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Functional POM-OFs

Modular Assembly of a Functional Polyoxometalate-Based Open Framework Constructed from Unsupported $Ag^I\cdots Ag^I$ Interactions**

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Polyoxometalates (POMs), anionic transition-metal oxide clusters,[1] represent a vast class of inorganic materials with a virtually unmatched range of physical and chemical properties relevant for applications as diverse as medicine and biology,[2] magnetism,[3] materials science,[4] and catalysis.[5] It is this unique range of properties which qualifies POM-based materials as prime candidates for the designed construction of molecular-framework materials. Polyoxometalates cover an enormous range in size and structure[1b,c,6] and thereby provide access to a huge library of readily available and controllable secondary building units (SBUs)[7] which can be interconnected by an electrophilic linker. This crucial step in the assembly of functional POM frameworks has so far been achieved by using organic linkers[8] or by ligand-supported transition-metal bridges;[9] both approaches however are limited by the reduced framework stability intrinsic to metal–organic framework materials. In contrast, the assembly of purely inorganic POM-based frameworks offers high potential for the formation of a new type of porous materials which combines the thermodynamic stability of zeolites and mesoporous silicas[10] with the sophistication and versatility of metal–organic frameworks (MOFs).[7,11]

The key to the work reported herein is the ability to form structurally supporting $\{Ag_2\}^{2+}$ building blocks, and we have recently shown that careful solvent and ligand control can be used to encourage the formation of such interactions.[12] This approach has stimulated us to exploit this tendency and to investigate the potential of silver(I) dimers to act as linking units in conjunction with larger isopolyoxometalates to construct 3D frameworks.

Herein we present the modular assembly of a 3D porous framework: $[Ag(CH_3CN)_4]\subset\{[Ag(CH_3CN)_2]_4[H_3W_{12}O_{40}]\}$ (**1**). Single-crystal X-ray diffraction studies revealed that the two principal SBUs, protonated α-metatungstate[13] clusters $[H_3W_{12}O_{40}]^{5-}$ ($\{W_{12}\}^{5-}$) and dimeric $\{[Ag(CH_3CN)_2]_2\}^{2+}$ ($\{Ag_2\}^{2+}$) bridging units (Figure 1), are linked such as to enclose two sets of colinear channels. T_d-symmetric $[Ag(CH_3CN)_4]^+$ units are located in the channels and appear to act as templates in the self-assembly of the framework, so **1** can be represented as $\{Ag\}\subset[\{W_{12}\}\{Ag_2\}_{8/4}]$.

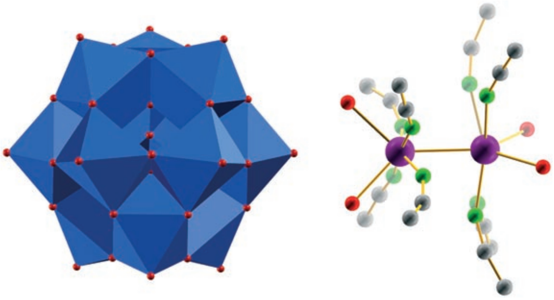

Figure 1. Illustration of the secondary building units of **1**. Left: The $\{W_{12}\}^{5-}$ Keggin type isopolyoxotungstate $[H_3W_{12}O_{40}]^{5-}$; WO_6 octahedra blue, O ligands red. Right: The dimeric $\{Ag_2\}^{2+}$ linker unit; note that each acetonitrile molecule is disordered over two positions. C gray, N green, Ag purple, O red; this color scheme is used throughout the text.

The reaction of ten equivalents $AgNO_3$ and one equivalent $(nBu_4N)_4[H_4W_{12}O_{40}]$ in acetonitrile in the presence of aqueous HNO_3 resulted in the isolation of the infinite 3D framework **1** in 60% yield, which was fully characterized. Structurally, the framework can be described as an infinite array of $\{W_{12}\}^{5-}$ α-metatungstate clusters which are connected to eight $\{Ag_2\}^{2+}$ cations by coordination through the terminal $W{=}O_t$ oxygen ligands. The formation of these W-O-Ag bridges provides flexibility but also stability to allow the assembly of an infinite purely inorganic framework. The key to the framework assembly is the ability of the silver ions to connect the particular clusters by self-organizing into $\{Ag_2\}^{2+}$ dimers with short silver–silver ($Ag^I\cdots Ag^I$) contacts which are stabilized by argentophilic metal–metal interactions (see Figure 2).[14] Each dimeric $\{Ag_2\}^{2+}$ motif cross-links four $\{W_{12}\}^{5-}$ clusters. To encourage the formation of the Ag···Ag interactions it is vital to exclude coordinating ligands. In other words, we have found that the absence of bridging ligands such as DMSO or 4,4′-bipyridine, which disrupt framework growth by capping the silver linkers and result in the isolation of low-dimensionality structures, can be used to encourage unsupported Ag···Ag interactions. This strategy represents a subtle yet significant departure from our previous synthetic approaches.[12] This new approach allows us to isolate the first example of a framework system constructed by utilizing

