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Design and Analysis of Chain and Network Structures from Organic Derivatives of Polyoxometalate Clusters

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Polyoxometalate (POM) clusters derivatized with aniline groups exhibit distinct interactions with counterions and with each other. These interactions lead to the assembly of the clusters into chains and networks upon crystallization. Two cluster types were examined, $[W_6O_{25}H(AsC_6H_4\text{-}4\text{-}NH_2)_2]^{5-}$ and $[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}NH_2)_4]^{4-}$. The X-ray crystal structures were solved for the mixed salts containing $[C(NH_2)_3]^+/Na^+$, Ag^+/H^+, or Cu^{2+}/H^+ as counterions. The X-ray crystal structures reveal that the POM clusters are linked together by hydrogen bonds or POM–metal ion–POM linkages. The roles of the counterions, solvents, and organic groups in the formation of specific crystalline architectures are discussed. Strongly interacting counterions form bonds to the oxo ligands of the POM and connect them into tetrameric units and/or into one-dimensional chains. The hydrogen bonding strength of the solvent influences the formation of hydrogen bonds between the aniline groups and oxo ligands of the cluster. The aniline groups played differing roles in the final structures: they were either nonbonding, bonded to a counterion, or involved in hydrogen bonding. Depending on the bonding interactions, the architecture of the cluster salts may be significantly altered.

Introduction

The assembly of molecular building blocks into specific architectures has recently been an active area of research.[1–11] Currently, we are studying the use of organically modified polyoxometalate clusters (POM) as building blocks for designed three-dimensional architectures.[12] 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 geometrically rigid clusters as building blocks with a set number of bonding locations and with directionality to the bonding interactions, a certain amount of control over the architecture of the product is introduced. Because of this, it may be possible to predetermine with more accuracy the final connectivity and architecture of the crystalline material. Organically modified POM clusters, $[Mo_{12}O_{46}(AsR)_4]^{4-}$ or $[M_6O_{25}H_y(AsR)_2]^{x-}$ (M = Mo, x = 4, y = 2; M = W, x = 5, y = 1)[13–18] contain multiple organic groups, which can be tailored and used as directional linking points. By controlling the solvophilicity of the organic moiety, the type of counterion, and the hydrogen bonding strength of the solvent, interesting archi-

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

	1	**2**	**3**
chemical formula[a]	$C_{32}H_{74}N_{28}Na_2O_{50}As_4W_{12}$	$C_{40}H_{54}N_{12}O_{48}Ag_2As_4Mo_{12}$	$C_{24}H_{28}N_4O_{46}As_4Mo_{12}$
fw	4203.05	3137.65	2559.48
cryst syst	triclinic	monoclinic	tetragonal
cryst size, mm	$0.40 \times 0.27 \times 0.20$	$0.31 \times 0.19 \times 0.12$	$0.55 \times 0.13 \times 0.06$
space group	$P\bar{1}$	$P2_1/n$	$I\bar{4}2d$
Z	2	4	4
a, Å	12.9018(2)	14.9291(2)	26.8869(1)
b, Å	18.9366(1)	23.1597(3)	26.8869(2)
c, Å	21.4854(2)	23.7897(1)	11.7327(1)
α	90.941(1)	90	90
β, deg	94.258(1)	96.174(1)	90
γ	92.595(1)	90	90
V, Å^3	5228.3(1)	8177.7(2)	8481.6(1)
d_{calc}, g/cm^3	2.670	2.549	2.004
R_1 (wR_2)	0.0363 (0.0873)	0.0446 (0.0957)	0.0542 (0.1234)
largest difference peak and hole, eÅ^{-3}	5.204, −2.461	2.632, −2.338	1.036, −1.089

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

tectures may be constructed. Linkages are formed between cluster oxo ligands and counterions, between organic groups through hydrogen bonds, or between organic groups and cluster oxo ligands. This paper describes three structures, which contain either chains or networks, and elucidates the parameters that control the assembly of these organically modified POM clusters into specific architectures.

