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Decatantalate—The Last Member of the Group 5 Decametalate Family

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Supporting Information

ABSTRACT: A tetra-*n*-butylammonium (TBA) salt of $[Ta_{10}O_{28}]^{6-}$ was synthesized by heating $TBA_6[H_2Ta_6O_{19}]$ in toluene for a prolonged period. X-ray structural analysis of $TBA_6[Ta_{10}O_{28}]\cdot 6H_2O$ revealed that the anion has the decametalate structure and is isostructural with the decavanadate and decaniobate anions [a = 15.8517(8) Å, b = 19.364(1) Å, c = 21.935(1) Å, β = 93.638(1)°, V = 6719.4(6) Å^3, Z = 2, and space group $P2_1/n$ at 292(2) K].

Decavanadate has been known for some time.[1] Both its structure and solution chemistry are well documented.[2−5] Many salts of different protonation states are now isolated.[6] Our knowledge on decaniobate, on the other hand, is still very limited. Yet, we already know it has the same structure as decavanadate thanks to the crystal structure analysis reported in 1977.[7] Unfortunately, development of its chemistry had been stalled for some time, largely because the original synthesis had some problem with reproducibility.[8,9] However, decaniobate is attracting renewed and growing interest lately, and now some of its reactions are known as well as its reproducible preparation.[10,11] What do we know about decatantalate, then? Very little.[8,9] Some evidence of its existence in solution has been published very recently,[8] but that is virtually the only piece of information we have so far. Tantalum belongs to the same group of the periodic table as vanadium and niobium. One would expect it to exhibit chemistry similar to those of the other two, especially to that of niobium. Tantalum and niobium have very similar atomic and ionic radii. The existence of decatantalate has long been anticipated.[12] Still, its isolation has never been reported up to now.

Recently, we reported the synthesis of $[TeO_4]^{2-}$, the tetrahedral tellurate.[13] This simple and basic homologue of sulfate had long been missing and deemed nonexistent. The key that led us to the isolation of this molecular oxide was the use of a quaternary organoammonium cation. The cation allowed us to leave the traditional playground for inorganic chemists, i.e., aqueous solution, and work with the system in nonaqueous media. This cation also minimizes the effects of hydrogen-bonding and the interactions between the cations and anionic molecular oxides, which often make the systems complicated. By applying the same technique and strategies to the tantalate system, we have successfully isolated $[H_2Ta_6O_{19}]^{6-}$, the first protonated hexatantalate.[14] This conceptually simple compound also has long eluded chemists' grasp. We found out that the tetra-*n*-butylammonium (TBA) salt of this protonated hexatantalate yields decatantalate $[Ta_{10}O_{28}]^{6-}$ when heated in toluene.[15,16]

Figure 1 shows the structure of the decatantalate.[17] The $[Ta_{10}O_{28}]^{6-}$ anion is isostructural with $[V_{10}O_{28}]^{6-}$ and $[Nb_{10}O_{28}]^{6-}$. The anion ideally has an *mmm* (D_{2h}) symmetry, which it closely approximates. There are three types of symmetrically nonequivalent Ta atoms and seven types of O atoms in the *mmm* structure, and the atoms are labeled accordingly in Figure 1. Not only are they isostructural, $[Ta_{10}O_{28}]^{6-}$ and $[Nb_{10}O_{28}]^{6-}$ are virtually identical. Their metal−oxygen bond lengths in these anions are almost the

