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Long Hydrogen-Bonded Rod of Molecular Oxide: A Hexatantalate Tetramer

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Supporting Information

ABSTRACT: A tetra-*n*-butylammonium (TBA) salt of $[H_{4.5}(Ta_6O_{19})]^{3.5-}$ was synthesized by reacting hydrous tantalum oxide with TBAOH. X-ray structural analysis of $TBA_{3.5}[H_{4.5}(Ta_6O_{19})]\cdot 2THF\cdot 5.5H_2O$ (THF = tetrahydrofuran) revealed that this compound consists of a hydrogen-bonded, rod-shaped tetramer of hexatantalate that is almost 30 Å long together with TBA cations and solvent molecules of crystallization [$a = 20.6354(5)$ Å, $b = 25.5951(7)$ Å, $c = 37.2058(8)$ Å, $\alpha = 77.092(1)^\circ$, $\beta = 86.177(1)^\circ$, $\gamma = 88.683(1)^\circ$, $V = 19110.9(8)$ Å^3, $Z = 8$, and space group $P\bar{1}$]. ^1H NMR spectra showed that this tetrameric structure is maintained in solution.

When a molecule has both highly polarized hydrogen atoms and atoms of high electronegativity on its periphery, it can form hydrogen-bonded polymers. A typical example is the dimer of acetic acid, which is described in almost every textbook of basic chemistry. A simple electrostatic argument predicts the formation of linear, rod-shaped polymers. However, such rodlike polymers are observed only in crystals where factors other than the hydrogen-bonding energy dictate the actual structure. Rod-shaped polymers are seldom, if ever, observed in the gas phase or in solution, where more compact structures better optimize the interactions between molecules. Thus, even hydrogen fluoride, whose molecule has a shape and dipole moment ideal for the formation of linear polymers, exists as cyclic hexamers of puckered structure reminiscent of the chair conformer of cyclohexane in the gas phase at room temperature.[1] A notable exception is hydrogen cyanide (HCN). It has been known for some time that HCN forms both linear and cyclic trimers in the gas phase.[2,3] More recently, the formation of longer rods up to heptamers has been observed, but in this case at very low temperature in superfluid helium.[4] The formation of long rod-shaped, hydrogen-bonded polymers in more normal solutions is still not yet known.

In this study, we show that an anionic molecular oxide of tantalum, $[Ta_6O_{19}]^{8-}$, forms a hydrogen-bonded linear tetramer that measures almost 30 Å in length. Not only does it form a discrete linear tetramer in crystals but it maintains this supramolecular form in solution. The formation of hydrogen-bonded polymers of molecular oxides has been observed in the solid state for some time.[5] However, with the single exception of $[(H_3V_{10}O_{26})_2]^{6-}$,[6] none of these polymers has been observed in solution.

When hydrous tantalum oxide, obtained by treating $K_8[Ta_6O_{19}]\cdot 17H_2O$[7] with hydrochloric acid,[8] is reacted with an aqueous TBAOH solution (TBA = tetra-*n*-butylammonium), a colorless, highly hygroscopic compound is obtained. If this compound is dissolved in toluene and, after the addition of an appropriate amount of Et_2O, is allowed to stand at ambient temperature, a TBA salt of diprotonated hexatantalate $TBA_6[H_2(Ta_6O_{19})]$ is obtained.[8] However, when this hygroscopic compound was dissolved in toluene and the solution was kept at 85 °C, microcrystals of a different compound precipitated out from the solution after some time.[9]

Single-crystal diffraction studies revealed that this compound is a TBA salt of $[H_{4.5}(Ta_6O_{19})]^{3.5-}$.[10] As is shown in Figure 1, the $[H_{4.5}(Ta_6O_{19})]^{3.5-}$ anion forms a discrete, linear tetramer, so it may be better formulated as $[H_{18}(Ta_6O_{19})_4]^{14-}$. Here, four Ta_6O_{19} units are connected by 18 hydrogen bonds to form a rod-shaped supramolecule that is almost 30 Å long. These 18 hydrogen bonds can be divided into two groups. Nine of them are of moderate strength, with O···O distances in the range 2.69−2.74 Å (green and blue bonds in Figure 1). The other nine, shown in yellow and red in Figure 1, are stronger, with O···O distances in the range 2.43−2.53 Å.[11] The former links doubly bridging O_B atoms and the latter terminal O_C atoms of Ta_6O_{19} units. These hydrogen bonds stack four Ta_6O_{19} units right above and below each other in a face-to-face manner to make a rodlike tetramer. The triangular faces of adjacent Ta_6O_{19} units align in the same direction.

