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Layered Assemblies of a Dialuminum-Substituted Silicotungstate Trimer and the Reversible Interlayer Cation-Exchange Properties

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Supporting Information

ABSTRACT: Two polyoxometalate assemblies, $TBA_9[\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3]$ (**1**; TBA = tetra-*n*-butylammonium) and $TBA_6Li_3[\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3]\cdot 18H_2O$ (**2**), were synthesized by trimerization of a dialuminum-substituted silicotungstate monomer. Both **1** and **2** possessed a layered structure composed of a basal sheet unit $[TBA_3\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3]^{6-}$ and interlayer cations. The interconversion between **1** and **2** reversibly took place through interlayer cation exchange.

Polyoxometalates (POMs) are a large family of anionic metal−oxygen clusters consisting of the group V and VI metals in their highest oxidation states and have a diverse range of applications such as catalysis, magnetism, biology, medicine, and material science.[1] Their chemical properties and structures can be finely tuned;[1] for example, various metal-substituted POMs with controlled active sites (molecular catalysts) have been synthesized by using lacunary POMs as structural motifs, which can realize many green catalytic functional group transformations.[1] In addition, various high-nuclearity POMs, e.g., POM polymers and giant isopolyoxometalates, can readily be synthesized.[2] Thus, POMs are ideal prefunctionalized anionic molecular building units and can be assembled with appropriate cations including metal cations, organic cations, and cationic organometallic complexes, resulting in the construction of sophisticated hierarchial nanoarchitectures.[3]

Recently, we have successfully synthesized a dialuminum-substituted silicotungstate monomer $TBA_3[\gamma\text{-}HSiW_{10}O_{36}\{Al(H_2O)\}_2(\mu\text{-}OH)_2]\cdot 4H_2O$ (**3**, where TBA = tetra-*n*-butylammonium; Figure S1 in the Supporting Information, SI).[4a] Aluminum-containing POMs are some of the least reported compounds.[4] The aluminum centers in **3** could act as Lewis acid sites and chemo- and diastereoselectively catalyze the intermolecular cyclization of citronellal derivatives.[4a] Herein, we demonstrate that it is possible to generate POM-based layered assemblies from the POM monomer. In organic media (nonaqueous solvents), the dehydrative condensation of **3** proceeded to afford a trimer anion $[\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3]^{9-}$. One trimer anion and three TBA cations were densely arranged to form a negatively charged basal sheet unit $[TBA_3\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3]^{6-}$, and the negative charge was compensated for by TBA cations (interlayer cations), resulting in the construction of a layered assembly **1**. By trimerization of **3** in the presence of lithium cations ($LiClO_4$), we also successfully synthesized a lithium-containing layered assembly **2** with the same basal sheet unit as that of **1**. In addition, we found that interconversion between **1** and **2** is possible through interlayer cation exchange.

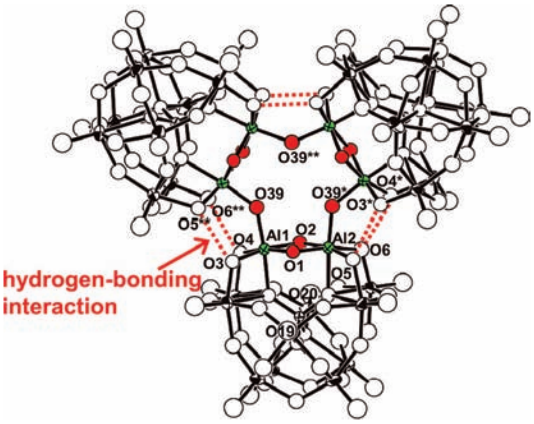

Figure 1. ORTEP representation of the anion part of **1**. The thermal ellipsoid was set at 50% probability.

