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Synthesis and Characterization of 2D and 3D Structures from Organic Derivatives of Polyoxometalate Clusters: Role of Organic Moiety, Counterion, and Solvent

Bret J. S. Johnson, Rick C. Schroden, Changcheng Zhu, and Andreas Stein*

Department of Chemistry, University of Minnesota, 207 Pleasant Street SE,
Minneapolis, Minnesota 55455

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New organic derivatives of “inverse-Keggin” polyoxometalate (POM) clusters, $[Mo_{12}O_{46}(AsR)_4]^{4-}$ (R = C_6H_4-4-COOH, C_6H_3-4-OH-3-NO_2, C_6H_4-4-OH), have been synthesized. Structures of the corresponding sodium or iron salts were elucidated by single-crystal X-ray diffraction and shown to be 3D structures connected through hydrogen bonds and/or O−Na−O linkages. Parameters which influence the final solid-state architecture, such as the crystallizing solvent, organic moiety, and counterions, have been examined. The hydrogen-bonding ability of the solvent affects the connectivity of the POM clusters through interactions with the organic group and the inorganic core. The organic groups influence the structure through hydrogen bonds to other organic groups, to neighboring clusters, and/or to solvent molecules. Hydrogen bonding between the organic groups and the solvent appears to inhibit some possible connectivity patterns, such as the hydrogen-bonded dimerization of carboxylic acid groups. Na^+ ions were found directly bonded to the cluster oxo ligands and provided linkages between clusters. Larger cations, such as transition metals, did not show this interaction, and other bonding methods dominated.

Introduction

The systematic construction of specific architectures from molecular building blocks has been an area of active research over the past few years.[1−3] Examples range from coordination polymers[4−14] to molybdenum oxide/organic nanocomposites[15−17] to larger cluster-based building blocks.[18−39] The difficulty with such “crystal engineering” has always been predicting the outcome of the structure. Small changes in the synthetic technique, such as solvent or counterion, can lead to different

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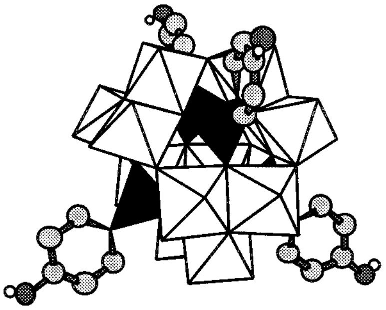

Figure 1. View of the tetrahedral cluster anion from **3** as a representative example of organically modified POMs. White octahedra: MoO_6. Black tetrahedra: AsO_3R. Light gray circles: carbon. Dark gray circles: oxygen. Hollow circles: hydrogen.

products.[40,41] The production of kinetically stable, crystalline networks requires that the bonding interactions be strong enough to connect the clusters, but also labile enough to permit reorganization into ordered, crystalline structures. By employing well-defined clusters, with a set number of bonding sites and with directionality to the bonding interactions, as building blocks, it may be possible to predetermine with more accuracy the final connectivity and architecture of the crystalline material. Clusters of the type $[Mo_{12}O_{46}(AsR)_4]^{4-}$ (R = CH_3, C_2H_4OH, C_6H_5, *p*-$C_6H_4NH_3^+$, *p*-C_6H_4CN)[42−46] have been previously synthesized, but have not been utilized as molecular blocks. They possess a tetrahedral arrangement of organic groups (Figure 1), which can be modified for a variety of characteristics such as solvophilicity/solvophobicity, reactivity, or size. This paper describes the crystal structures of three different salts of organic derivatives of POM clusters and the influences that affect the connectivity and the formation of networks or frameworks from these molecular building blocks.

Experimental Section

Materials. All chemicals were used as obtained without further purification: (*p*-hydroxyphenyl)arsonic acid, (4-hydroxy-3-nitrophenyl)arsonic acid (TCI America), sodium molybdate dihydrate (Strem, Inc.), arsenic trioxide, copper(II) nitrate trihydrate (Mallinckrodt), 4-aminobenzoic acid, sodium nitrite, iron(III) nitrate nonahydrate, (Aldrich), potassium chloride (Fisher). All water used was distilled and deionized.

$H_2O_3AsC_6H_4$-4-COOH. (*p*-Carboxyphenyl)arsonic acid was synthesized by the Bart method.[47] 4-Aminobenzoic acid (4.00 g, 14.9 mmol) was dissolved in 150 mL of H_2O and acidified with 7.50 mL of concentrated HCl at 0 °C. To the cold solution, a solution of 2.21 g (32.0 mmol) of $NaNO_2$ in 20 mL of cold H_2O was added dropwise (solution 1). (**CAUTION:** Dry diazonium salts can be explosive; they should be kept in solution.) Solution 2, consisting of 4.33 g (21.9 mmol) of As_2O_3, 5.25 g (0.131 mol) of NaOH, and 25 mL of H_2O, was prepared. Solution 1 was added to solution 2 dropwise with rapid stirring. Upon addition, N_2 was released and the solution turned orange. The solution was acidified to pH ∼ 3 with concentrated HCl and filtered to remove any red precipitate. The yellow solution was then acidified to pH 1 with concentrated HCl, filtered again, and boiled to reduce the volume of the solution to 75 mL. Upon cooling, an off-white precipitate was collected and washed with acetone. The product was recrystallized from ethanol/H_2O. FT-IR (KBr): 3099, 3061, 2850, 1708, 1090, 800 cm^{-1}. ^1H NMR (DMSO): ∼9 broad (1H), 8.10 (2H), 7.86 (2H) ppm.

