ABSTRACT: By using solubility control to crystallize the prenucleation clusters of hydrosol, a family of titanium-oxo clusters possessing the \( \{\text{Ti}_{18}\text{O}_{27}\} \) core in which the 18 Ti(IV)-ions are uniquely connected with \( \mu \)-oxo ligands into a triple-decked pentagonal prism was obtained. The cluster cores are wrapped by external sulfate and aqua ligands, showing good solubilities and stabilities in a variety of solvents including acetonitrile and water and allowing their solution chemistry being studied by means of electrospray ionization mass spectroscopy, \(^{17}\text{O}\) NMR, and vibrational spectroscopy. Furthermore, this study provides new titanium oxide candidates for surface modifications and homogeneous photocatalysis.

Metal oxide clusters constitute a large and rapidly growing class of discrete molecular materials that are useful in a variety of applications such as homogeneous catalysis, solution chemistry studies, and surface functionalization. Among them, titanium-oxo clusters are especially attractive for their roles as prenucleation clusters and as molecular analogues of titanium oxides such as \( \text{TiO}_2 \), which has been the most important photocatalyst to date. Over the past six decades, most titanium-oxo clusters were produced as isolated intermediates from nonaqueous solvothermal synthesis of \( \text{TiO}_2 \) nanomaterials. These compounds are passivated with alkoxide ligands or chelating carboxylate ligands and are sensitive to \( \text{H}_2\text{O} \) and oxidative environments, which largely limit their potential applications like solar light harvesting. However, titanium-oxo clusters isolated from water without any additional (chelating) ligands, which can be regarded as the prenucleation clusters of titinate hydrosol, are very rare, while those among them that can be redissolved as stable and individual ions in solvents like water have not been reported.

\( \text{TiOSO}_4 \) and \( \text{TiCl}_4 \) are the most common precursors for the aqueous sol−gel synthesis of titinate nanomaterials. We recently demonstrated that even when they are dissolved as clear aqueous solutions under highly acidic conditions Ti(IV) spontaneously hydrolyze and condensate into titanium-oxo oligomers. With the coexisting ions to lower the solubilities, some low-nuclearity prenucleation titanium-oxo clusters could be selectively isolated. Herein, we have moved a big step forward and report a new type of 18-nuclear titanium-oxo clusters (e.g., \( [\text{Ti}_{18}\text{O}_{27}(\text{OH})_{3}\text{SO}_{4}]_{6}\text{Cl}_{6}\cdot 6\text{TBAC} \)) exhibiting a \( \{\text{Ti}_{18}\text{O}_{27}\} \) core structure was isolated by precipitation of the 18 Ti atoms, and \( \{\text{Ti}(\text{Ti}_5)\} \) pentagonal building unit, in the structure of \( [\text{Ti}_{18}\text{O}_{27}(\text{OH})_{3}\text{SO}_{4}]_{6}\text{Cl}_{6}\cdot 6\text{TBAC} \) (1a). Color scheme: Ti, blue; O, red; S, yellow. For clarity, hydrogen atoms at the aqua ligands are omitted. In panels a and b, Ti atoms are at the centers of the green octahedra and the blue pentagonal bipyramids, and oxygen atoms lie at the vertices of the polyhedra.

Figure 1. (a) Side and (b) top views, (c) the triple-decked arrangement of the 18 Ti atoms, and (d) the \( \{\text{Ti}(\text{Ti}_5)\} \) pentagonal building unit, in the structure of \( [\text{Ti}_{18}\text{O}_{27}(\text{OH})_{3}\text{SO}_{4}]_{6}\text{Cl}_{6}\cdot 6\text{TBAC} \) (1a). Color scheme: Ti, blue; O, red; S, yellow. For clarity, hydrogen atoms at the aqua ligands are omitted. In panels a and b, Ti atoms are at the centers of the green octahedra and the blue pentagonal bipyramids, and oxygen atoms lie at the vertices of the polyhedra.

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that none of the bridging O atoms is protonated, and meanwhile, the 30 terminal-O are actually aqua ligands, related to the very low acidity of an aqua ligand bonded to the cluster surface (Table S1). Cluster 1a is also capped with six bridging bidentate SO$_4^{2-}$ ligands on the longitude surface of the Ti$_{18}$O$_{27}$ core. Due to the locations of the SO$_4^{2-}$ ligands, 1a internally possesses planar chirality (Figure S1). Both enantiomers are present in the unit cell, leading 1 to a racemic material.