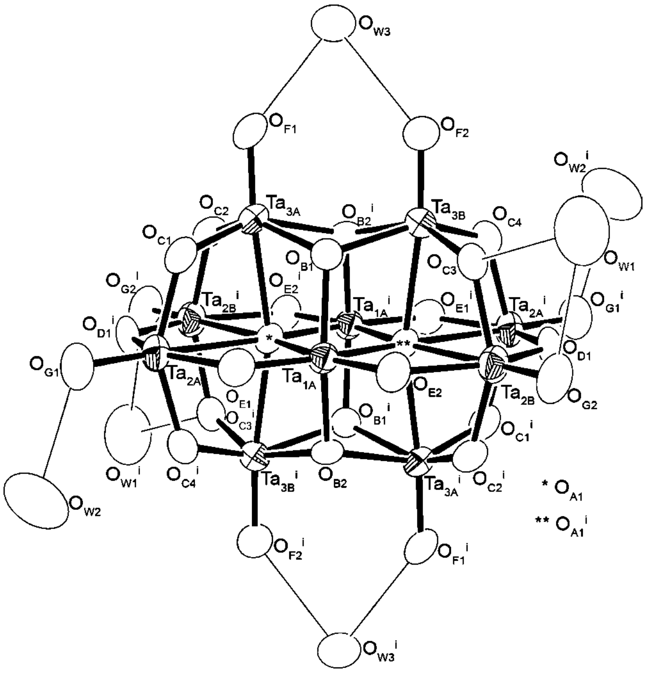

Figure 1. Structure of the $[Ta_{10}O_{28}]^{6-}$ anion (292 K). Oxygen atoms of the water molecules that are hydrogen-bonded to the anion are also depicted. The ellipsoids are drawn to encompass 50% probability levels. Atoms labeled with a superscripted i are related to those labeled without it by the crystallographic inversion center at (0, 0, 1/2). Thin lines indicate hydrogen-bonding interactions. Hydrogen-bond distances (Å): $O_{W1}\cdots O_{C3}$, 2.90(1); $O_{W1}\cdots O_{G2}$, 2.86(1); $O_{W2}\cdots O_{G1}$, 2.67(1); $O_{W3}\cdots O_{F1}$, 2.678(9); $O_{W3}\cdots O_{F2}$, 2.798(8).

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same (Figure 2). A noticeable difference is observed only for the two longest bonds, i.e., $Ta_{2A}-O_{A1}$ and $Ta_{2B}-O_{A1}^{i}$. Figure 2 also shows that both $[Ta_{10}O_{28}]^{6-}$ and $[Nb_{10}O_{28}]^{6-}$ are significantly larger than $[V_{10}O_{28}]^{6-}$.

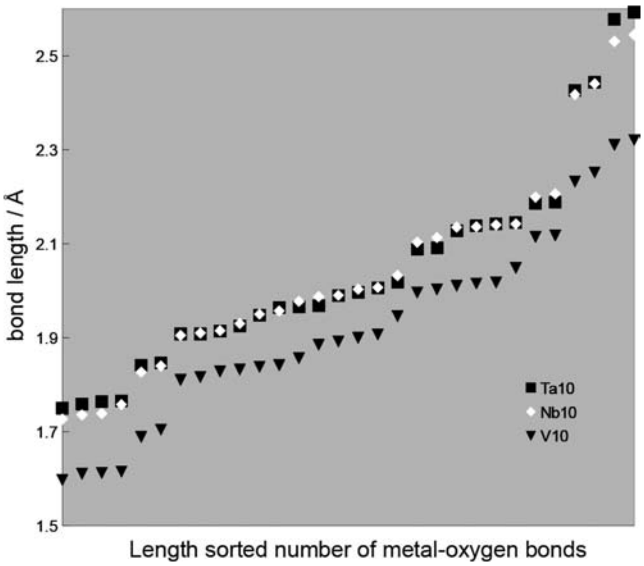

Figure 2. Comparison of the metal−oxygen bond lengths in decatantalate (Ta10), decaniobate (Nb10), and decavanadate (V10). The metal−oxygen bonds of each decametalate are sorted and plotted in the order of their lengths.

As shown in Figure 1, the $[Ta_{10}O_{28}]^{6-}$ anion is hydrogen-bonded to six molecules of water. Two of them, O_{W3} and O_{W3}^{i}, are chelated by two O_F atoms. The same mode of bonding between the decametalate anion and water molecules has also been observed for $[Nb_{10}O_{28}]^{6-}$.[10] In addition to these two, four more water molecules are hydrogen-bonded to the $[Ta_{10}O_{28}]^{6-}$ anion. Two of them, O_{W1} and O_{W1}^{i}, bridge a terminal O_G atom and bridging O_C atom. The remaining two, O_{W2} and O_{W2}^{i}, are bonded to terminal O_G atoms only. All eight terminal oxygen atoms are engaged in hydrogen-bonding in $[Ta_{10}O_{28}]^{6-}$. This fact demonstrates the high basicity of the decatantalate anion and terminal oxygen atoms in the structure.

