo group (O(7)−H) involved in the stronger H-bonding. The relatively sharper band at 3578 cm^{-1} is due to O(8)−H stretchings involved in the weaker H-bonding. In cases where the water molecules are missing, the structure may require more cations in order to "hold" cluster anions in place. This explains why the cesium content increases from the structures of **1** to **2** upon dehydration.

In contrast to **1**, structure **2** consists of six crystallographically independent Cs sites with coordination numbers ranging from 5 to 10. According to the bond-length bond-strength calculations,[12] the valence sums for all Cs cations except Cs(6) are greater than 1, indicating that five Cs sites are tightly bound to anions. Cs(6) is only loosely bound to anions with an average distance greater than 3.3 Å. From a structural point of view, the cation Cs(6) in **2** occupies the same site as water molecules in **1** (Figures 1 and 2). By excluding two cations associated with the Cs(6) sites, the content of **2** becomes "$Cs_5Mo_8O_{26}$-AsO_4", differing from **1** by only two hydroxo H atoms. It is also noticed that **1** readily dissolves in basic solutions. Therefore, taking into account the possibility of breaking two O−H bonds by heating, transformation from **1** to **2** can take place at a higher temperature. The unit cell of **2** keeps the same *b* axial length as that in **1** whereas the other two axes are altered according to the relations $\boldsymbol{a_2} = \boldsymbol{a_1} - \boldsymbol{c_1}/2$ and $\boldsymbol{c_2} = 2\boldsymbol{a_1} + \boldsymbol{c_1}$. It is worth mentioning that the five-coordinated Cs(6) in a square-pyramidal geometry is rarely observed. Because of the fifth coordination of the μ_4-O(7) atom, the presence of the larger Cs(6) instead of a hydroxo H apparently compresses the μ_4-O atom more toward the Mo_4 plane, i.e., ~0.74 Å in **1** and 0.56 Å in **2**. In addition, the Mo···Mo distances (Table 4) vary significantly from the anions $[AsMo_8O_{30}H_2]^{5-}$ to $[AsMo_8O_{30}]^{7-}$, indicating different effects of cesium cations relative to water molecules and hydrogen bonds. Variations in the Mo···Mo distances due to the influence of hydroxo hydrogens[19] and different cation structures have been observed in other polyoxoanions.[20]

Table 4. Comparison of the $[AsMo_8O_{30}H_2]^{5-}$ and $[AsMo_8O_{30}]^{7-}$ Cluster Anions[a]

	$[AsMo_8O_{30}H_2]^{5-}$	$[AsMo_8O_{30}]^{7-}$
anion symmetry	*m2m*	2
core symmetry	*m2m* in $\{Mo_4O_{15}H\}$	*1* in $\{Mo_4O_{15}\}$
Mo···Mo (bw face-sharing)	3.193, 3.188 Å	3.113 Å
Mo···Mo (bw edge-sharing)	3.510, 3.342 Å	3.235 Å
Mo···Mo (bw two cores)	5.350 Å	5.532 Å
μ_4-O···Mo_4 plane	0.722, 0.751 Å	0.566 Å

[a] bw = between.

A three-stage weight-loss scheme was observed on the TGA curve of **1** (Figure 4). The first stage, which occurs from ~110 to ~320 °C, is attributed to the loss of the two lattice water molecules. The second stage, which is not resolved well from the first step, occurs between temperatures of ~320 and ~450 °C. During this stage one water molecule is released from the $[AsMo_8O_{30}H_2]^{5-}$ cluster anion as the observed total weight loss (3.44%) of the first two stages can be compared well with the calculated value (3.46%) based on the above interpretation. Powder X-ray diffraction measusrements reveal that compound **2** exists in the product of the thermal treatment of compound **1** at 450 °C. It is proposed that the $[AsMo_8O_{30}H_2]^{5-}$ cluster anions may lose H^+ cations to form $[AsMo_8O_{30}]^{7-}$, from which the structure of **2** emerges. The $[AsMo_8O_{30}H_2]^{5-}$ anions may as well lose OH^- groups to give $\{AsMo_8O_{28}\}$, an intermediate species that decomposes to Cs_3AsO_4 and MoO_3 by a prolonged heating to 550 °C. The small endothermic peak at ca. ~385 °C on the DTA curve may account for the breaking of Mo−OH and O−H bonds. Considering bonding interactions (see Table 3), the $[AsMo_8O_{30}H_2]^{5-}$ anion may be alternatively described as an AsO_4^{3-} group linking two Mo_4O_{12} rings with two OH^- groups on the opposite sides of the rings by weak (>2.3 Å) Mo−O bonds, yielding the structural formula $(AsO_4^{3-})[(Mo_4O_{12})(OH^-)]_2$, which in turn implies potential lability with respect to dissociation of AsO_4^{3-}.[21] Furthermore, the Mo_4O_{12} ring is composed of four distorted MoO_4 tetrahedra sharing corners.[22] Along with the dissociation of AsO_4^{3-}, the