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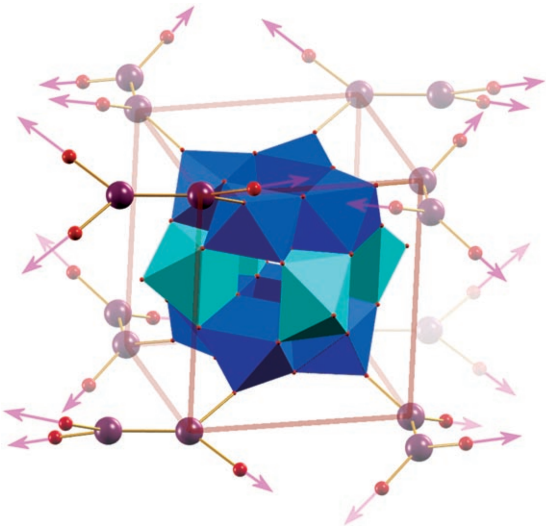

Figure 2. Representation of the principal cubic coordination environment in **1**: one $\{W_{12}\}^{5-}$ cluster (blue) linked to eight $\{Ag_2\}^{2+}$ bridges (purple), forming the open framework structure. Note that the $\{Ag_2\}^{2+}$ dimers are located on two distinct faces of the cluster (light blue octahedra) whereas the terminal oxygen atoms in the central belt remain noncoordinated to the Ag atoms (cyan octahedra). The purple arrows emphasize the direction of framework growth. The red cube highlights the cubic arrangement of the silver dimers around the $\{W_{12}\}^{5-}$ cluster. Solvent molecules are omitted for clarity.

unsupported metal–metal interactions and demonstrates the stability and versatility of this self-assembled SBU.

Topologically, the structure can be rationalized as a 4,8-connected 3D net in which each silver dimer links four clusters and each $\{W_{12}\}^{5-}$ unit is surrounded by eight $\{Ag_2\}^{2+}$ bridges. Interestingly, this distinct cubic arrangement of the eight silver moieties around the central $\{W_{12}\}^{5-}$ unit results in a central belt of four noncoordinating WO_6 octahedra (see Figure 2). Both the top and the lower sections of the cluster are made up of edge-sharing tetranuclear $\{W_4\}$ fragments, and each section is linked to four $\{Ag_2\}^{2+}$ units through terminal $W{=}O_t$ bridges, thereby connecting the clusters in all three dimensions. Consequently, the coordination mode of each $\{Ag_2\}^{2+}$ unit corresponds to a μ_4-bridging unit, in which each dimer coordinates to four clusters through both silver(I) ions. Closer inspection of the $\{Ag_2\}^{2+}$ dimers reveals a set of three different donor ligands: The principal coordination environment around each silver center is formed by two oxygen atoms from two $\{W_{12}\}^{5-}$ units which are engaged in coordinative Ag–O bonds, providing stability to this framework. Furthermore, two disordered acetonitrile molecules coordinate to the central silver ion to fill the coordination sphere. However, these ligands do not support the framework and do not add to its stability.