It is interesting to note that the average charge per Ta atom of the decatantalate is very similar to that of recently reported $[H_{18}(Ta_6O_{19})_4]^{14-}$.[18] The former is −0.6, while the latter is −0.58. This means that these two molecular oxides with totally different structures need about the same amount of acid or protons to form. The decatantalate was obtained after prolonged heating of the solution. In the synthesis of $[H_{18}(Ta_6O_{19})_4]^{14-}$, the reaction solution was also heated but only overnight. Kinetic control seems to be an important factor in the formation of different polytantalates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format for $TBA_6[Ta_{10}O_{28}]\cdot 6H_2O$. 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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(15) A solution of $TBA_6[H_2Ta_6O_{19}]\cdot 10H_2O$ (0.80 g, 0.26 mmol) in 4.0 mL of toluene was heated at 85 °C for 30 h. After allowing this solution to cool to ambient temperature, 80 mL of Et_2O was added to the solution with stirring. The mixture was left stirred for 5 min and then filtered to remove a small amount of oil that formed. Colorless microcrystals formed when the clear filtrate was stirred for 1 h. The mixture was allowed to stand at −20 °C for 2 days, after which period the microcrystals were collected by filtration, washed with 3 × 2 mL of Et_2O, and dried under vacuum for 30 min to yield 0.083 g (0.022 mmol, 14%) of $TBA_6[Ta_{10}O_{28}]\cdot 6H_2O$. Single crystals suitable for X-ray structural analysis were prepared by dissolving 0.10 g of the microcrystals in 2.5 mL of toluene, adding 2.5 mL of Et_2O with stirring, and then allowing the solution to stand for 2 days at ambient temperature. The highly hygroscopic crystals were collected by filtration, washed with 3 × 2 mL of Et_2O, and dried under vacuum for 30 min to yield 0.045 g (0.012 mmol) of the product. Anal. Calcd for $C_{96}H_{228}N_6O_{34}Ta_{10}$: C, 30.18; H, 6.02; N, 2.20; Ta, 47.4. Found: C, 29.84; H, 5.96; N, 2.05; Ta 47.5. IR (Nujol mull, 1000 − 400 cm^{-1}): 893 (m), 818 (m), 791 (m), 752 (s), 705 (m), 596 (w), 565 (w), 543 (w), 513 (m), 446 (m), 419 (m).

(16) The average charge per Ta atom of $[H_2Ta_6O_{19}]^{6-}$ is −1, while that of $[Ta_{10}O_{28}]^{6-}$ is −0.6. This means some acid is needed to form the latter from the former. We still do not know exactly where this acid comes from. Some possibilities are (1) water in the solvent, (2) atmospheric CO_2, and (3) disproportionation of $[H_2Ta_6O_{19}]^{6-}$.

(17) Single crystals of $TBA_6[Ta_{10}O_{28}]\cdot 6H_2O$ were monoclinic, space group $P2_1/n$, with $a = 15.8517(8)$ Å , $b = 19.364(1)$ Å, $c = 21.935(1)$ Å, $\beta = 93.638(1)°$, $V = 6719.4(6)$ Å^3, and $Z = 2$ at 292(2) K and $a = 15.5165(3)$ Å, $b = 19.4161(4)$ Å, $c = 21.6413(5)$ Å, $\beta = 95.139(1)°$, $V = 6493.7(2)$ Å^3, and $Z = 2$ at 150(1) K. Diffraction data were collected on a Rigaku SCX mini (292 K) and Rigaku Raxis Rapid (150 K) diffractometers using Mo Kα radiation. The structures were solved by the direct methods and refined by full-matrix least-squares with the *SHELX*-97 program suite. The final agreement factors were $R = 0.049$ for 9166 reflections with $F^2 > 2\sigma(F^2)$ and $wR(F^2) = 0.106$ for 15 351 unique reflections collected at 292(2) K and $R = 0.056$ for 10 295 reflections with $F^2 > 2\sigma(F^2)$ and $wR(F^2) = 0.149$ for 14 900 unique reflections collected at 150(1) K. Crystallographic data have been

deposited with Cambridge Crystallographic Data Centre under deposition numbers CCDC 929071 and 929072.

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