$Na_vH_w[Mo_{12}O_{46}(C_6H_4As\text{-}4\text{-}COOH)_4]\cdot xH_2O$ (1). (*p*-Carboxyphenyl)arsonic acid (0.123 g, 0.50 mmol) and $Na_2MoO_4\cdot 2H_2O$ (0.363 g, 1.50 mmol) were dissolved in 20 mL of water. The solution was adjusted to pH 1 with dilute sulfuric acid, refluxed for 30 min, and cooled to room temperature. To this solution was added 0.125 g (0.50 mmol) of $CuSO_4\cdot 5H_2O$. The resulting solution was transferred to a 23 mL Teflon-lined autoclave and heated at 120 °C overnight. The solution was then allowed to evaporate slowly for 3 weeks, during which time yellow crystals formed. Elemental anal. (wt % found/calcd for $Na_vH_w[Mo_{12}O_{46}(C_6H_4As\text{-}4\text{-}COOH)_4]\cdot xH_2O$ [$v = 3$; $w = 1$; $x = 34$]): Mo (34.24/34.32), As (9.81/8.93), Na (2.26/2.06), Cu (0.23/0.00). FT-IR (KBr): 1076, 979, 953, 917, 871, 764, 712, 584 cm^{-1}. ^1H NMR (DMSO): 9.07 (2H), 7.92 (2H) ppm.

$Na_4[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}OH\text{-}3\text{-}NO_2)_4]\cdot xH_2O$ (2). (4-Hydroxy-3-nitrophenyl)arsonic acid (0.132 g, 0.50 mmol) and $Na_2MoO_4\cdot 2H_2O$ (0.363 g, 1.50 mmol) were dissolved in 20 mL of water. The pH of the solution was lowered to 1 with dilute sulfuric acid, and the solution was heated to reflux for 30 min and cooled to room temperature. The solution was then allowed to evaporate slowly for 3 months, during which time yellow crystals were produced. Elemental anal. (wt % found/calcd for $Na_4[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}OH\text{-}3\text{-}NO_2)_4]\cdot xH_2O$ [$x = 49$]): Mo (36.99/36.91), As (9.16/9.61), Na (3.31/2.94). FT-IR (KBr): 1081, 979, 953, 927, 871, 840, 764 cm^{-1}. DR−UV−vis: 375 nm. ^1H NMR (D_2O): 9.673 (1H), 8.83 (2H), 7.26 (2H) ppm.

$Fe_vH_w[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}OH)_4]\cdot xH_2O\cdot y$DMSO (3). (*p*-Hydroxyphenyl)arsonic acid (4.00 g, 18.3 mmol) was dissolved in 200 mL of H_2O. To this was added 13.30 g (55.0 mmol) of solid $Na_2MoO_4\cdot 2H_2O$. The resulting solution was brought to a boil and then acidified to pH 1 by the dropwise addition of concentrated HNO_3. Solid KCl (1.36 g, 18.3 mmol) was added to the solution. The volume was reduced to 25 mL and cooled to room temperature. Upon cooling, off-white crystals of $K_{2.75}Na_{1.25}[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}OH)_4]$ precipitated. Crystals of **3** were grown by a diffusion method: $K_{2.75}Na_{1.25}[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}OH)_4]$ (0.136 g, 0.050 mmol) was dissolved in 5 mL of DMSO. $Fe(NO_3)_3\cdot 9H_2O$ (0.027 g, 0.067 mmol) was dissolved in 3 mL of H_2O. H_2O (2 mL) was carefully layered on top of the POM solution in a 5 dram vial. The iron nitrate solution was then carefully added to the water layer at the top of the vial. At the solution interface a purple color formed almost immediately. After 3 days, large yellow-brown, blocky crystals appeared at the bottom of the vial. A few of the crystals were isolated and washed with EtOH and the remainder left within the mother liquor. Elemental anal. (wt % found/calcd for $K_{2.75}Na_{1.25}[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}OH)_4]\cdot xH_2O$ [$x = 42$]): Mo (39.19/39.29), As (9.73/10.23), K (3.67/3.67), Na (1.42/0.98). FT-IR (KBr): 979, 952, 932, 871, 845, 589 cm^{-1}. ^1H NMR (DMSO): 9.96 (1H), 8.76 (2H), 6.72 (2H) ppm. Elemental anal. (wt % found/calcd for $Fe_vH_w[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}OH)_4]\cdot xH_2O\cdot y$DMSO [$v = 1.2$; $w = 0.4$; $x = 2.2$; $y = 14.5$]): Mo (32.99/32.98), As (8.12/8.58), Fe (2.12/1.92), K (0.03/0.00), Na (0.00/0.00). FT-IR (KBr): 947, 948, 923, 867, 845, 594, 582, 519, 482, 463, 391, 336, 282, 266, 241, 201 cm^{-1}. UV−vis (DMSO/H_2O): 262, 350 sh, 506 nm. ^1H NMR (D_2O): 8.64 (2H), 6.98 (2H) ppm.

