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Nanosized Alkali-Metal-Doped Ethoxotitanate Clusters

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Supporting Information

ABSTRACT: The synthesis and crystallographic characterization of alkali-metal-doped ethoxotitanate clusters with 28 and 29 Ti atoms as well as a new dopant-free Ti_{28} cluster are presented. The light-metal-doped polyoxotitanate clusters in which the alkali-metal atom is the critical structure-determining component are the largest synthesized so far. Calculations show that doping with light alkali atoms narrows the band gap compared with the nondoped crystals but does not introduce additional energy levels within the band gap.

The preparation of metal-doped alkoxotitanate complexes has received much attention because of their catalytic properties,[1−4] as single-source precursors for the synthesis of perovskite titanium-based electroceramic oxides,[5−9] and as model systems for porous anatase anodes widely used as photovoltaic cells.[10−12] Small molecular complexes have been readily generated and structurally identified, whereas this is not the case for sensitizer-functionalized larger clusters. We have recently succeeded in synthesizing and crystallizing large polyoxotitanate clusters with up to 34 Ti atoms with and without attached chromophores[13−15] and have discussed chromophore binding modes in some detail.[13] Their structures have features typical for the TiO polymorphs anatase and brookite but also show distortions and titanium coordination more likely to occur in surface layers of the bulk compounds. Of additional interest are clusters doped with other atoms, which have the potential of significantly affecting the band structure of the complexes. Recently, high-nuclearity polyoxotitanates containing lanthanides have been reported.[16] We describe here related complexes doped with sodium and lithium and a new "pure" Ti_{28} cluster, which unlike the previously reported polyoxotitanate complex $Ti_{28}O_{40}(O^tBu)_{20}(OAc)_{12}$[14] ($O^tBu$ = *tert*-butoxide; OAc = acetate) does not have the structural features of a Ti_{14} dimer.

In a solvothermal reaction of $Ti(OEt)_4$ (OEt = ethoxide) with isonicotinic acid in a sealed glass tube, a small amount of sodium-doped ethoxypolyoxotitanate with average composition $Ti_{28+\delta}NaO_{38}(OEt)_{39}$ was obtained with $\delta \sim 0.5$, in addition to the targeted pure compound $Ti_{28}O_{34}(OEt)_{44}$. The sodium presumably originated from impurities in the starting materials or from leaching of sodium from the glass reaction vessels. To explore the formation of this unexpected product, we added sodium acetate to the reaction mixture and obtained $Ti_{28+\delta}NaO_{38}(OEt)_{39}$ in a better yield (see the Supporting Information, SI). The presence of sodium is confirmed by scanning electron microscopy (SEM)/energy-dispersive spectrometry (EDS) microanalysis (Figure S1 in the SI). Careful crystallographic analysis indicates that the triclinic crystals (space group $P\bar{1}$, $Z' = 1$) are a periodic array of a superposition of three clusters with compositions $[Ti_{28}NaO_{37}(OEt)_{39}]$, $[Ti_{29}NaO_{39}(OEt)_{39}]$, and $[Ti_{29}NaO_{40}(OEt)_{37}]$ in a ratio of 0.55:0.25:0.20. The three clusters share the same core of ethoxy-substituted polyoxotitanate $[Ti_{28}NaO_{37}(OEt)_{37}]$ and differ only by substitutions at a single site on the periphery of the cluster. They can be formulated as $[Ti_{28}NaO_{39}(OEt)_{37}](Et\text{-})_2$, $[Ti_{28}NaO_{39}(OEt)_{37}]Ti(29)(OEt)_2$, and $[Ti_{28}NaO_{39}(OEt)_{37}]Ti(29)O$ because they share the same core but respectively contain two ethyl groups bound to a cluster O atom, a Ti(29) atom coordinated by two ethoxy groups, and Ti(29) coordinated by a double-bonded O atom.

As shown in Figure 1a, the structure of the $[Ti_{28}NaO_{37}(OEt)_{39}]$ core is of the Keggin type, built around a central four-coordinated Ti atom. The cluster contains 3 six-coordinated Ti atoms in its inner layer, 3 five-coordinated Ti atoms surrounding the Na^+ position, 3 seven-coordinated Ti atoms, and 18 six-coordinated Ti atoms in its outer layer. The average Ti−O bond length is 1.992(11) Å, which agrees well with commonly observed Ti−O bond lengths.[17] The polyoxotitanate cluster's core has approximate C_{3v} symmetry, with the pseudo-3-fold axis connecting the Na atom and the central four-coordinated Ti atom (Figure 1b). The upper part of the $[Ti_{28}NaO_{37}(OEt)_{39}]$ cluster is similar to the structure of $Ti_{17}O_{24}(O^iPr)_{20}$ (Figure S2 in the SI).[15] The presence of the Ti_{29} atom (Figure 1c) increases the similarity between the Ti_{28} core and $Ti_{17}O_{24}(O^iPr)_{20}$ cluster. The similar conical shape of the three species in $Ti_{28+\delta}NaO_{38}(OEt)_{39}$ favors the observed cocrystallization. The size of the clusters as measured from the extreme of the ethoxides is about 1.6 × 1.6 × 1.7 nm.