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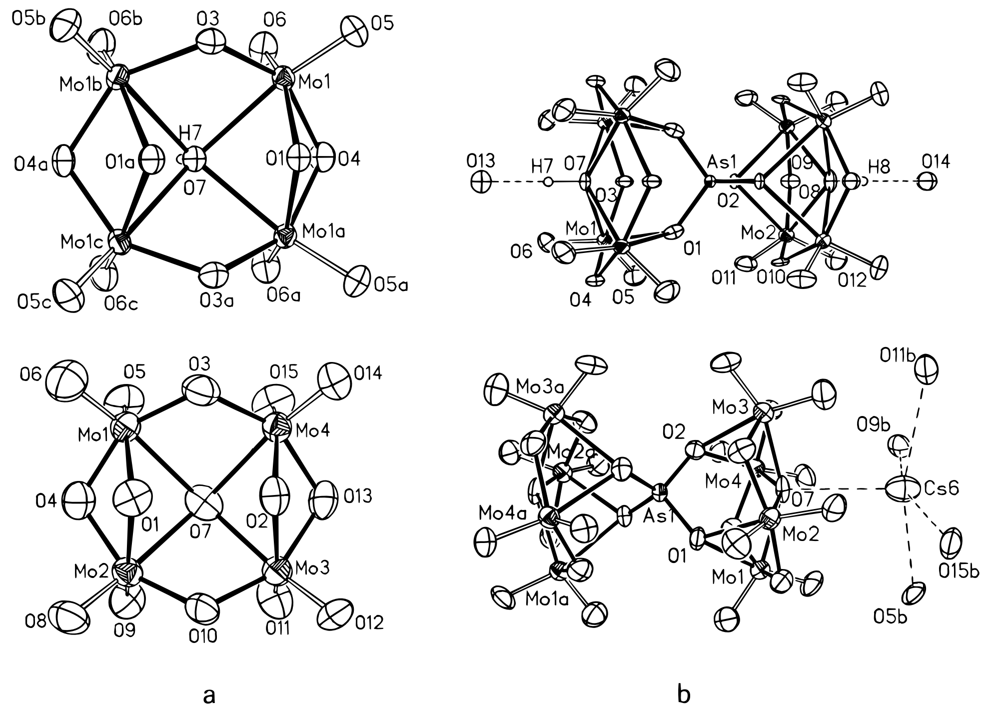

Figure 2. ORTEP drawings with atomic labeling of the cluster anions and their component Mo_4 cores: (a) $\{Mo_4O_{15}H\}$ (top) and $\{Mo_4O_{15}\}$ (bottom); (b) $[AsMo_8O_{30}H_2]^{5-}$ with hydrogen-bonded water oxygens (top) and $[AsMo_8O_{30}]^{7-}$ with the cation Cs(6) in a square-pyramidal geometry (bottom). Thermal ellipsoids are shown at the 50% probability level.

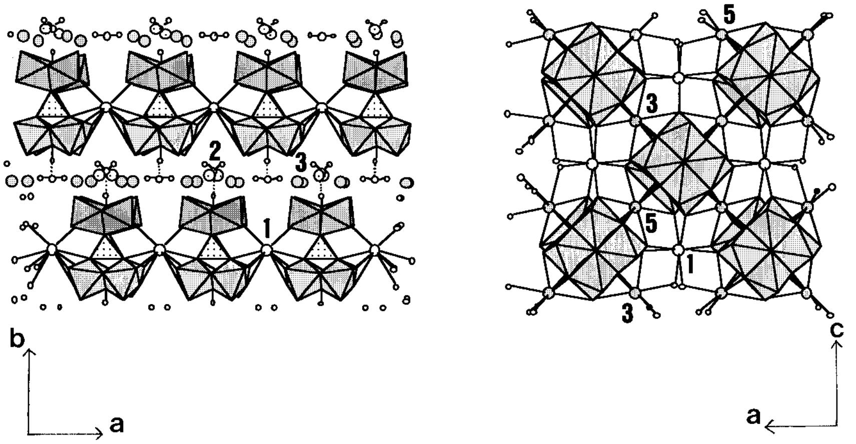

Figure 3. Cluster anions are connected by Cs cations. Left: The $[AsMo_8O_{30}H_2]^{5-}$ anions are bridged together into 1-D strings running along the *a* axis. Right: The $[AsMo_8O_{30}]^{7-}$ anions are connected by cations Cs(1), Cs(3), and Cs(5) to form a cation−anion 2-D net perpendicular to the *b* axis.