X-ray Crystallography. Suitable single crystals were mounted onto the tip of a 0.2 mm diameter glass capillary and positioned on a Bruker SMART system for data collection. The data collection was carried out using Mo Kα radiation. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å (for **1** and **2**) or 0.77 Å (**3**). Three major sections of frames were collected with 0.30° steps in ω at three different ϕ settings and a detector setting of −28° in 2θ. The space groups were determined on the basis of systematic absences and intensity statistics. Direct-methods solutions were calculated, which provided most non-hydrogen atoms from the *E*-map. Full-matrix least squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group, if appropriate) isotropic displacement

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Table 1. Crystallographic Data for Compounds **1**−**3**

	1	**2**	**3**
chemical formula[a]	$C_{28}H_{36}O_{62}Na_3As_4Mo_{12}$	$C_{24}H_{40}N_4O_{70}Na_4As_4Mo_{12}$	$C_{24}H_{20}O_{50}As_4Mo_{12}$
fw	2884.5	3047.52	2559.36
cryst syst	monoclinic	tetragonal	tetragonal
space group	$P2/c$	$I\bar{4}$	$I4_1/amd$
Z	4	2	4
a, Å	12.0087(2)	17.802(5)	28.450(3)
b, Å	15.7150(3)	17.8024(5)	28.450(3)
c, Å	21.8718(2)	11.8281(4)	11.645(2)
β, deg	101.3380(10)		
V, Å^3	4047.01(11)	3748.6(2)	9425(2)
d_{calcd}, g/cm^3	2.367	2.700	1.804
R1 (wR2)	0.0609 (0.1385)	0.0288 (0.0649)	0.0382 (0.1011)

[a] The chemical formulas listed here represent those determined by X-ray crystallography. Disordered atoms (solvent, counterions) are not included.

Table 2. Bond Distance Ranges of Compounds **1**−**3**

	distance (Å)
Mo−O (terminal)	1.679−1.712
Mo−O (doubly bridging)	1.87−1.91
Mo−O (triply bridging, 3 Mo)	2.028−2.055
Mo−O (triply bridging, 2 Mo, 1 As)	2.268−2.315
As−O	1.68−1.701
As−C	1.897−1.923

parameters. The data sets were corrected for disordered solvent with the program PLATON/SQUEEZE. Crystallographic data are listed in Table 1.

Spectroscopic and Chemical Analysis. FT-IR spectra were collected on a Nicolet Magna 760 FT-IR with 2 cm^{-1} resolution. Samples were prepared as KBr pellets for mid-IR (4000−400 cm^{-1}) and polyethylene pellets for far-IR (700−75 cm^{-1}). UV−vis absorption spectra were collected on a Hewlett-Packard 8452A diode array UV−visible spectrophotometer with a Labsphere RSA-HP-84 reflectance spectroscopy accessory. Reflectance data were converted to $f(R_\infty)$ using the Kubelka−Munk equation. ^{1}H NMR spectra were collected on a Varian Unity Inova 300 MHz spectrometer operating at 299.957 MHz. Spectra were recorded from samples in 5 mm (o.d.) tubes and referenced to tetramethylsilane. Carbon, nitrogen, and hydrogen analyses were performed by Atlantic Microlabs, Norcross, GA. All other elements were determined either by the Department of Geology, University of Minnesota, using an inductively coupled plasma source and mass spectrometry (ICP/MS) or at the Research Analytical Laboratory in the Department of Soil, Water and Climate, University of Minnesota, using an inductively coupled plasma source and atomic emission spectroscopy (ICP/AES).

Results

General Considerations. The structure of the POM cluster, $[Mo_{12}O_{46}(AsR)_4]^{4-}$, is nearly identical in all three compounds synthesized here and the same as that described in the literature,[42−46] with the exception of the organic groups. The cluster has been described as an "inverse-Keggin" cluster,[44,48] where the tetrahedral heteroatoms are located on the surface of the structure, as opposed to the interior. The charge on the cluster is −4 when the organic groups are neutral. The organic moieties attached to the arsenic atoms are arranged in a tetrahedral fashion around the Mo−As−O core. The bond distances for Mo−O and As−O bonds are presented in Table 2. The MoO_6 octahedra are distorted with the Mo atoms displaced outward, while the AsO_3R tetrahedra are normal.