The Na cation is coordinated by six O atoms at a mean distance of 2.67(12) Å (Figure S3a in the SI), in an almost planar arrangement at the bottom of the cluster. Its coordination geometry is similar to that of the Na^+ ion in crown-6 ether complexes, as tabulated in the Cambridge Structural Database.[18] The average distance from the Na cation to the surrounding Ti atoms is 3.53(2) Å. The Na-centered ring is capped by a water atom located outside the cluster.

The Na cation and the surrounding atoms cover a Ti/O-lined cage located toward the center of the cluster (Figure S3a in the SI).

Replacing sodium acetate trihydrate with lithium acetate dihydrate in the synthesis described above produced a lithium analogue of $Ti_{28+\delta}NaO_{38}(OEt)_{39}$. The presence of lithium was confirmed by ^7Li NMR (Figure S4 in the SI). Crystals of $Ti_{28+\delta}LiO_{38}(OEt)_{39}$ are isostructural with $Ti_{28+\delta}NaO_{38}(OEt)_{39}$

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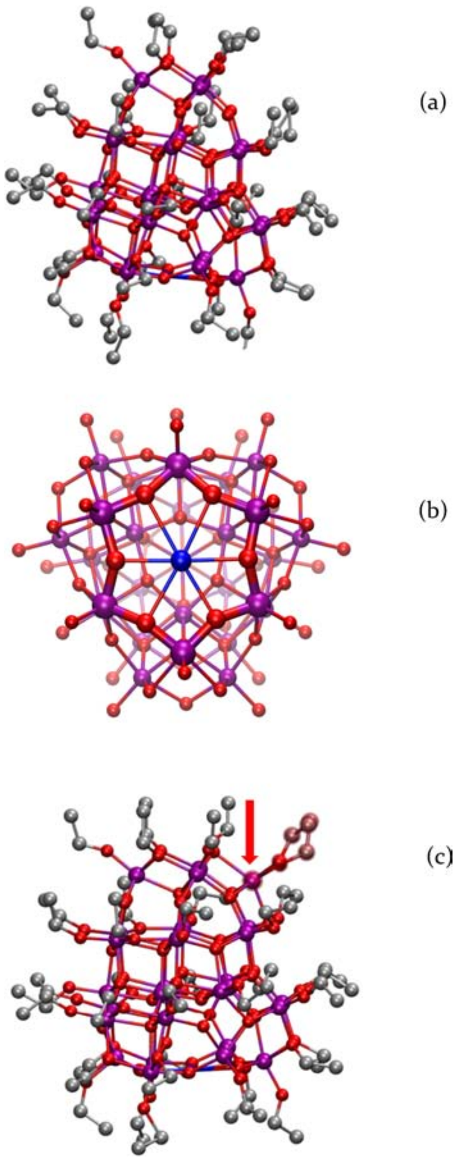

Figure 1. (a) Atomic arrangement of $Ti_{28+\delta}NaO_{38}(OEt)_{39}$. Color code: Ti, purple; O, red; C, gray; Na, blue. (b) Perspective view of the $Ti_{28}NaO$ core of the cluster along its approximate C_{3v} axis (C omitted for clarity). (c) Cluster structure of $Ti_{29}NaO_{40}(OEt)_{37}$. The extra Ti atom is indicated by the arrow. H atoms are omitted for clarity in all figures.

with identical cell dimensions and space groups. As is the case for the sodium-containing clusters, the crystals consist of an overlay of species with identical shapes differing by the exact titanium content, which is due to the presence of a Ti_{29}-occupied surface site. In the lithium case, the central four-coordinated Ti position is also partially occupied. The ethoxy groups are strongly disordered with less than full occupancy at several sites. It is not possible to assign each of the ethoxy groups to one or the other of the overlapping species. This interferes with a reliable evaluation of a charge balance of each of the complexes.

As may be expected, the sodium and lithium coordinations differ, as illustrated in Figure S3 in the SI. Whereas the Na atom is located 0.139 Å toward the outside, above the plane of the coordinating O atoms, the smaller Li atom is disordered over two sites with partial occupancies of 0.499 and 0.301 and distances of 0.49 Å above and 0.32 Å below the plane of the O atoms, respectively. The Li−O coordination of the most highly occupied site is similar to that in known lithium crown-6 structures, as shown in Figure S3b in the SI. In addition to the surrounding cluster O atoms, lithium is coordinated by a water molecule located outside the cluster.