Experimental Section

Materials. All chemicals were used as obtained without further purification from the sources indicated: *p*-arsanilic acid and sodium hydroxide (Aldrich); sodium molybdate dihydrate and sodium tungstate dihydrate (Strem, Inc.); silver nitrate, copper(II) nitrate trihydrate, and cobalt(II) nitrate hexahydrate (Mallinckrodt); and guanidine hydrochloride (Matheson Coleman and Bell). [Mo$_{12}$O$_{46}$-(AsC$_6$H$_4$-4-NH$_3^+$)$_4$] was synthesized according to the literature.[16] All water used was distilled and deionized.

Na[C(NH$_2$)$_3$]$_4$[W$_6$O$_{25}$H(AsC$_6$H$_4$-4-NH$_2$)$_2$]·xH$_2$O (1). *p*-Arsanilic acid (2.2 g, 0.01 mol) was dissolved in 250 mL of H$_2$O at 55 °C. Sodium tungstate dihydrate (9.9 g, 0.03 mol) was dissolved in 40 mL of H$_2$O and added to the *p*-arsanilic acid solution. The pH of the solution was reduced to 6 by the dropwise addition of concentrated HCl. Guanidine hydrochloride (2.4 g, 0.025 mol) was added to the solution. The solution was boiled to reduce the volume to 150 mL. After solvent evaporation for 4 days in an open beaker, 8.73 g of an off-white crystalline material was obtained. Crystals suitable for X-ray diffraction were grown over a period of 2 weeks by slow solvent evaporation of a 100 mL solution of 0.5 g of the off-white crystalline material and 0.2 g of cobalt(II) nitrate hexahydrate. Anal. Calcd for Na[C(NH$_2$)$_3$]$_4$[W$_6$O$_{25}$H(AsC$_6$H$_4$-4-NH$_2$)$_2$]·xH$_2$O, $x = 14.5$: W, 46.69; As, 6.34; Na, 1.09. Found: W, 46.67; As, 6.41; Na, 1.11. FT-IR (KBr): 3415, 3346, 3249, 3172, 1093, 950, 938, 891, 832, 697, 661, 599, 536, 514 cm^{-1}. ^{1}H NMR (D$_2$O): δ 7.96 (2H), 7.72 (2H), 6.74 (6H, [C(NH$_2$)$_3$]$^+$) ppm.

Ag$_2$[Mo$_{12}$O$_{46}$(AsC$_6$H$_4$-4-NH$_2$)$_2$(AsC$_6$H$_4$-4-NH$_3^+$)$_2$]·2H$_2$O·8CH$_3$CN (2). [Mo$_{12}$O$_{46}$(AsC$_6$H$_4$-4-NH$_3^+$)$_4$] (1.05 g, 0.41 mmol) was dissolved in a hot solution of 15 mL of CH$_3$CN and 5 mL of H$_2$O. AgNO$_3$ (0.141 g, 0.83 mmol) was dissolved in 5 mL of CH$_3$CN and added dropwise to the solution of the POM cluster. A precipitate that formed upon addition of the AgNO$_3$ solution quickly dissolved. The solution was heated slowly to boiling without stirring for 15 min. During the heating process, yellow crystals suitable for X-ray crystallography appeared at the bottom of the reaction vessel. Anal. Calcd for Ag$_2$[Mo$_{12}$O$_{46}$(AsC$_6$H$_4$-4-NH$_2$)$_2$(AsC$_6$H$_4$-4-NH$_3^+$)$_2$]·2H$_2$O·8CH$_3$CN: Mo, 36.69; As, 9.55; Ag, 6.88. Found:

Mo, 37.62; As, 9.18; Ag, 7.11. FT-IR (KBr): 3460, 3064, 2602, 1622, 1592, 1497, 1414, 1384, 1328, 1190, 1088, 981, 952, 926, 866, 587, 500, 390, 373, 336, 285, 265, 244, 206 cm^{-1}. NMR data was not collected due to the poor solubility of this compound in standard solvents.