In the coordination chemistry of transition metals, the {M(M$_5$)} (M = metal) pentagonal unit is a very important transferable building block in the formation of metal-oxide clusters. They are normally seen in molybdates and are rare for other iso-polyoxometalates. Although recently the {M(M$_5$)} units are also seen in W$_7^{-}$, Nb$_7^{-}$ and Ti$_{12}^{-}$ oxo complexes, they prevalently form the highly curved outer surfaces of spheroidal clusters like the Keiplerite {M$_7$O$_{12}$} and the fulleren-like {Ti$_{12}$} oxoalkoxide by appropriate linkers or sharing edges. Herein the triple-decked geometry of the pentagonal building blocks in 1a demonstrates their potential for construction of nonspheroidal molecular structures.

Compound 1 could be readily dissolved in common polar solvents like acetonitrile (MeCN, 300 mM), water (150 mM in 1.0 M HCl), methanol (180 mM), ethanol (140 mM), isopropanol (80 mM), acetone (140 mM), tetrahydrofuran (80 mM), nitrormethane (100 mM), and benzy alcohol (50 mM). ESI-MS was then used to investigate the stability of 1a in MeCN. Association/dissociation of H$_2$O, SO$_4^{2-}$, Cl$^-$, TBA$^+$, and H$^+$ can occur during desolvation (180 °C by ESI) of the polycationic {Ti$_{18}$O$_{27}$} clusters, resulting in both positively and negatively charged species. In the ESI$^-$ mode (Figure 2A), the two ensembles of related clusters in the range from 750 to 950 are attributed to the species {Ti$_{18}$O$_{27}$} and [[{Ti$_{18}$O$_{27}$} + TBAC]$^{3+}$], respectively. The species in the range of 1260 to 2250 are all $\sim$2 charged species with continuously increasing numbers of TBAC molecules (Table S2). Observation of the ensembles of the related clusters with differing numbers of TBAC, which follow both the −2 and the −3 species, strongly supports the assignments. The ESI-MS in the positive mode was also performed, and the data agree well with the structural stability of 1a (Figure S3).

To gain further insight into the solution chemistry of 1a, $^{17}$O NMR spectroscopy on $^{17}$O-labeled 1 was carried out. $^{17}$O-labeled 1 was conveniently prepared following the same protocol as normal 1 but using 10% $^{18}$O enriched water. The $^{17}$O NMR spectrum of 1 in MeCN (Figure 2B, curve a) shows five resonances related to the O-ligands. The relatively broad peak at 0 ppm is assigned to the quickly exchanging aqua ligands and solvent water. The peak at 528 ppm is assigned to the 10 $\mu$-O in the top and the bottom (Ti(Ti$_5$)), while that at 569 ppm is assigned to the five $\mu$-O in the middle (Ti(Ti$_5$)) (see the cartoons in Figure 2B). The two peaks at 738 and 793 ppm are assigned to the 10 $\mu$-O near the surface and the two buried in the Ti$_{18}$O$_{27}$ framework, respectively. Their relative intensity, defined as ratio of the peak area, is close to the expected 42:10:5:10:2 (from the high field to the low field; both the O-ligands and the solvent water in 1 are accounted). The well-resolved peaks and the match of the experimental peak area ratio to the solid-state measurements. A downfield-shifted resonance of the bridging-O atoms buried in the Ti$_{18}$O$_{27}$ framework relative to those near the surface is observed (e.g., 569 vs 528 ppm of the $\mu$-O), which can be attributed to a weaker shielding effect of the titanium-oxo framework to the buried O atoms, originating from the stronger bonding with Ti. Broadening of the signals is attributed to the magnetic nonequivalence and/or the high nuclear quadrupole relaxation of the O atoms. The $^{17}$O NMR spectrum of a fully hydrated, free SO$_4^{2-}$ ion has a sharp signal at 162 ppm (Figure S4), but this was not seen in the $^{17}$O NMR of 1, and instead, a very broad signal near this region is observed, suggesting SO$_4^{2-}$ ligands are not dissociated from the Ti$_{18}$O$_{27}$ framework.