cyclic Mo_4O_{12} ring is dissected into MoO_3 by breaking the stronger Mo−O bonds. This bond-breaking process accounts for the large endothermic peak at ca. 520 °C on the DTA curve which has no counterpart on the TGA curves. Finally, the sharp fall in weight loss on the TGA curve suggests vaporization of MoO_3 beyond 780 °C. Taking into account all our experiments, the following decomposition path for **1** is proposed:

$$2Cs_5Mo_8O_{24}(OH)_2\ AsO_4{\cdot}2H_2O \xrightarrow{\sim 230\ °C} 2\text{“}Cs_5Mo_8O_{24}(OH)_2\ AsO_4\text{”} + 4H_2O(\uparrow)$$

$$\xrightarrow{\sim 385\ °C} Cs_7Mo_8O_{26}AsO_4 + 2H_2O(\uparrow) + \text{“}Cs_3(AsO_4^{\ 3-})(Mo_4O_{12})_2\text{”}$$

$$\xrightarrow{\sim 520\ °C} Cs_7Mo_8O_{26}AsO_4 + Cs_3AsO_4 + 8MoO_3$$

$$\xrightarrow[MoO_3(\uparrow)]{\sim 780\ °C} MoO_3(\uparrow)$$

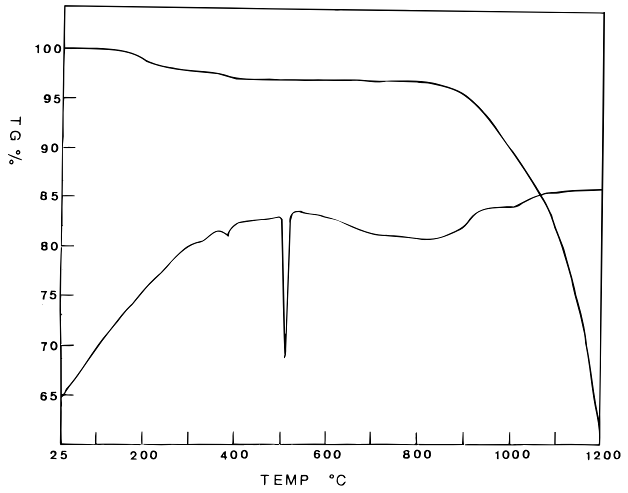

Figure 4. Thermal analysis of $Cs_5Mo_8O_{24}(OH)_2AsO_4{\cdot}2H_2O$: TGA and DTA curves.

In conclusion, two molybdenum(IV) arsenates containing unprecedented polyheteroanions $[AsMo_8O_{30}H_2]^{5-}$ and $[AsMo_8O_{30}]^{7-}$ have been prepared and their structures characterized. Structure **1** was synthesized by a high-temperature, high-pressure hydrothermal method, while structure **2** was obtained from the dehydration product of **1** at 550 °C. Our study shows that the two structures are closely related to each other. The spatial arrangements of the cluster anions in the unit cells are influenced by the coordination geometries of the cesium cations. Water molecules in **1** can be replaced by additional cesium cations as observed in **2**. One of the most interesting results obtained from TGA/DTA and powder X-ray diffraction study of **1** is that the lability with respect to dissociation of $AsO_4{}^{3-}$ from the $[AsMo_8O_{30}H_2]^{5-}$ cluster anion is first shown in the solid state. The hydrothermal technique that we have employed is useful for the crystal growth of novel metal arsenates. Further research on the hydrothermal synthesis of new molybdenum(VI) arsenates is in progress.

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Supporting Information Available: Tables giving detailed crystal data, bond distances and angles, and anisotropic thermal parameters for $Cs_5Mo_8O_{24}(OH)_2AsO_4{\cdot}2H_2O$ and $Cs_7Mo_8O_{26}AsO_4$ (17 pages). Ordering information is given on any current masthead page.

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