Cu$_{v}$[Mo$_{12}$O$_{46}$(AsC$_6$H$_4$-4-NH$_3^+$)$_4$]·xH$_2$O·yCH$_3$CN (3). [Mo$_{12}$O$_{46}$-(AsC$_6$H$_4$-4-NH$_3^+$)$_4$] (0.5 g, 0.19 mmol) was dissolved in 75 mL of CH$_3$CN and 25 mL of H$_2$O. To this was added dropwise a solution of Cu(NO$_3$)$_2$·3H$_2$O (0.07 g, 0.29 mmol) in 50 mL of CH$_3$CN. The resulting solution was then placed in a refrigerator at 4 °C. After 10 days, yellow-green needle crystals appeared, which were collected by filtration and washed with CH$_3$CN. The crystal structure of this compound was modeled with four anilinium groups as counterions; however, residual electron density and analysis results suggest that fractional Cu^{2+} ions are also present as counterions. Anal. Calcd for Cu$_v$H$_w$[Mo$_{12}$O$_{46}$(AsC$_6$H$_4$-4-NH$_2$)$_4$]·xH$_2$O·yCH$_3$CN [using estimates of $v = 0.25$, $w = 3.5$, $x = 2.3$, and $y = 5$], where H$_w$ represents protons bound to the aniline groups: Mo, 40.67; As, 10.59; Cu, 0.90. Found: Mo, 40.67; As, 10.11; Cu, 0.98. FT-IR (KBr): 3460, 3064, 2970, 2924, 2859, 1088, 981, 952, 926, 866, 587, 500 cm^{-1}. ^{1}H NMR (D$_2$O/CD$_3$CN): δ 9.78 (2H), 6.77 (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. 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. 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 electron 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 parameters. The data sets were corrected for a disordered solvent with the program PLATON/SQUEEZE.[19] 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.

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Organic Derivatives of Polyoxometalate Clusters

Samples were prepared as KBr pellets for mid-IR (4000−400 cm^{-1}) and polyethylene pellets for far-IR (700−75 cm^{-1}). Elemental analysis was performed 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

Two different clusters were examined as building blocks in this study: a difunctional cluster, $[W_6O_{25}H(AsR)_2]^{5-}$ (R = C_6H_4-4-NH_2), and a tetrafunctional cluster, $[Mo_{12}O_{46}$-$(AsR)_4]^{4-}$ (R = C_6H_4-4-NH_3^+). The former is isostructural with the previously reported phenyl derivative[17] and similar to the molybdenum derivatives, $[Mo_6O_{24}(AsC_6H_4NH_2)_2]^{4-}$.[18] The cluster consists of a ring of six WO_6 octahedra connected by three shared edges, two corners, and one face. The aniline groups cap the faces of the ring. The angle between aniline moieties is 151°. The larger cluster, $[Mo_{12}O_{46}(AsC_6H_4$-4-$NH_3^+)_4]$, is known from the literature and has been described as an "inverse-Keggin" cluster in which the heteroatoms are located on the surface of the cluster, as opposed to the interior.[15,20] The cluster consists of four units of three edge-sharing MoO_6 octahedra. The organoarsenic groups form bridges between units and are arranged around the cluster in a tetrahedral fashion. Both of the clusters used in this paper are normal examples of these organically modified POMs, and all bond angles and distances are typical. The differences in the structures from those seen previously in the literature are their solid-state architecture and connectivity. The materials presented here contain significant cluster−cluster, organic−organic, cluster−organic, and cluster−ion inter-actions, which connect the clusters into one- or two-dimensional polymeric structures. The source of these interactions is similar for each of the POM clusters despite the differences in overall structure.