In the published crystal structure of the zwitterionic cluster $[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}NH_3^+)_4]\cdot 10CH_3CN\cdot 6H_2O$,[45] the clusters do not directly bond to one another, but the charged anilinium groups hydrogen bond to water present in the structure. Since interactions between neighboring organic groups and between clusters and organic groups are small, the crystalline architecture is governed mostly by packing considerations and organic group/solvent interactions. In the derivatives synthesized here, interactions between the organic group, the solvent, and neighboring clusters all affect the final crystalline architecture, and there are significant cluster−cluster, organic−organic, and cluster−organic interactions.

Crystal Structure of 1. The benzoic acid derivative (Figure 2) was crystallized as a Na$^+$ salt from aqueous solution in the presence of Cu^{2+}. The carboxylic acid groups were found with two different C−O bond lengths, C═O double bonds average 1.19 Å, and C−OH distances were 1.34 Å. Protons of two of the carboxylic acids of one POM are hydrogen bonded to carboxylic acids of two adjacent clusters at distances of 2.17 Å. The hydrogen bond is not a typical donor−acceptor carboxylic acid dimer. Water disrupts the hydrogen-bonding dimerization, and all of the remaining hydrogen-bonding sites on the carboxylic acids are satisfied by water molecules (see Scheme 1). The O−H···O angle between carboxylic acids is 114.9°, which allows each POM to be hydrogen bonded diagonally to four others that are within the same *ab* plane. The hydrogen-bonding scheme of a single plane is pictured in Figure 3. This plane is constructed of two independent networks. Within each of these networks, POMs hydrogen bond to clusters diagonally to any chosen cluster. Along the 110 plane (squares 7, 5, 3 in the schematic of Figure 3) the hydrogen-bonded carboxylic acids are angled below the cluster, while along $\bar{1}\bar{1}0$ (squares 1, 5, 9), the hydrogen-bonding carboxylic acids are above the POM. Sodium cations occupy two sites within the unit cell, free of the cluster and solvated by water, or bonded to oxo ligands of the cluster. Two solvent waters were located around the solvated Na$^+$ ions, and residual electron density indicates that other solvent sites are present, but disordered. A total of eight water molecules were located by crystallography, but additional disordered water appears to be present, on the basis of elemental analysis. A second Na$^+$ ion is in a pseudo-octahedral environment directly bonded to four terminal oxo ligands of the POMs at distances of 2.37, 2.92, 2.54, and 2.31 Å (two from one POM and two from a neighboring cluster). The octahedron is completed by two water ligands at an average distance of 2.31 Å. Only three Na$^+$ ions were located, and the additional positive charge is assumed to be from a disordered proton. Cu^{2+}, which had been added to the crystallization media as a potential linking ion, was not observed by crystallography. Additionally, DR−UV−vis spectroscopy did not reveal an absorption for Cu^{2+}. Along the *c*-axis, there are two O−Na−O linkages between each POM, which connect them into zigzag chains. Because of the undulation of POM−Na−POM chains, channels are formed, which can be viewed down the *a*-axis;

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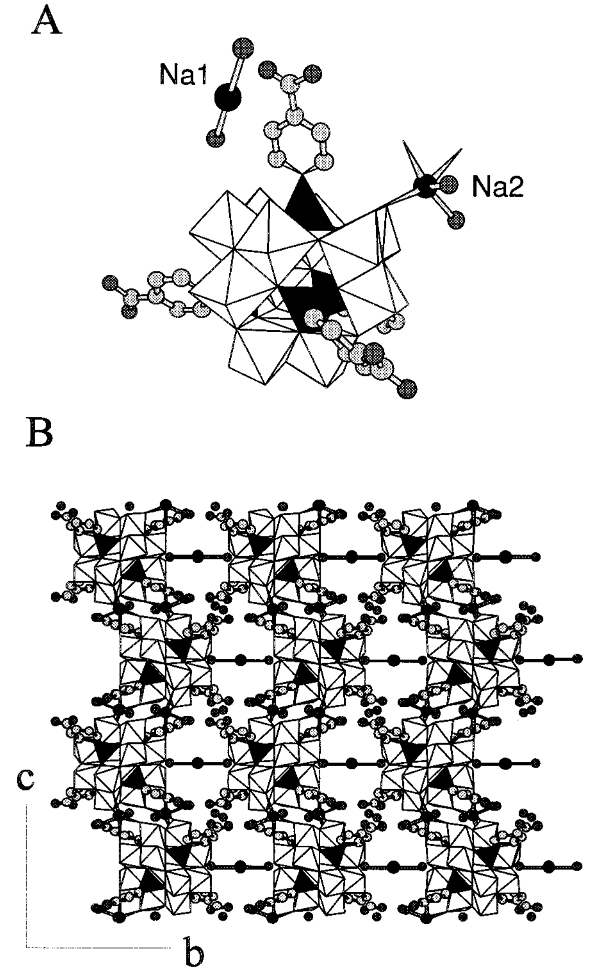
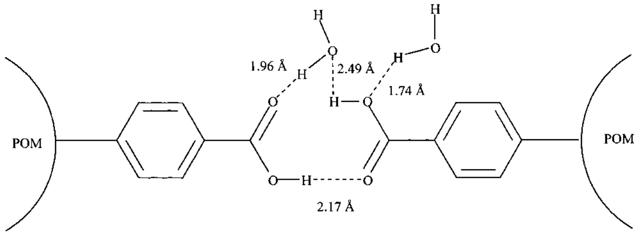