Where are these protons? Unfortunately, the protons could not be located directly from the X-ray diffraction data. However, the locations of those on the anions 2 and 3, the Ta_6O_{19} units at both ends of the rodlike tetramer, can reasonably be inferred from bond length comparison and bond valence sum calculations.[12,13] The Ta−O_B bonds involving O_{B22}, O_{B23}, and O_{B26} atoms of anion 2 and O_{B31}, O_{B34}, and O_{B36} atoms of anion 3 are all significantly longer than the other Ta−O_B bonds. The bond valence sums of these oxygen atoms are 1.1−1.2, which are significantly smaller than those of other O_B atoms and much smaller than the ideal value of 2. The Ta−O_C bonds involving O_{C21}, O_{C22}, and O_{C26} atoms of anion 2 and O_{C31}, O_{C34}, and O_{C36} atoms of anion 3 are all significantly longer than 1.8 Å, while the other Ta−O_C bonds are shorter than 1.8 Å. The bond valence sums of these terminal oxygen atoms are 1.2−1.3. Thus, 12 of the 18 protons can be assumed to be on these O_B and O_C atoms.

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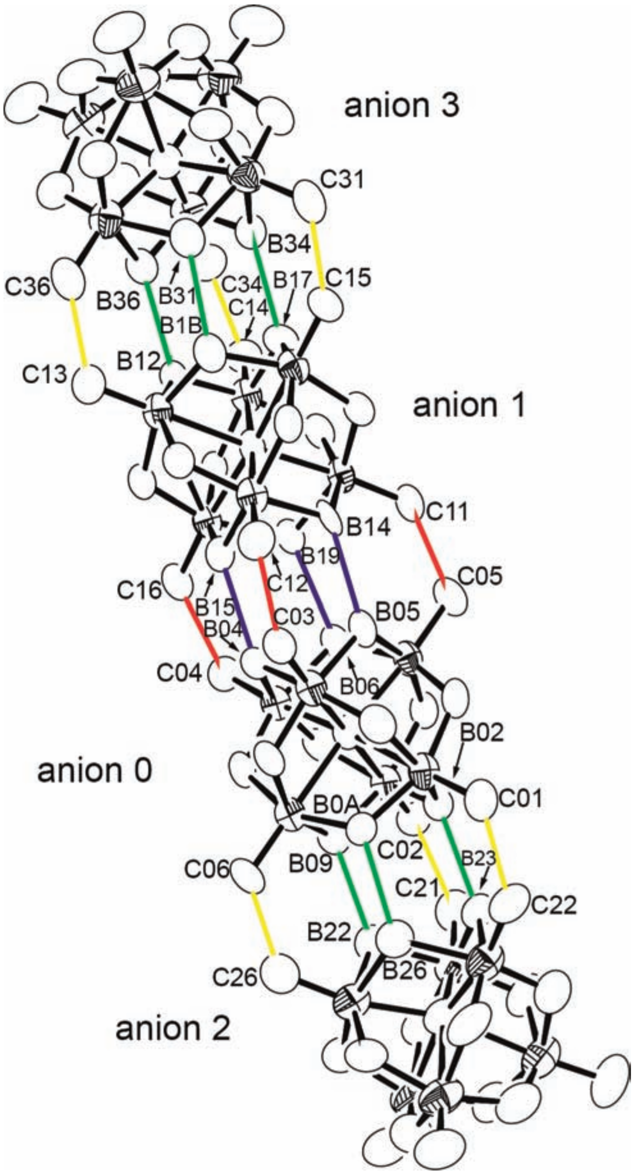

Figure 1. Structure of the tetrameric molecular oxide anion $[H_{18}(Ta_6O_{19})_4]^{14-}$. Tantalum and oxygen atoms are represented by shaded and open ellipsoids, which are drawn to encompass 50% probability levels. Hydrogen bonds are color-coded to indicate their different nature (see the text). Hydrogen-bonded oxygen atoms are labeled with their subscripts.