Crystal Structure of (1). The difunctional cluster $[W_6O_{25}H$-$(AsC_6H_4$-4-$NH_2)_2]^{5-}$ has been previously synthesized, but the crystal structure was not determined.[17] The individual cluster unit is pictured in Figure 1A. The compound was crystallized from an aqueous solution in the presence of guanidinium ions to induce hydrogen bonding between the guanidinium and cluster oxo ligands and/or the aniline moiety. Compound **1** crystallized as a mixed salt of four guanidinium ions and one sodium ion. No hydrogen bonds were observed between aniline groups and solvent molecules or between aniline hydrogens and guanidinium ions. POMs were linked together through bridging guanidinium and sodium ions. Eight guanidinium ions near the POM clusters form a total of 34 hydrogen bonds to oxo ligands of four different POM clusters with distances from the guanidinium nitrogens to the oxo ligands ranging from 2.83 to 3.32 Å. The result is a hydrogen bonded unit of four POM clusters in a slanted "X" motif (Figure 1B). The remaining guanidinium ions are not bonded to the POM cluster and form no hydrogen bonds.
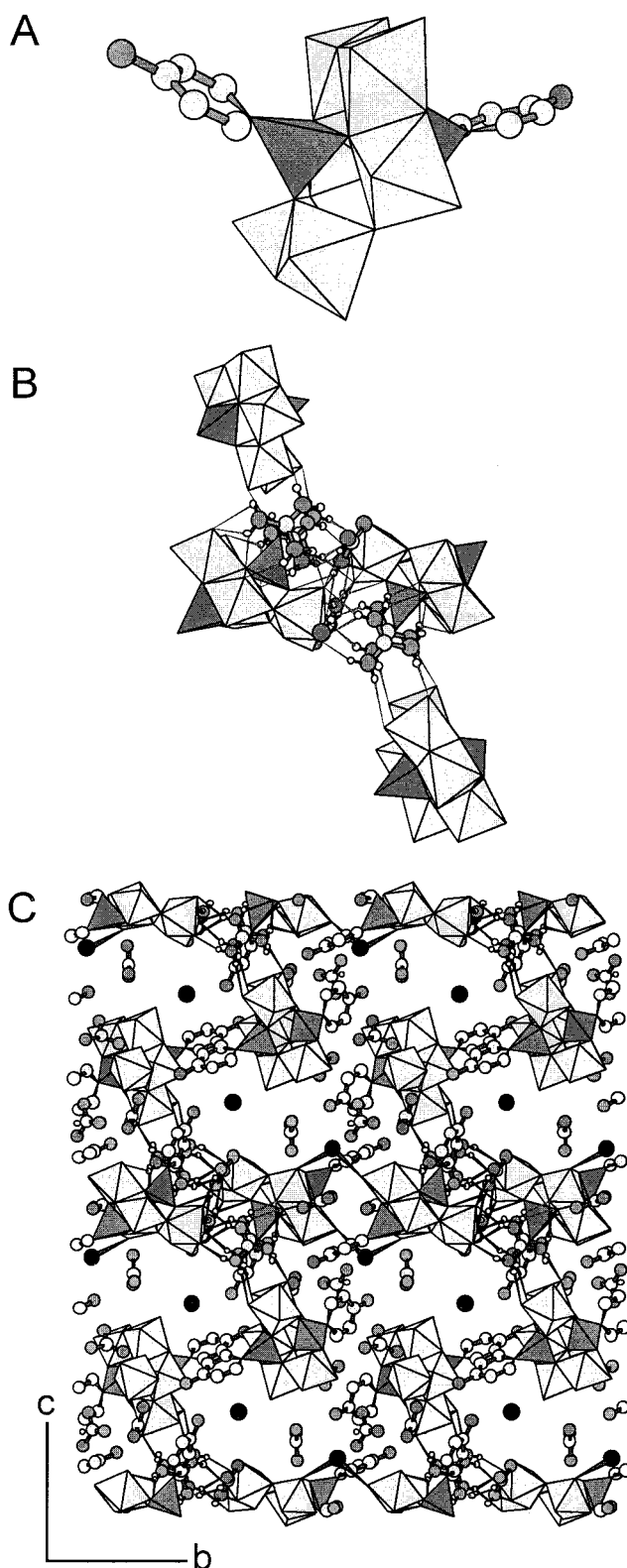
(20) Keggin, J. F. *Nature* **1933**, *131*, 908.

Figure 1. Crystal structure of **1**. (A) Discrete POM unit. (B) Hydrogen bonded tetrameric unit, bridged by eight $[C(NH_2)_3]^+$ ions. Aniline groups are omitted to make the hydrogen bonding scheme clearer. (C) Full structure showing the one-dimensional chains linking the tetramers through Na$^+$ cations along the *b*-axis. Light gray octahedra, MoO_6; dark gray tetrahedra, AsO$_3$R; light gray circles, carbon; dark gray circles, nitrogen; white circles, hydrogen; black circles, sodium.

There are two sodium sites within the unit cell. One is located outside of the bonding distance to the cluster oxo

ligands and is surrounded by disordered, solvating H_2O molecules, evidenced by the presence of residual electron density observed by X-ray crystallography. In addition, there is a potential disordered solvent void of 951 $Å^3$ containing 413 electron counts as determined by the PLATON/SQUEEZE[19] programs. The reflection file was modified to account for this disordered electron density, improving the R factor by 0.05%. The second sodium site acts as a bridge between POM tetramer units and coordinates to cluster oxo ligands at distances of 2.80 and 2.84 Å. The result is a one-dimensional chain of tetrameric POM units running along the *b*-axis. The chains are interdigitated with solvated Na^+ and non-hydrogen bonding guanidinium ions located in the space between chains.