Figure 2. Crystal structure of **1**. (A) View of individual cluster with two Na^+ ions. Na1 is free and solvated by water. Na2 is bonded to the POM at two adjacent oxo ligands of neighboring molybdenum atoms. Open bonds are to the neighboring cluster. (B) Crystal structure viewed down the *a*-axis. The POM−Na−POM chains zigzag along the *c*-axis. White octahedra: MoO_6. Black tetrahedra: AsO_3R. Light gray circles: carbon. Dark gray circles: oxygen. Black circles: sodium.

Scheme 1



these are approximately 5.6 Å in diameter, including the van der Waals radius of the closest oxo ligands. These channels contain the solvated Na^+ cations. The overall structure is constructed of two independent, interpenetrating 3D frameworks containing hydrogen-bonded 2D sheets held together along the third axis by O−Na−O linkages. The two frameworks pack together closely, with H_2O molecules occupying space between clusters.

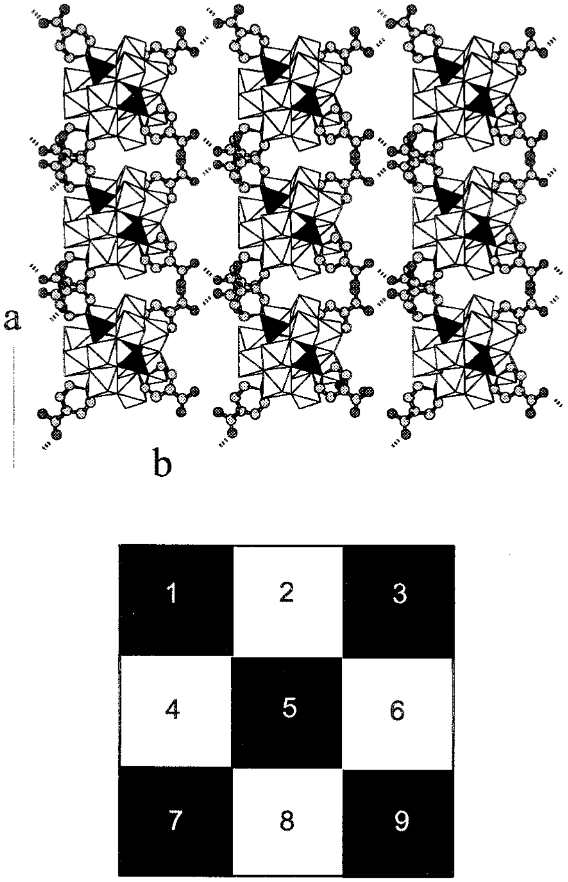


Figure 3. Hydrogen-bonding scheme of **1**. View down the *c*-axis showing one plane of the hydrogen-bonded sheets of POM clusters. POMs interact diagonally, but not adjacent. The solvent molecules and counterions have been omitted for clarity. The schematic portrays the connectivity pattern of the two interpenetrated networks. Squares represent POM clusters. Black squares are bonded to each other, as are white squares, but there are no bonds to opposite colored squares.

Crystal Structure of 2. The 4-hydroxy-3-nitrophenyl derivative has a less open structure than **1**, but similar motifs are observed. Crystals of the sodium salt were obtained from aqueous solution (Figure 4). There are no hydrogen bonds between organic groups. One hydrogen bond is formed between each nitro group and a water molecule at a distance of 2.17 Å. Eight water molecules were located by X-ray crystallography, but analysis of the crystalline sample indicates that more disordered water may be present. The Na^+ cations are again in a pseudo-octahedral environment, which in **2** consists of two terminal oxo ligands from one POM at distances of 2.63 and 2.62 Å, three waters (average distance 2.33 Å), and one terminal oxo ligand of a second POM at 2.51 Å. The clusters are connected through O−Na−O linkages into a three-dimensional structure that has channels (approximately 3.6 Å diameter, including the van der Waals radius of the closest O−O distances) occupied by disordered solvent. The POM clusters are packed into a body-centered cubic lattice. Each POM is connected by O−Na−O bonds to eight nearest neighbors. Two body-centered cubes joining along one side create the channels along the adjoining edge. The 4-hydroxy-3-nitrophenyl groups fill space between clusters with no direct interactions to neighboring clusters. Diffuse reflectance UV−visible spectroscopy of this cluster shows only a broad absorption at 375 nm corresponding to an oxygen-to-molybdenum charge transfer band.