The $^{17}$O NMR of 1 in $^{17}$O-enriched 1.0 M HCl solution shows five resonance peaks whose locations are consistent with the peaks of 1a in MeCN (Figure 2B). Due to the high concentration of $^{17}$O in the solvent, phase correction cannot be precisely performed. The relative peak intensity of the $\mu$-O on the surface and those buried in the Ti$_{18}$O$_{27}$ framework is near to 5:1, and meanwhile, the relative peak intensity of the $\mu$-O on the surface and those buried in the titanium-oxo framework is nearly 2:1, both indicating the integrity of the Ti$_{18}$O$_{27}$ framework in acidic water.

The Fourier transform infrared spectroscopy (FTIR) of 1 in MeCN solvent is well-consistent with that of the authentic solid sample. The frequencies at 839 and 738 cm$^{-1}$ assigned to Ti-(O$_5$) and Ti-(OH$_2$)$_0$ of 1 (Figure S5), respectively, are slightly shifted to higher frequencies upon dissolution in MeCN, and meanwhile, the absorbance and the concentration follow the Beer–Lambert law (Figure S6). Air-drying of the solution gives a
solid whose IR indicates it is 1. In the Raman spectra, the frequencies of the SO$_4^{2-}$ ligands in the ranges of 400–600 and 930–1030 cm$^{-1}$ and those of Ti–O in the range of 100–250 cm$^{-1}$ are maintained in MeCN solution. Further, the solution vibrational spectra remained unchanged upon aging for a few months under ambient conditions, indicating the stability of 1 in MeCN with time. The above solution stability results are consistent with the ESI-MS and the $^{17}$O NMR data. Based on these, vibrational spectroscopy have also been applied to study the solution chemistry of 1 in other solvents like 1.0 M HCl, acetone, methanol, ethanol, isopropanol, tetrahydrofuran, nitromethane, and benzyl alcohol (Figures S7–S11). It was found that under ambient conditions, 1 is stable in these solvents, too.

Compound 1 was synthesized by one-pot reaction of TiCl$_4$ (1.0 M), H$_2$SO$_4$ (0.33 M), and TBAC (1.0 M) in water under ambient conditions. The yield is ca. 69% (based on Ti). Increasing the concentration of H$_2$SO$_4$ to 1.0 M yielded 2, while using 2.0 M (TBA)$_2$SO$_4$ gave 3 (see SI for full formula of 2 and 3), both having the same Ti$_{18}$O$_{27}$ cluster cores (Figure 3). 2 contains two cluster structures, [Ti$_{18}$O$_{27}$(OH$_2$)$_{26}$(SO$_4$)$_9$]$_{8}^{2-}$ (2a) and [Ti$_{18}$O$_{27}$(OH$_2$)$_{31}$(SO$_4$)$_{9}$]$_{8}^{3-}$ (2b). In 2a there are six SO$_4^{2-}$ ligands in the same locations as in 1a and another two monodentate SO$_4^{2-}$ binding to the two seven-coordinated Ti-atoms, respectively, while in 2b there are five SO$_4^{2-}$ ligands at the side faces (of the Ti$_{18}$O$_{27}$ framework) and one more at the top face as monodentate ligand. 3 contains a cluster [Ti$_{18}$O$_{27}$(OH$_2$)$_{24}$(SO$_4$)$_9$]$_{8}^{3-}$ (3a) with nine SO$_4^{2-}$ ligands, of which seven are bidentate bridged to the side faces and the other two are monodentate bounded to the six-coordinated Ti-atoms at the top face. Both 2 and 3 are soluble and stable in 1.0 M HCl, MeCN, and acetone (Figures S12 and S13). When H$_2$SeO$_4$ was used instead of H$_2$SO$_4$, compound 4 (see SI for full formula) containing [Ti$_{18}$O$_{27}$(OH$_2$)$_{24}$(SeO$_4$)$_9$]$_{8}^{3-}$ of nine SeO$_4^{2-}$ ligands was exclusively obtained regardless of SeO$_4^{2-}$ concentration in which the nine bridging bidentate SeO$_4^{2-}$ ligands are located at the top and the bottom circumferences of the {Ti$_{18}$O$_{27}$} pentagonal prism. 4 is of low solubility in acidic water but is very soluble and stable in alcohols (Figure S14).