While the presence of Co^{2+} was required for crystal growth of **1**, no cobalt ions were found in the structure. Elemental analysis revealed the presence of a small amount of Co in the sample (0.58 wt %); however, attempts to incorporate Co into the structure using partial occupancy models with the Na sites led to large thermal parameters and poor *R* values.

Crystal Structure of (2). A reaction between the tetrahedral cluster, $[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}NH_3^+)_4]$, and Ag^+ ions was conducted to probe the possibility of connecting the clusters through linear linkages between the aniline nitrogens and a transition metal. Silver was chosen because of its propensity to form linear two-coordinate complexes.[21] The resulting crystalline material (Figure 2) contained two Ag^+ sites within the unit cell. One had a distorted tetrahedral geometry with bonds to an aniline nitrogen (2.26 Å), two CH_3CN molecules (average distance of 2.32 Å), and one oxo ligand of a neighboring POM at 2.65 Å. Through these bridging Ag^+ ions, the POM clusters are linked into one-dimensional chains along the 110 direction of the crystal. The second Ag^+ site has nearly tetrahedral geometry and is bonded to one oxo ligand of the cluster at 2.57 Å and three CH_3CN molecules at an average distance of 2.24 Å. Two of the four aniline groups were modeled with protonated amine groups to satisfy the counterion requirements.

A total of three additional acetonitrile and two water molecules were also located in the spaces between POM chains. Four free acetonitrile sites were found; however, two of these were disordered. The disordered molecules were refined anisotropically with partial occupancies of 0.59 and 0.41 to total a single acetonitrile disordered over two sites. The protons of the water molecules could not be located, but they have been included in the chemical formula.

Crystal Structure of (3). A second reaction using a transition metal as a potential linking ion was performed with Cu^{2+}. Reaction of $[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}NH_3^+)_4]$ with Cu^{2+} in aqueous acetonitrile solution yielded a structural architecture very different from that found in **2** (Figure 3). The four aniline groups were modeled with protonated amine groups to satisfy the counterion requirements. No Cu^{2+} sites could be located by X-ray crystallography, and instead of

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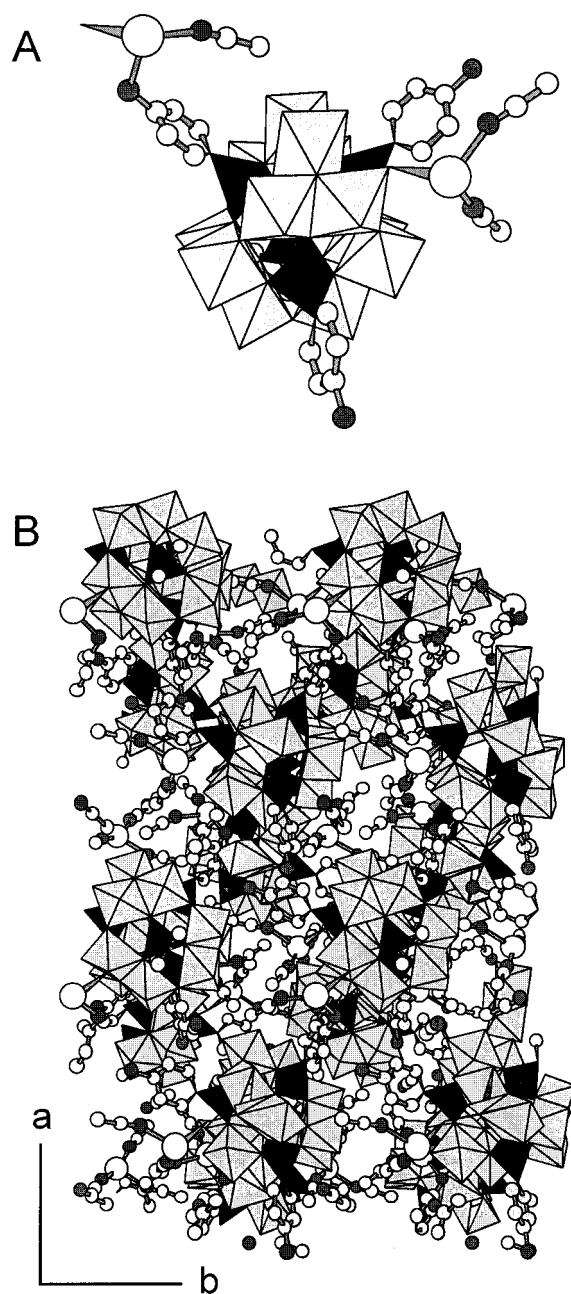
Figure 2. Crystal structure of **2**. (A) Individual POM unit. Open bonds are to the neighboring cluster oxo ligand. (B) Crystal structure viewed down the *c*-axis. POM chains are arranged diagonally across the unit cell. Grey octahedra, MoO_6; black tetrahedra, AsO_3R; light gray circles, carbon; dark gray circles, nitrogen; large white circles, silver.