Compound **3** was dissolved in acetonitrile, and the successive addition of dimethyl carbonate to the solution yielded single crystals of **1** suitable for X-ray crystallographic analysis (76% yield based on **3**; see the SI).[5,6] As shown in Figure 1, the anion part of **1** consisted of three fused dialuminum-substituted silicotungstate monomers, and this is the first example of the aluminum-substituted POM-based trimerized (polymerized) structure. It was confirmed by bond valence sum (BVS) calculations that O39 was a mono-μ-hydroxo ligand bridging two monomer units and that O4 and O5 were monoprotonated. Both of the O4···O6** and O5···O3* distances were 2.78(2) Å, showing the existence of hydrogen-bonding interaction.[7] Thus, each monomer unit was closely connected with the μ-hydroxo ligand and the hydrogen-bonding interaction. The **1** anion possessed a clover-leaf-shaped Al−O core $\{Al_6(\mu\text{-}OH)_9\}^{9+}$ surrounded by three lacunary $[\gamma\text{-}H_2SiW_{10}O_{36}]^{6-}$ units. In the Al−O core, six aluminum atoms and three oxygen atoms of the mono-μ-hydroxo ligands bridging two monomer units (O39, O39*, and O39**) were coplanar. To date, several γ-Keggin silicotungstate trimers, e.g., $[Fe_6(OH)_9(H_2O)_2L_2(\gamma\text{-}SiW_{10}O_{36})_3]^{n-}$ (L = OAc, n = 17 or L =

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$(H_2O)_2$, $n = 15)$[8a,b] and $[M_6(O_2)_6(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ (M = Zr or Hf)[8c,d] have been reported. In particular, zirconium/hafnium-POM trimers possessed a structure similar to that of **1** except for the bridging ligands (μ-hydroxo ligands for **1** and peroxo groups for those trimers).[8c,d] The results of X-ray, elemental, and thermogravimetric analyses show that the formula of **1** is $TBA_9[\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3]$. Compound **1** is formed by the dehydrative condensation of three monomers, and the formation can be expressed by eq 1.

$$3TBA_3[\gamma\text{-}HSiW_{10}O_{36}\{Al(H_2O)\}_2(\mu\text{-}OH)_2] \rightarrow TBA_9[\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3] + 3H_2O \quad (1)$$

One trimer anion and three TBA cations were arranged parallel to the *ab* plane to form a negatively charged closely packed honeycomb-like sheet with a basal unit $[TBA_3\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3]^{6-}$ (Figures 2a and S2 in the SI). There were six TBA cations per one basal unit to compensate for the negative charge, resulting in the construction of the densely packed layered structure. Each negatively charged basal sheet was stacked along the *c* axis with lattice translations, and **1** possessed three sheets in the unit cell (ABC-stacking pattern; Figure 2b). The thickness of the basal sheet was 10.3 Å, and the interlayer distance was 4.1 Å.

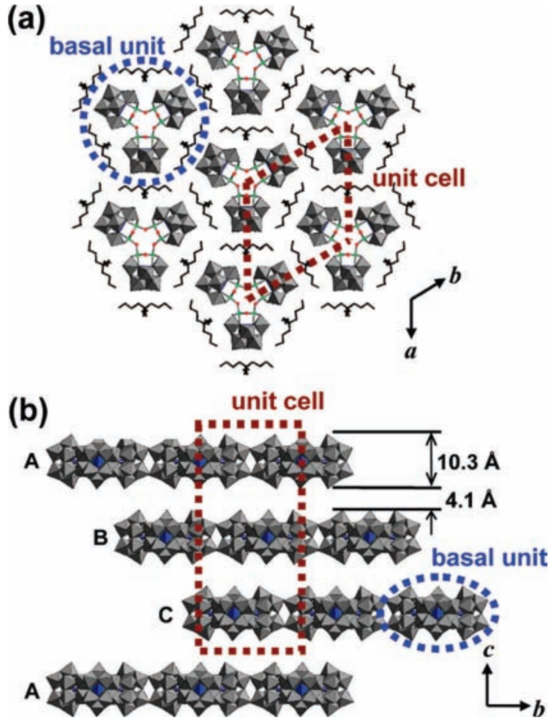

Figure 2. Polyhedral representation of **1**: (a) negatively charged sheets (view along the *c* axis) and (b) the stacking (view along the *a* axis, ;TBA cations are omitted for clarity). Green and red spheres represent aluminum and oxygen atoms, respectively. Gray and blue polyhedra showed $\{WO_6\}$ and $\{SiO_4\}$ units, respectively. Black sticks represent TBA cations.