The locations of the remaining six protons are less clear. The bond valence sums for O_{B04}, O_{B05}, and O_{B06} atoms of anion 0 and O_{B14}, O_{B15}, and O_{B19} atoms of anion 1 are all 1.5 or lower. However, these oxygen atoms are facing each other, and it is not possible to put protons on all of them. Only three of these six O_B atoms should be protonated. Unfortunately, it is not possible to tell which three from the data. The last three protons should be on terminal O_C atoms. The $O_{C03}\cdots O_{C12}$, $O_{C04}\cdots O_{C16}$, and $O_{C05}\cdots O_{C11}$ distances are roughly 2.5 Å and suggest the existence of relatively strong hydrogen bonds.[11] However, the Ta−O_C bond lengths involving those terminal oxygen atoms, and hence their bond valence sums, are very similar, with the exception of O_{C04}, and do not allow us to determine which of these oxygen atoms are protonated.[14]

A very interesting feature of this supramolecular molecular oxide is that it maintains its teterameric structure in solution. The ^1H NMR spectra of $TBA_{14}[H_{18}(Ta_6O_{19})_4]$ in tetrahydrofuran (THF-d_8) show four peaks at 8.59, 8.99, 13.88, and 14.15 ppm in a 2:1:2:1 intensity ratio in addition to those of TBA cations, THF, and water. The unusually large chemical shifts of these peaks strongly suggest that they are from protons that are involved in hydrogen bonds.[15] Both the chemical shift and intensity ratio of these peaks are consistent with the tetrameric structure shown in Figure 1. Of the 18 hydrogen bonds, 9 are between the O_B atoms and are of moderate strength (green and blue). The other nine are stronger and are between the O_C bonds (yellow and red). The peaks at 14.15 and 13.88 ppm (peaks a and b in Figure 2, respectively) are assigned to the protons that are responsible for the stronger hydrogen bonds between the O_C atoms. The other two peaks at 8.99 and 8.59 ppm (peaks c and d in Figure 2, respectively) are assigned to the protons that form hydrogen bonds of moderate strength between the O_B atoms. These two groups of nine hydrogen bonds are both further divided into two groups, six (green or yellow) that unite the Ta_6 units at both ends of the rod to the central two and three (blue or red) that unite the central two Ta_6 units. Thus, peak d is assigned to three protons that unite O_B atoms of anions 0 and 2 and another three that unite those of anions 1 and 3 (green bonds in Figure 1). Peak c is assigned to three protons that unite O_B atoms of the central two Ta_6 groups, i.e., anions 0 and 1 (blue bonds in Figure 1). Similarly, peak b is assigned to two groups of three protons that unite the O_C atoms of anions 0 and 2 and anions 1 and 3 (yellow bonds in Figure 1). Finally, peak a is assigned to three protons that are responsible for the hydrogen bonds between

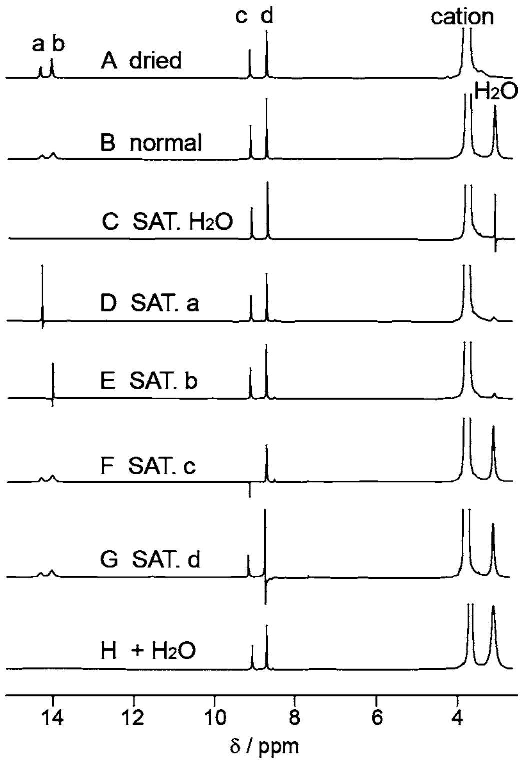

Figure 2. ^1H NMR spectra of $[H_{18}(Ta_6O_{19})_4]^{14-}$ in THF-d_8 (1 mM). The large peak of the TBA cation is amputated. (A) Normal spectrum of a dried sample. (B) Normal spectrum of a nondried sample. Spectra C−G were obtained under the same conditions as those of spectrum B but with selective saturation of the resonance indicated. In spectrum H, a small amount of water was added to the solution.

the O_C atoms of the central two Ta_6 groups (red bonds in Figure 1).