the POM clusters linking together through bridging ions as in **1** and **2**, they are connected by hydrogen bonds between aniline groups and cluster oxo ligands at distances of 2.81−2.96 Å from the aniline protons to the oxo ligands. The structure can be considered a hydrogen bonded two-dimensional sheet of POM clusters with the sheets stacked directly on top of one another. The POMs are packed into a two-dimensional network that has a bricklike arrangement of channels. These channels have a potential solvent volume of 39% of the unit cell volume and contain a large amount of residual electron density (2865 electron counts). This large value suggests that there is not only disordered solvent (CH_3CN and H_2O) but also some solvated copper species
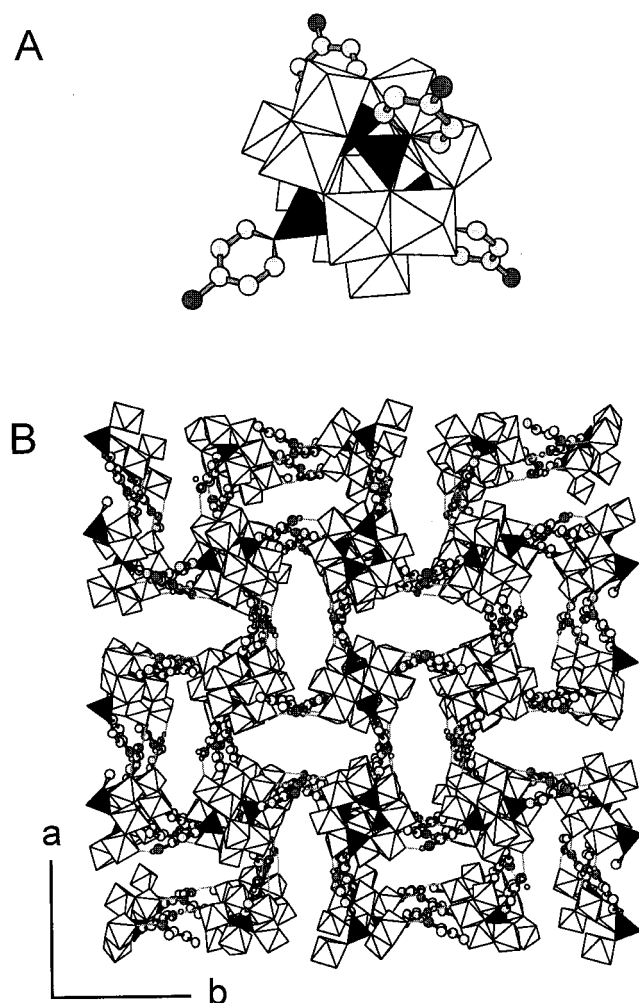
A

B

Figure 3. Crystal structure of **3**. (A) Individual POM unit. (B) Crystal structure viewed down the *c*-axis. Subsequent layers are directly above and below. 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, nitrogen.

filling these pores as well. The reflection file was modified to account for this disordered electron density by the PLATON/SQUEEZE[19] programs, improving the *R* factor by 2%.