Crystal structure of 3. The open-structured *p*-phenol derivative (Figure 5) was grown from a solution of DMSO and H_2O in the presence of Fe^{3+}. The clusters in this structure are packed in 2D sheets held together along the *a*- and *b*-axes by hydrogen bonds between phenol hydrogens and terminal oxo ligands of the neighboring cluster. Along the *c*-axis, the clusters are within close contact of each other (2.86 Å between oxo ligands). The

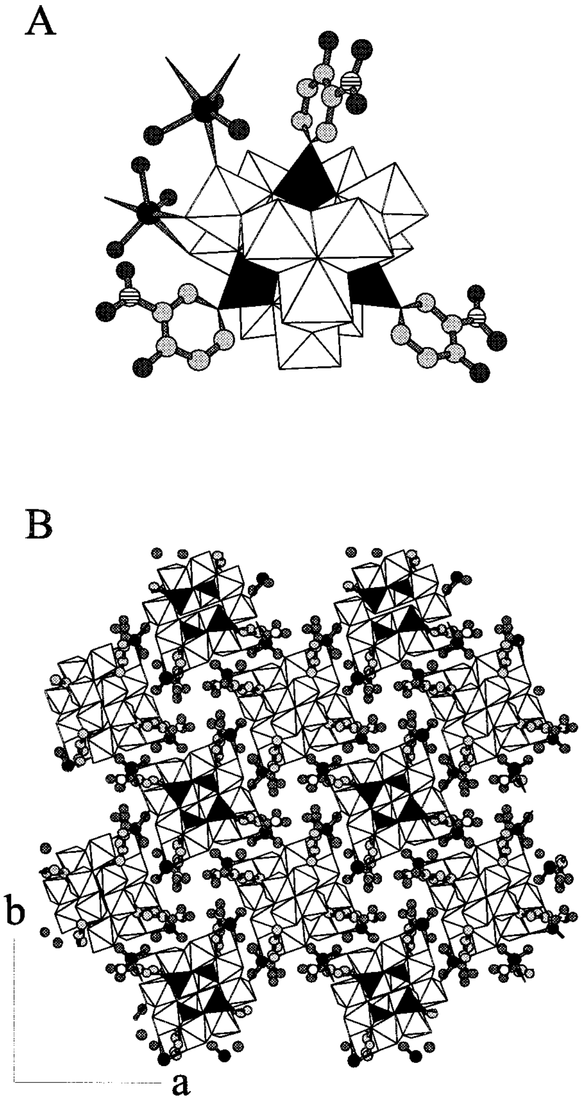


Figure 4. Crystal structure of **2**. (A) View of an individual POM cluster with two bonded Na^+ ions. (B) Crystal structure viewed down the *c*-axis. Clusters are arranged in a bcc lattice linked by POM−Na−POM bonds. The small pores are filled with disordered solvent, omitted for clarity. White octahedra: MoO_6. Black tetrahedra: AsO_3R. Light gray circles: carbon. Dark gray circles: oxygen. Black circles: sodium.

phenol hydrogen is shared equally over two equivalent sites of two separate oxo ligands of a neighboring cluster at a distance of 2.17 Å. Adjacent clusters are rotated by 90°, which results in the hydrogen-bonding scheme depicted in Figure 6. The channels (approximately 8 Å diameter, including the van der Waals radius of the closest oxygen atoms) are filled with disordered solvent and counterions, which could not be modeled. The solvent-accessible volume is 46% of the unit cell volume and contains a significant amount of residual electron density (1684 electrons). Elemental analysis reveals the presence of Fe in the sample. However, no Fe was located in the crystal structure. The low R1 value (0.0382) for this structure leads us to believe that there are no heavy, disordered cations such as Fe^{3+} within the channels and that the counterions on the cluster may be protons. The Fe found by elemental analysis is more likely to be due to excess Fe^{3+} present on the surface of the crystals even after washing. The channels contain large numbers of disordered molecules, presumably DMSO and H_2O. The number of solvent molecules present could not be determined accurately by X-ray crystallography; an approximate number was calculated from the elemental analysis data. This type of counterion and solvent disorder is also found for coordination network materials, where the framework is well modeled, but the counterions and solvent molecules are not.[4] The entire structure is constructed of 2D sheets, which stack immediately upon each other through close POM−POM contacts. Solution UV−visible spectroscopy of the DMSO solution prior to crystallization reveals three absorptions. The band at 262 nm and the shoulder at 350 nm are assigned to phenol−cluster charge transfer, while the third absorbance at 506 nm is assigned to Fe^{3+} ligated with phenolate ligands. UV−visible spectroscopy does not show the presence of Fe^{2+} in the solution, or the reduction of the POM.