When trimerization of **3** was carried out in the presence of $LiClO_4$ (3 equiv with respect to **3**; the other conditions were the same as those for the synthesis of **1**), a lithium-containing trimer **2** was obtained (71% yield based on **3**; see the SI).[5] The local structure of the **2** anion was identical with that of **1** (Figure S3 in the SI). The results of X-ray, elemental, and thermogravimetric analyses show that the formula of **2** is $TBA_6Li_3[\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3]\cdot 18H_2O$. The formation of **2** can be expressed by eq 2.

$$3TBA_3[\gamma\text{-}HSiW_{10}O_{36}\{Al(H_2O)\}_2(\mu\text{-}OH)_2] + 3Li^+ \rightarrow TBA_6Li_3[\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3] + 3TBA^+ + 3H_2O \quad (2)$$

As shown in Figure 3, **2** also possessed the layered structure composed of the same negatively charged basal sheet unit $[TBA_3\{\gamma\text{-}H_2SiW_{10}O_{36}Al_2(\mu\text{-}OH)_2(\mu\text{-}OH)\}_3]^{6-}$ as that of **1**. TBA and lithium cations likely exist in the interlayer with a molar ratio of 1:1 to compensate for the negative charge.[9] Each sheet was stacked along the *c* axis without lattice translations (AA-stacking pattern; Figure 3b), and the stacking pattern was different from that of **1** (Figure 2b). The interlayer distance of **2** (2.8 Å) was shorter than that of **1** (4.1 Å).

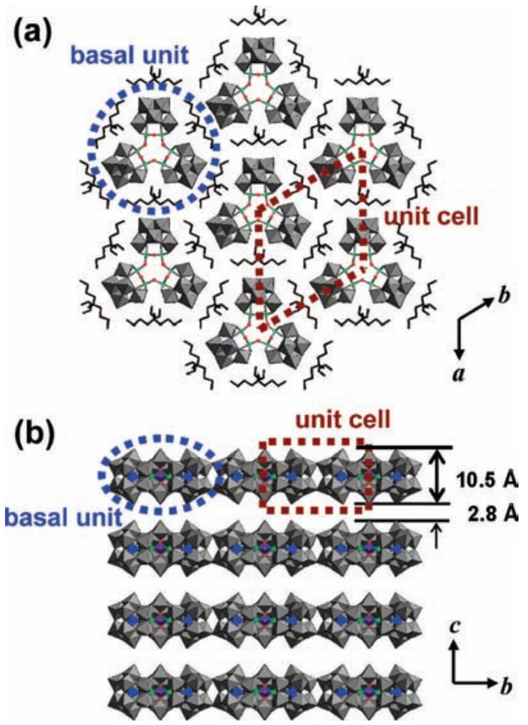

Figure 3. Polyhedral representation of **2**: (a) negatively charged sheets (view along the *c* axis) and (b) the stacking (view along the *a* axis; TBA cations are omitted for clarity). Green and red spheres represent aluminum and oxygen atoms, respectively. Gray and blue polyhedra showed $\{WO_6\}$ and $\{SiO_4\}$ units, respectively. Black sticks represent TBA cations.