Figure 3f demonstrates that the clusters featuring the Ti$_{18}$O$_{27}$ core are formed under a relatively wide range of conditions in the TiCl$_4$/XO$_4^{2-}$ aqueous system (X = S or Se), which is one of the most important systems for titanate hydrosol/nanoparticle synthesis. It appears both SO$_4^{2-}$ and the alkyl chain length of the R$_n$N$^+$ ions are dominating the formation and crystallization of the polycationic titanium-oxo clusters from water. We consider that near the surfaces of the polycationic Ti$_{18}$O$_{27}$ clusters, both the SO$_4^{2-}$ ligands and the Cl$^-$ counterions (Cl$^-$ is hydrogen-bonded to the aqua ligands$^{8b}$) can associate with the coexisting TBA$^+$ cations via electrostatic interaction, which is the key in synthesis of the Ti$_{18}$O$_{27}$ clusters.

The present {Ti$_{18}$O$_{27}$} cluster compounds can be used to functionalize nanomaterial surfaces (e.g., GO) and electrode surfaces. Adsorption of 1 on the GO surface was performed by adding GO sample to an MeCN (or 1.0 M HCl) solution of 1, and ultrafiltration gave a wet solid residue, which was dried under vacuum. FTIR of the sample was measured (Figure 4A), and the data indicates the structural integrity of the Ti$_{18}$O$_{27}$ framework. This observation is consistent with the solution stability of 1, as well as the thermogravimetric analysis results (Figure S15), which suggests that terminal aqua ligands are hardly lost at $<$200 °C. Due to the ultrathin nature of the GO sheet (1.1 nm), the 1/GO nanocomposite is suitable for characterization of 1 with transmission electron microscopy (TEM). The TEM images show that on the surface of GO, there are many electron dense objects of ca. 1.5 nm (Figure 4B,C) consistent with the dimension of 1a. Energy dispersive spectroscopy (EDS) was used to confirm these objects are molecules of 1 (Figure 4D).

The UV–vis absorption spectra of MeCN solutions of 1 (Figure S16) show that the absorption onset occurs at
approximately 420 nm. The extinction coefficient is 270 M$^{-1}$ cm$^{-1}$ at 380 nm and is 1.03 × 10$^4$ M$^{-1}$ cm$^{-1}$ at 242 nm. Hence, we examined the photocatalytic activity of 1 under UV irradiation. First, 1 was adsorbed on a TiO$_2$/FTO photoanode surface following the analogous protocol as that for preparing the 1/GO nanocomposite (see SI for experimental details). The obtained photoanode, 1/TiO$_2$/FTO, was then used for the short-circuit photocurrent test, and a dramatic enhancement of the photocurrent was observed (by up to 200% comparing to the unmodified TiO$_2$/FTO photoanode; Figure S18). This might be attributed to the enhancement of surface roughness and/or of the photoabsorption properties of the photoanode by 1a. 1 was also found to be an active homogeneous photocatalyst to activate molecular O$_2$ for selective oxidation of benzyl alcohol to benzaldehyde.$^{17}$ Conversion reached ca. 41% after 140 min, corresponding to a turnover number (TON; defined as n(converted benzyl alcohol)/n(1)) of 67, giving benzaldehyde as a major kinetic product (yield = 40%). It is worth noting that during the above photocatalytic reactions, no precipitate or colloidal was formed, and the vibrational spectroscopic analysis confirmed the stability of 1 (Figures S19–S21).

In summary, a new family of \[\{\text{Ti}_x\text{O}_{2-x}\}\] titanium-oxo clusters, which possess a unique pentagonal-prismatic framework, are reported herein. Their ESI-MS, $^{17}$O NMR, and vibrational spectroscopy have been elucidated. This type of molecular titanium oxide exhibits good photoactivities and photostabilities under oxidative and aqueous conditions. The above features will make them as promising titanium oxide molecular materials for many applications.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06290.

Experimental details, structural views, characterization, catalysis, and more analysis (PDF)

X-ray crystallographic data (CIF)

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**Notes**

The authors declare no competing financial interest.

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