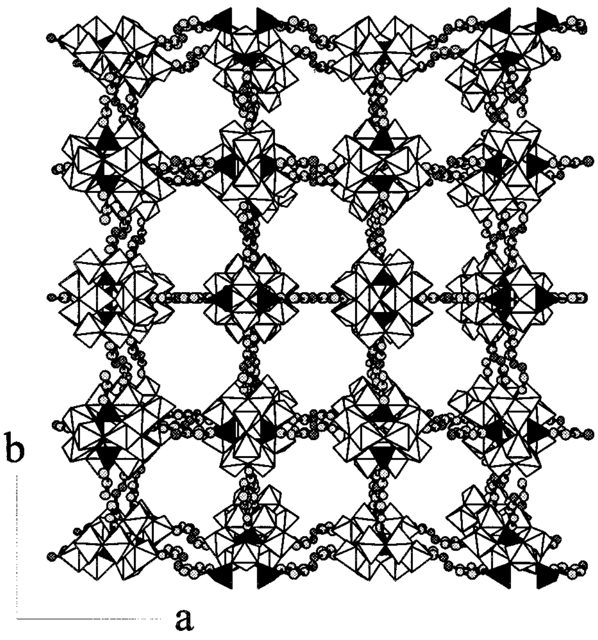


Figure 5. Crystal structure of **3**. Subsequent layers are directly above and below. The channels are filled with disordered solvent and counterions, not shown for clarity. White octahedra: MoO_6. Black tetrahedra: AsO_3R. Light gray circles: carbon. Dark gray circles: oxygen.

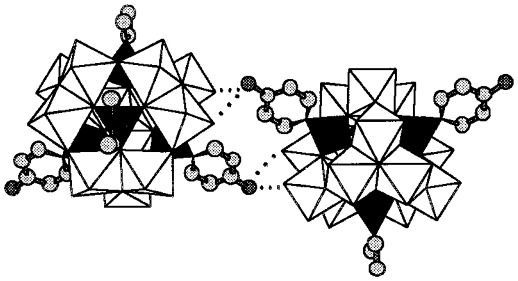


Figure 6. Hydrogen-bonding scheme in **3**. The phenol hydrogen is shared equally over two oxo ligand sites. The bonding is identical along the *a*- and *b*-axes.

Discussion

To be able to predict the final structure of a material based on the self-assembly of molecular building blocks, some patterns of interaction and connectivity must be established. The influences on the solid-state structure of organic derivatives of POM clusters include the organic functionality, the solvent, and the counterion. These are discussed individually below.

Influence of Organic Moiety. The influence of the organic group attached to the POM clusters is dependent on the solvophilicity and hydrogen bond donor−acceptor strength. The benzoic acid group of **1** is apt to form intermolecular hydrogen bonds;[49] this is evident in the formation of hydrogen bonds between adjacent carboxylic acids of neighboring clusters. Hydrogen bonding to free solvent is also observed. It is difficult to determine if the interactions between carboxylic acid groups are directing the structure, or if the formation of the hydrogen bonds results from the cluster packing and counterion interactions. If the clusters assemble around free, solvated counterions, the clusters may be placed in the correct orientation for interaction between two carboxylic acids, and the hydrogen bonds form after the packing considerations force them into certain orientations. However, if hydrogen bonding is a strong influence on the structure, carboxylic acid dimers might be expected, resulting in a diamondoid network. Regular dimers are not observed and appear to have been disrupted by water. The effect of the carboxylic acid seems to be related to its hydrophilicity. Complete hydrogen bond dimers may be impossible to establish due to the presence of H_2O. The bent mode of hydrogen bonding observed in **1** may be favored by packing considerations, whereby any empty voids formed are filled with clusters.

The 4-hydroxy-3-nitrophenyl group in **2** has almost no effect on the 3D architecture; its presence appears to be space filling. There are no bonding interactions between the organic group and other POMs. Effects from the counterions and solvent most likely have a greater influence on this structure. The lack of interaction of the organic functional groups with neighboring clusters or with other organic groups may have to do with the fact that the 4-hydroxy-3-nitrophenyl group has a greater tendency to form *intramolecular* rather than *intermolecular* hydrogen bonds.[49] This is seen by the formation of a hydrogen bond between the phenolic hydrogen and both O and N of the nitro group at distances of 1.87 and 2.49 Å, respectively.

In contrast, the phenol functionality in **3** has a significant effect on the connectivity of the clusters, but it is unclear whether it is directing the structure. Two scenarios are possible. The hydrogen bonds between oxo ligands and phenol hydrogens may begin to form in solution because of the lower hydrogen-bonding capability of the DMSO solvent. This would result in the observed two-dimensional sheets. Solvated counterions then fill the space left between hydrogen-bonded clusters. It is also plausible that the phenol groups are forced into this configuration by the packing of the clusters around the solvated cations. The packing then aligns the phenol ligands for interaction with the neighboring cluster. Despite the fact that the phenol group is attracted to both H_2O and DMSO, these are not located within bonding distance of the phenol.