The two $\{Ag(O)_2(CH_3CN)_2\}$ fragments are held together by argentophilic Ag···Ag interactions, which in turn form the dimeric $\{Ag_2\}^{2+}$ structure with short silver–silver contacts of 2.9075(2) Å. The UV/Vis spectrum of **1** provides further evidence for the presence of attractive argentophilic interactions: An absorption band at $\lambda = 270$ nm is indicative of close Ag···Ag interactions and has been observed previously.[15] The result of this complex arrangement of $\{W_{12}\}^{5-}$ and $\{Ag_2\}^{2+}$ building units is the formation of a 2D network of microporous channels which propagate along the crystallographic *a* and *b* axes (Figure 3). The walls of these micropores are made up by a distinct cagelike assembly of four $\{W_{12}\}^{5-}$ clusters and two $\{Ag_2\}^{2+}$ dimers, resulting in ellipsoidal voids with dimensions of about 6.1×9.1 Å^2 which are located at the intersection of two channels. These cavities are formed around a cationic $[Ag(CH_3CN)_4]^+$ group, which does not only act as a charge-balancing unit but directs the formation of the porous structure by templating the channels. Intriguingly, the structure of this complex cation resembles the structure of quaternary alkyl ammonium groups, which are often used in the templated synthesis of zeolites.[16] Thermogravimetric desolvation studies indicated that all acetonitrile solvent molecules can be removed from the structure at moderate temperatures, resulting in a large accessible pore volume. Calculations based on the desolvated crystal structure estimated the accessible pore volume to be 1321 Å^3, which corresponds to 39.9% of the unit-cell volume (3307 Å^3).[17] Further calculations based on the crystallographic results indicate a surface area of about 1006 $m^2 g^{-1}$. These preliminary theoretical results encouraged a detailed experimental investigation to study the sorption capabilities of **1**.

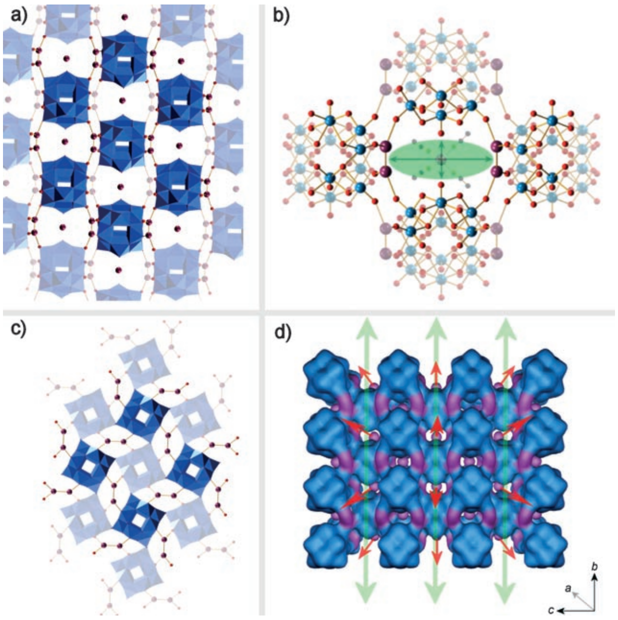

Figure 3. Illustration of the framework **1**. a) View along the crystallographic *a* axis, showing the spatial arrangement of the $\{W_{12}\}^{5-}$ units (blue) and $\{Ag_2\}^{2+}$ dimers (purple) to form channels in which the $[Ag(CH_3CN)_4]^+$ counterions are located. b) Detailed illustration of the channels; the pore dimensions are highlighted by a green ellipsoid. c) View along the crystallographic *c* axis, illustrating the bridging mode of the $\{Ag_2\}^{2+}$ dimers. d) Space-filling representation of **1**, indicating the propagation of the channels along the crystallographic *a* axis (red arrows) and the crystallographic *b* axis (green arrows). Solvent molecules are omitted for clarity.

Thermogravimetric sorption studies using acetonitrile as the sorbate were conducted to investigate the porosity of the framework. The material was desolvated at 150 °C until no further weight loss was observed. Thereafter, the material was stored in an atmosphere of acetonitrile for 24 h to allow re-adsorption of the solvent, and the desorption cycle was subsequently repeated to confirm the reversibility of the sorption process. After the first cycle, the material showed a weight loss of 10.7 wt %, which decreased to 8.7 wt % after run 5 (Figure 4). Interestingly, the decrease in absorbed solvent shows a linear dependence on the number of runs and suggests a gradual blockage of the solvent-accessible pore volume, which is most likely due to the thermal treatment during the desorption process.

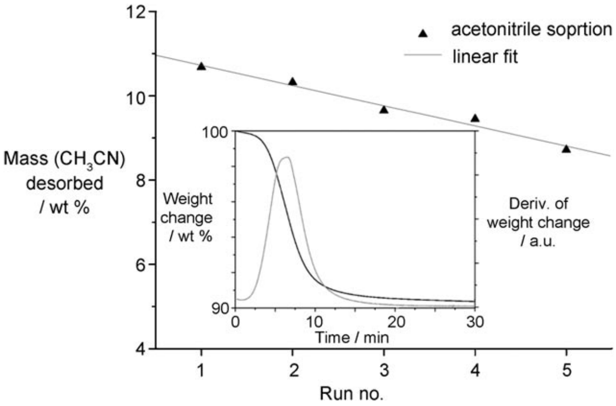

Figure 4. Thermogravimetric study of the reversible sorption capabilities of **1**. The main graph depicts the linear decrease in acetonitrile desorption observed over five sorption–desorption cycles. The inset shows a typical thermogravimetric desorption (weight change: black line, derivative of weight change: gray line).