The undoped Ti_{28} polyoxotitanate cluster $Ti_{28}O_{34}(OEt)_{44}$ obtained as the main product of the first synthesis has a completely different structure, as illustrated in Figure 2. Its structural features are similar to those of $Ti_{16}O_{16}(OEt)_{32}$.[6,19] It can be constructed as a superposition of two $Ti_{16}O_{16}(OEt)_{32}$ clusters[6,19] in which four Ti/O octahedral units coincide (Figure S5 in the SI). In contrast to the doped structures, none of the Ti atoms in these two clusters show the five-coordination of surface Ti atoms, which is needed for functionalization by sensitizer molecules.[13] This provides another example of modification of the chemical and physical properties of the polyoxotitanates by substitutional doping, as pointed out in earlier publications.[20,21]

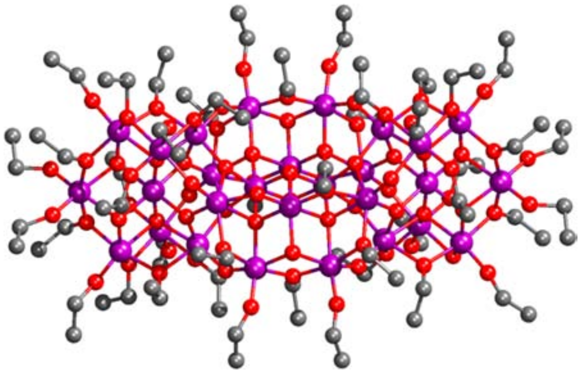

Figure 2. Crystal structure of $Ti_{28}O_{34}(OEt)_{44}$. Color code: Ti, purple; O, red; C, gray. The H atoms are omitted for clarity.

The band structures of the clusters were calculated using *Gaussian09*[22] with the B3LYP functional and a 6-31G basis set.[22] Results are shown in Figure 3 for $Ti_{28}O_{40}(O^tBu)_{20}(OAc)_{12}$, $Ti_{28}O_{34}(OEt)_{44}$, $Ti_{28}LiO_{37}(OEt)_{39}$, and $Ti_{28}NaO_{37}(OEt)_{39}$. The Na and Li orbitals only occur in the conduction band and do not penetrate the band gap, as is the case for heavier atoms according to model calculations.[21] However, there is a noticeable reduction of the band gap by about 1 eV in the doped structures compared with the undoped Ti_{28} clusters, as is evident in Figure 3. We are

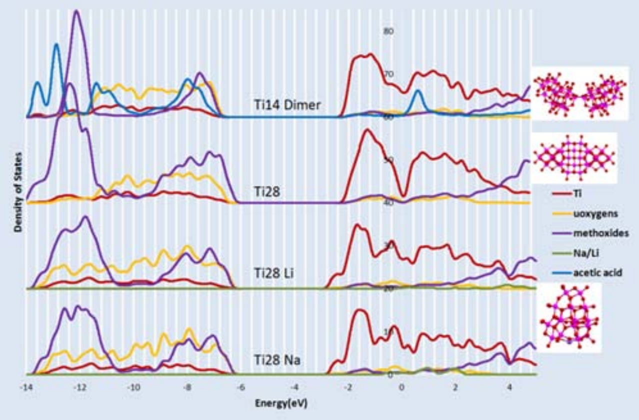

Figure 3. Calculated band structures of $Ti_{28}O_{40}(OBu^t)_{20}(OAc)_{12}$[14] ($Ti_{14}$ dimer, top), $Ti_{28}O_{34}(OEt)_{44}$ (second from above), $Ti_{28}LiO_{37}(OEt)_{39}$ (second from below), and $Ti_{28}NaO_{37}(OEt)_{39}$ (lowest).

synthesizing additional doped structures to further explore bandgap modification by substitutional doping.

In conclusion, we present the synthesis and characterization of alkali-metal-doped ethoxotitanate clusters. They are the largest light-metal-doped polyoxotitanate clusters synthesized and crystallized to date, in which the alkali-metal atom is the critical structure-determining component. We note that the structures of the lithium- and sodium-doped cages are very closely related to the recently reported lanthanide-doped cages, as is the observation of superimposition of the Ti_{28} and Ti_{29} cages in the solid state.[16] Calculations show that doping with light-atom alkali atoms narrows the band gap but does not introduce additional energy levels within the gap. It should be noted that structural differences induced by the doping may make a considerable contribution to this variation. The relationship between the structure of the nanoclusters and those of the known TiO_2 phases was discussed in one of our previous publications.[14]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files for the three structures, experimental section, and supplementary figures including an EDS spectrum of $Ti_{28+\delta}NaO_{38}(OEt)_{39}$, ^{7}Li NMR spectra of $Ti_{28+\delta}LiO_{38}(OEt)_{39}$, and structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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