Solvent Effects. The influence of the solvent can be examined by comparing structures **1** and **2**, which were grown from water, to **3**, grown from DMSO/water. While the solvent present in all three structures interacts with both the POM and the organic groups, the major effect of the solvent on the crystal structure appears to be one of competition with hydrogen-bonding interactions between organic functional groups and neighboring POM clusters, depending on the solvent's affinity for the organic groups and on the solvation of the counterions. The presence of water in **1** and **2** leads to hydrogen bond formation between the organic moiety and the water, a process which interferes with direct intermolecular hydrogen bond formation between organic groups. The open structure of **3** is at least partially due to the nature of the DMSO present during crystallization. It is important to point out that the crystals of **3** grew in the DMSO layer of the solvent mixture. The weaker hydrogen-bonding strength of DMSO decreases the interaction between solvent and the phenol groups and therefore promotes interactions between the phenol groups and neighboring POM clusters.

Counterion Effects. The counterion to the cluster has a large effect on the final architecture of the structure. The presence of Na^+ in both **1** and **2** profoundly influences the connectivity, compared with that of **3**. The affinity of the Na^+ cation for the cluster oxo ligands leads to direct linking of the POM clusters through O−Na−O bonds in **1** and **2**. In **3**, no Na^+ is present in the synthesis, and cation−cluster interactions are absent in the crystalline product, suggesting that the K^+ counterion in the precursor has a lower affinity for the oxo ligands than Na^+.[50] Even though no Fe^{3+} was located in the crystal structure of **3**, this cation seems to play an important role during the formation of **3**. During the synthesis, a maroon color is observed at the reacting interface. This color change is indicative of a phenol−Fe^{3+} interaction and is often used in organic chemistry to identify phenol groups.[51] The crystals that form, however, are yellow, and the crystal structure shows no bonding between the phenol and Fe^{3+} centers. The interaction between the phenol and the iron center is an equilibrium between the iron-bonded phenoxide and the nonbonded phenol. In the absence of a base to remove the liberated protons, the phenoxide ligands can be reprotonated easily and yield the nonbonded phenol and free iron centers. The aqueous Fe^{3+} solution in the top layer has a pH value of 1, and, as protons diffuse into the DMSO layer, they react with the Fe^{3+}−phenoxide species, and ion exchange Fe^{3+} for H^+ as the counterion on the POM. This transient bonding interaction between the cluster phenol groups and the Fe^{3+} centers appears to aid in the expulsion of the K^+ cations and the subsequent reduction of interactions between the POM core and the cations present. By removing the cluster−cation interactions, the interactions between the phenol and the cluster oxo ligands are maximized, resulting in the formation of the channel structure. It is interesting to note that the size of a DMSO solvated iron center is approximately 10 Å in diameter,[52] on the order of the size of the channels present in **3**.

Conclusion

Three new salts of organic derivatives of polyoxometalate clusters have been synthesized: $[Mo_{12}O_{46}(AsR)_4]^{4-}$ (R = C_6H_4-4-COOH, C_6H_3-4-OH-3-NO_2, C_6H_4-4-OH), and the structures with countercations have been determined by single-crystal X-ray diffraction. It is found that the connectivity and packing of the clusters depends on the hydrogen bond capability and solvophilicity of the organic group, the hydrogen-bonding strength of the solvent, and the oxophilicity of the counterion. By comparing **1** and **2**, it is seen that an organic group such as a carboxylic acid, which is a strong hydrogen bond donor−acceptor, bonds to both solvent water and other carboxylic acids. Intercluster hydrogen bonding results in 2D nets in each successive plane along the *c*-axis. In **2**, where intermolecular hydrogen bonds are less likely, a close-packed structure is

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(49) Etter, M. C. *J. Phys. Chem.* **1991**, *95*, 4601−4610.

(50) Most X-ray crystal structures of organic derivatives of POM clusters prepared in our laboratory contain Na^+ ions coordinated to the terminal oxo ligands of the cluster if Na^+ ions were present during the reaction synthesis. Coordination of the oxo ligands to larger cations, such as K^+, has not been observed for these samples.

(51) Mayo, D. W.; Pike, R. M.; Butcher, S. S. *Microscale Organic Laboratory*; John Wiley & Sons: New York, 1989.

(52) Bennett, M. J.; Cotton, F. A.; Weaver, D. L. *Acta Crystallogr.* **1967**, *23*, 581−586.

formed. Counterions studied here other than Na^+ appear to have lower affinity for the oxo ligands of the clusters resulting in solvated counterions that do not interconnect clusters. The structure of **3** provides an example of how the utilization of the correct parameters can yield an interesting, open structure. For example, by providing hydrogen-bonding sites (phenol), cations with little affinity for the cluster oxo ligands (K^+/Fe^{3+}), and a weakly hydrogen bonding solvent (DMSO), a structure with bonds directly between clusters was formed. It is hoped that by weighing each of the influences discussed above it will become easier to predict the final structure before synthesis. Research on constructing predicted structures from organic derivatives of POM clusters by using aprotic solvents, less oxophilic counterions, and organic groups, which are hydrogen bond donor−acceptors or ligands, is ongoing in our laboratory.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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