The single crystals of **1** were immersed in a dimethyl carbonate solution of $LiClO_4$ (12 equiv with respect to **1**) at 32 °C for 24 h,[10] and then the crystals were retrieved by filtration. It was confirmed by elemental analysis that the lithium content of the retrieved crystals was 0.24 wt % and that the nitrogen content decreased from 1.05 (**1**) to 0.85 wt % (retrieved crystals).[11] These lithium and nitrogen contents were very similar to those of **2** (Li, 0.23 wt %; N, 0.90 wt %). Parts a and b of Figure 4 show the X-ray diffraction (XRD) patterns of **1** before and after the $LiClO_4$ treatment, respectively (Figure 4 in the SI). By this treatment, the peak positions of the *hk*0 reflections, e.g., 110, 330, 250, and 440, remained almost unchanged (Figures 4a,b and S4 in the SI). In contrast, the peak position of the 00*l* reflection of **1** (d_{003} = 14.4 Å; Figure

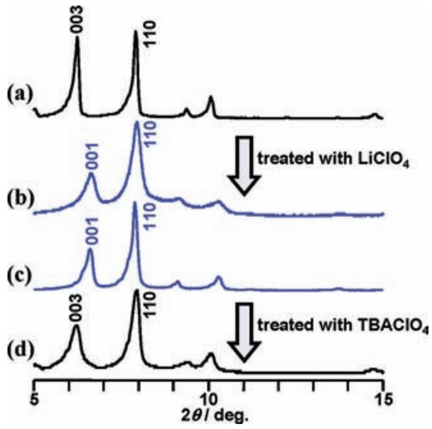

Figure 4. XRD patterns of (a) **1**, (b) **1** treated with $LiClO_4$, (c) **2**, and (d) **2** treated with $TBAClO_4$ (see also Figure S4 in the SI).

4a) shifted to the higher angle (d_{001} = 13.3 Å corresponds to the 001 reflection of **2**; Figure 4c), in accordance with shrinking of the interlayer distance and changing of the stacking pattern from ABC to AA stacking (Figures 2b and 3b). Therefore, half of the interlayer TBA cations in **1** were exchanged with lithium cations to form **2** by the above-mentioned treatment.

When the single crystals of **2** were immersed in a dimethyl carbonate solution of $TBAClO_4$ (12 equiv with respect to **2**) at 90 °C for 3 h (repeated three times),[10] the lithium content decreased from 0.23 to 0.018 wt % with increasing nitrogen content from 0.90 to 1.27 wt %.[11] The XRD pattern of **2** treated with $TBAClO_4$ was in good agreement with that of **1** (Figure 4a,d).[9] All of these results suggest that interconversion between **1** and **2** reversibly takes place through interlayer cation exchange. Although several POM-based layered compounds have been reported,[12] their reversible cation-exchange properties demonstrated herein have never been reported, to the best of our knowledge.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format for **1** and **2**, experimental procedures, Tables S1−S3, and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) The crystallographic data and selected bond lengths and angles are summarized in Tables S1 and S2 in the SI, respectively.

(6) Trimerization of the monomer **3** hardly proceeded in coordinating solvents such as acetonitrile, dimethylformamide, dimethyl sulfoxide (DMSO), and mixed solvents of acetonitrile/water and acetonitrile/DMSO.[4a] Upon the addition of nonpolar or low-polar solvents (e.g., dimethyl carbonate, toluene, chloroform, ethyl acetate, or diethyl ether) to an acetonitrile solution of **3**, trimerization proceeded to afford single crystals of **1**.

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(9) Although some TBA (except for those in the basal sheet unit) and lithium cations in **2** could not be crystallographically determined because of the high disorder and low electron density, respectively, these cations likely exist in the interlayer, taking the structural analogy between **1** and **2** into account. In addition to the hydrogen-bonded oxygen atoms, oxygen atoms with relatively lower BVS values (1.17 for O19 and 1.34 for O20) were found in **2**. Therefore, lithium cations in **2** are likely located between these oxygen atoms (interlayer).

(10) It was confirmed by the inductively coupled plasma atomic emission spectrometry analyses that compounds **1** and **2** were completely insoluble in dimethyl carbonate (see the SI for more details).

(11) Full elemental analysis data are summarized in Table S3 in the SI.

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