To establish the role of the $Ag^I\cdots Ag^I$ interactions, the electronic structure of a representative fragment, containing one $\{Ag_2\}^{2+}$ and four adjacent $\{W_{12}\}^{5-}$ groups, was estimated using single-determinant DFT (density functional theory) calculations.[18] The chosen (neutral) fragment, $Na_{18}[Ag(CH_3CN)_2)]_2[H_3W_{12}O_{40}]_4$, replaces the $[Ag(CH_3CN)_4]^+$ cations and the $\{Ag_2\}^{2+}$ groups that anchor the tetrahedral metatungstate tetramer into the solid-state structure of **1** with terminal Na^+ cations, thereby mimicking point charges. The size of this fragment limited the calculations to single-point estimates of the relative energies of the frontier orbitals and Mulliken population analyses. The latter reveal a bonding character of the Ag–Ag pairs equivalent to about a quarter of a covalent Ag–Ag bond; this result is in good agreement with similar $\{Ag_2\}$-linked polyoxometalates[12] and coordination complexes and illustrates the weak but significant binding contribution along the axial vector perpendicular to the equatorial coordination environment defined by the acetonitrile and tungstate oxo ligands. Examination of the energy gap between the HOMO and LUMO, both significantly centered on the $\{Ag_2\}^{2+}$ groups, and the density of states in the frontier orbital region leads to the prediction that electronic absorption related to the $\{Ag_2\}^{2+}$ group occurs in the range of 340 to about 250 nm, which is experimentally observed for compound **1**.

In conclusion, we have synthesized a truly porous 3D framework which is constructed from $\{W_{12}\}^{5-}$ and $\{Ag_2\}^{2+}$ building blocks to give an unprecedented, purely covalently connected framework that contains microporous channels, yet the framework does not require organic linkers. Therefore, we name this framework as the first in a series of polyoxometalate open frameworks (POM-OFs). Furthermore, this material shows reversible sorption capabilities which allow the sorption and desorption of small organic molecules. Further studies will be concentrated on investigating the functionality of **1** in more detail in terms of catalysis and sorption studies, as well as on extending this synthetic approach to develop a family of POM-OFs.

Experimental Section

All chemicals were of analytical grade and used as supplied. $(nBu_4N)_4[H_4W_{12}O_{40}]$ was prepared according to reference [19], except for the use of nBu_4NBr instead of nPr_4NBr. $(nBu_4N)_4[H_4W_{12}O_{40}]$ (500 mg, 131 μmol) and 10 equivalents $AgNO_3$ (222 mg, 1.31 mmol) were dissolved in acetonitrile (25 mL). HNO_3 (35 %, 1 mL) was added, and the mixture was heated at 80 °C for 24 h, cooled to room temperature, and filtered. Diffusion of acetone into the reaction mixture gave colorless crystals of **1** after about 4 days. Yield: 297 mg, 76.5 μmol, 59.7 % based on W. Elemental analysis (%) calcd for $C_{24}H_{39}N_{12}O_{40}Ag_5W_{12}$ (3881.22 $g\,mol^{-1}$): C 7.42, H 1.01, N 4.33, Ag 13.66, W 58.26; found: C 6.67, H 0.88, N 3.78, Ag 13.90, W 56.84, indicating the loss of 1.5 CH_3CN solvent molecules. FT-IR (KBr): $\tilde{\nu} =$ 3454 (vs, br), 1623 (m), 1384 (w), 1262 (w), 945 (s), 892 (vs), 768 cm^{-1} (vs).

Crystallographic data for **1**: $C_{24}H_{39}N_{12}O_{40}Ag_5W_{12}$, tetragonal, space group $P4/mnc$ (no. 128); $a = 13.4833(9)$, $c = 18.190(2)$ Å, $V = 3307.0(5)$ Å^3; $Z = 2$; $R1 = 0.0466$, $wR2 = 0.1201$ (all data). CCDC-651032 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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