Another interesting feature is the exchange behavior of those protons with water. The protons attached to O_B atoms and those attached to O_C atoms exhibit totally different exchange behavior. While those attached to O_C atoms show appreciable exchange with water, the protons on O_B atoms display virtually no exchange with water in THF solutions in the NMR time scale. When the crystals of $TBA_{14}[H_{18}(Ta_6O_{19})_4]$, which contains water as well as THF as solvents of crystallization, were dissolved in THF-d_8, peaks a and b were much broader than peaks c and d. However, if the crystals were dried under vacuum prior to dissolution, peaks a and b showed widths comparable to those of peaks c and d (Figure 2A,B). When the water peak was selectively saturated, peaks a and b vanished but peaks c and d remained intact. Conversely, when peaks a and b were selectively saturated, the intensity of the water peak was greatly reduced, but it was not affected by the selective saturation of peaks c and d. When a small amount of water was added to the solution, peaks a and b broadened extensively and almost vanished. On the other hand, the addition of water had no effect on peaks c and d.

Again, these observations are perfectly consistent with the rodlike structure shown in Figure 1. The protons attached to O_B atoms exist in the medial part of the rod, while those attached to O_C atoms are located in the lateral part of the rod. It would be much easier for water molecules to approach lateral O_C atoms than medial O_B atoms.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format for $TBA_{3.5}[H_{4.5}(Ta_6O_{19})]\cdot 2THF\cdot 5.5H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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(9) To a solution of $K_8[Ta_6O_{19}]\cdot 17H_2O$ (3.00 g, 1.49×10^{-3} mol) in 20 mL of H_2O was added 21 mL of aqueous 1.0 M HCl. The colorless precipitate that formed was collected on a fine-porosity filter paper with suction and washed with 5 × 20 mL of H_2O to thoroughly remove the byproduct KCl. After the precipitate was mixed with 22.4 mL of aqueous 10% TBAOH (0.40 M, 9.0×10^{-3} mol), the mixture was stirred for 72 h at 90 °C. A small amount of insoluble solid was then removed by centrifugation and filtration, and the clear filtrate was evaporated to dryness under vacuum. The tacky solid thus obtained was further dried under vacuum over P_2O_5 to yield 3.72 g of a colorless product. Under a dry N_2 atmosphere, 2.00 g of this product was dissolved in 2.0 mL of toluene at 85 °C. The microcrystals that formed after the solution was maintained at 85 °C for 16 h were collected by filtration and dried under vacuum to yield 1.39 g of $TBA_{3.5}[H_{4.5}(Ta_6O_{19})]$. Single crystals were obtained by dissolving 500 mg of this microcrystalline compound in 5.0 mL of THF, filtering the solution to remove any insoluble material, adding 4.4 mL of Et_2O to the filtrate, and then allowing the mixture to stand at 5 °C (161 mg, 6.48×10^{-2} mmol, 22.5% on Ta). Anal. Calcd for $TBA_{3.5}[H_{4.5}(Ta_6O_{19})]\cdot 2THF\cdot 5.5H_2O$: C, 30.92; H, 6.39; N, 1.97; Ta, 43.7. Found: C, 30.77; H, 6.23; N, 2.07; Ta, 43.8. IR (Nujol mull, 1000−400 cm^{-1}): 891 (sh), 880 (w), 793 (m), 720 (s), 544 (w), 529 (w), 519 (w). ^1H NMR (300 MHz, THF-d_8): δ 0.96 (t), 1.64 (m), 1.88 (m), 3.67 (m), 8.59 (s), 8.99 (s), 13.88 (s), 14.15 (s).

(10) Single crystals of $TBA_{3.5}[H_{4.5}(Ta_6O_{19})]\cdot 2THF\cdot 5.5H_2O$ are, at 110(2) K, triclinic, space group $P\bar{1}$, with a = 20.6354(5) Å, b = 25.5951(7) Å, c = 37.2058(8) Å, α = 77.092(1)°, β = 86.177(1)°, γ = 88.683(1)°, V = 19110.9(8) $Å^3$, and Z = 8. A colorless crystal of dimensions 0.40 × 0.40 × 0.30 mm^3 was used for data collection. Diffraction data were collected on a Rigaku R-Axis Rapid diffractometer using Mo Kα radiation. The final agreement factors were $R = 0.092$ for 38074 reflections with $F^2 > 2\sigma(F^2)$ and $R_w(F^2) = 0.224$ for 86973 unique reflections. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 864357.

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(14) The conclusion that anions 0 and 1 are triprotonated and anions 2 and 3 are hexaprotonated is not inconsistent with the size of each monomer. Anions 2 and 3 are thicker (both 4.87 Å) than anions 0 (4.79 Å) and 1 (4.83 Å). The thickness of each monomeric anion here is defined as the distance between two triangular planes that are virtually perpendicular to the long axis of the rod, each defined by three O_C atoms.

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