The relatively low R_1 value (0.0540) for this structure indicates that there are few heavy, disordered cations (i.e., Cu^{2+}) within the channels and that the majority of the counterions on the cluster are protons. The crystals were washed after synthesis, and their color is slightly green, indicating that some of the Cu^{2+} does populate the channels of the material. The presence of copper is further evidenced by elemental analysis, which indicates that there is approximately one Cu^{2+} ion for every four POM clusters.

Discussion

Crystallization of the structures presented here can be understood on the basis of the same guidelines that have been reported previously.[12] Despite differences in the POM framework, the structures all share similar connectivity and packing patterns, which are based on different counterions, solvents, and organic groups. Each of these plays a significant

role in the final structure. Because all of the organic groups were the same (aniline) in this study, the other parameters could be examined more closely. The purpose of investigating these parameters was to begin creating rules that govern the construction of predesigned crystalline arrays. The parameters below are studied with the idea that POM clusters can be linked through either bridging counterions or hydrogen bonds (between organic groups or between organic groups and cluster oxo ligands).

Organic Group. Aniline groups were chosen as the organic groups for their hydrogen bonding ability and possible use as ligands. In the structures presented here, aniline groups were observed to be either nonbonding, bonding to cations, or bonding to cluster oxo ligands. The type of bonding interaction observed in the product depended largely on the choice of cation and solvent. If the aniline was not solvated, bonding interactions, including dative and hydrogen bonding, could take place between the aniline and metal ions or hydrogen bond donor−acceptors.

Solvent Effects. For the present discussion, solvents can be classified by the strengths of two properties: Lewis acidity (hydrogen bonding) and Lewis basicity. The hydrogen bonding strength of the solvent may influence the degree of bonding between the aniline and other moieties. Solvents that have strong hydrogen bonding potential are able to form bonds to the organic moieties attached to the cluster, thus impeding them from other bonding interactions; weakly hydrogen bonding solvents are not observed interacting with the POM or its organic groups. Solvents that act as strong electron donors to the metal cations counterbalancing the POM passivate the coordination environment of the counterions.

Metal centers observed in structures presented here are partially solvated; the remaining coordination sites are occupied by cluster oxo ligands (**1**) or both oxo ligands and aniline nitrogens (**2**). In **1**, H_2O was used as the solvent and it was observed bonding to Na^+ ions. Although no hydrogen bonds were observed between aniline groups and water molecules, it is possible that bonds involving disordered solvent molecules between the POM chains were not detected by X-ray crystallography. The solvent system for both **2** and **3** was an aqueous acetonitrile solution. Acetonitrile is polar aprotic and, therefore, of comparatively weak hydrogen bonding strength, so it was not expected to impede any bonding interactions that might derive from the organic groups. This was true both for **2** and **3**. In **2**, there were no acetonitrile molecules associated with the aniline, but several solvated the Ag^+ ions. The connectivity of the clusters in **2** through the Ag^+ ions was facilitated by the presence of a weakly Lewis acidic solvent (CH_3CN), which did not interfere with bonding between the aniline and the Ag^+ center. The same is true for **3**: because there was no interference between acetonitrile and aniline, the hydrogen bonds between aniline hydrogens and cluster oxo ligands were free to form.

Counterion Effects. POM counterions can be categorized into two groups: those having a strong affinity for the oxo ligands of the POM and those that interact weakly with the

cluster. Counterions such as Na^+, Ag^+, or $[C(NH_2)_3]^+$ appear to interact significantly with the POM and were observed bonded to oxo ligands of the cluster or the organic group (aniline). Cluster-bonded counterions often acted as bridges between POM clusters. This is observed in the structures of both **1** and **2** and is also observed elsewhere in the literature.[12,22,23] Cations such as K^+ appear to have less affinity for the cluster. They are typically located as solvated ions and are not bonded to the POM.[12] In systems with such ions, it is expected that *intercluster* interactions are more significant. Cluster−cluster interactions could take the form of hydrogen bonding between organic groups[12] or between the organic moiety and the cluster oxo ligands, such as in **3**. A similar trend in cation coordination has also been observed for Keggin-type POMs,[22] where it is indicated that Na^+ ions prefer to coordinate to the terminal oxo ligands of POMs, while counterions such as K^+ do not. While it may be expected that transition metal ions would also bond to terminal oxo ligands because of larger electrostatic interactions between the divalent transition metals and the anionic POM, this has not been observed in the crystal structures described here.

Previous experiments performed using K^+ salts of the phenol-derivatized POM clusters and Fe^{3+} as potential linking ions[12] resulted in a product with a connectivity similar to **3**. Like **3**, no counterions were detected by X-ray crystallography. Transient bonding between the organic moiety and Fe^{3+} ions expelled K^+ and decreased cluster−counterion interactions. Reprotonation of the organic ligand left the structure with proton counterions and only organic group−cluster bonding interactions. A similar mechanism may take place during the formation of **3**, which could explain the role of the Cu^{2+} ion in the crystallization. Where transient bonds between Cu^{2+} ions and aniline may form, cluster−cluster interactions are maximized, and protons displace the Cu^{2+} ions from the product. However, there is little information on the mechanism of formation and the final structure only gives clues as to the actual course of the reaction. The precise role that Cu^{2+} plays in the crystallization of compound **3** is not known; however, crystallization into a hydrogen-bonded network does not take place in its absence and compound **3** is unique to Cu^{2+} addition.

Crystallization with ions that have significant affinity for the POM cluster ($[C(NH_2)_3]^+$/Na^+) yielded a structure (**1**) in which the cations are bonded to the cluster oxo ligands, connecting them into one-dimensional chains. The structure of **2** was directed by the strong affinity Ag^+ has for the POM cluster. Bonds formed between both cluster oxo ligands and aniline groups to the metal. The Lewis basicity of the acetonitrile resulted in the formation of bonds to the Ag^+ and possibly prevented further bonding to oxo ligands or aniline groups. The channel structure of **3** formed by the choice of appropriate counterion and solvent in combination with an organic group capable of hydrogen bonding. Provid-

ing a counterion that was not observed bonded to the POM (Cu^{2+}) and a solvent with a lower hydrogen bonding capacity (aqueous CH_3CN) allowed intercluster hydrogen bonds between aniline moieties and between aniline and cluster oxo ligands to be obtained.

The Cu^{2+} ion must also play a role in the formation of the final structure; if **3** is compared to the crystal structure of $[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}NH_3^+)_4]\cdot10CH_3CN\cdot6H_2O$,[16] the only difference between the crystallization procedures is the presence of Cu^{2+} in the solution. In this known crystal structure, no hydrogen bonds exist between anilinium groups and cluster oxo ligands, but they are observed in **3** when $[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}NH_3^+)_4]$ is crystallized in the presence of Cu^{2+}. Previous examples provided us with a starting point based on transient bond formation between the transition metal ion and the organic group; a similar mechanism may be working here involving replacement of protons for Cu^{2+} ions during the reaction.

Conclusion

Three crystal structures of organic derivatives of POM clusters were solved, and the roles of the counterions, solvent, and organic group were studied. It is observed from these examples and those investigated earlier[12,16,22] that several parameters control the structure of crystalline materials synthesized from organic derivatives of POM clusters. These parameters concern the affinity of the cation for the cluster oxo ligands and the organic group of the cluster, the hydrogen bonding strength and Lewis basicity of the solvent, and the hydrogen bonding donor−acceptor ability of the organic group. In compound **1**, the presence of both Na^+ and $[C(NH_2)_3]^+$, which interact with the cluster oxo ligands, link the POM clusters into tetrameric units and one-dimensional chains. Compound **2** is dominated by the affinity of Ag^+ for the POM cluster. Strong interactions between Ag^+ and both the oxo ligands and the aniline groups link the clusters into one-dimensional chains. The Lewis basicity of acetonitrile also plays a role in this structure, as it passivates many of the Ag^+ coordination sites. The structure of **3** shows the significance of selecting a weaker hydrogen bonding solvent (CH_3CN/H_2O) in the presence of a transition metal (Cu^{2+}), which did not bond to the cluster oxo ligands. The bonding interactions between clusters are maximized in the absence of solvent and cation interactions, leading to an open structure. While the goal of tailoring the crystal structures of organically modified POM clusters to have predictable geometries has yet to be realized, it is hoped that the understanding of some parameters affecting the crystallization will yield more open-framework or porous structures.

Supporting Information Available: A full CIF file of each structure. This material is available free of charge via the Internet at http://pubs.acs.org..

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