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[Ti₂Ta₈O₂₈]⁸⁻ and [Ti₁₂Ta₆O₄₄]¹⁰⁻

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Polyoxometalates

Titanium-Substituted Polyoxotantalate Clusters Exhibiting Wide pH Stabilities: $[\text{Ti}_2\text{Ta}_8\text{O}_{28}]^{8-}$ and $[\text{Ti}_{12}\text{Ta}_6\text{O}_{44}]^{10-}$ Jung-Ho Son^{*,[a]} and William H. Casey^[a, b]

Abstract: Two new substituted polyoxotantalate clusters, $[\text{Ti}_2\text{Ta}_8\text{O}_{28}]^{8-}$ and $[\text{Ti}_{12}\text{Ta}_6\text{O}_{44}]^{10-}$, considerably expand the pH range where tantalates persist in aqueous solution. The structures of $[\text{Ti}_2\text{Ta}_8\text{O}_{28}]^{8-}$ and $[\text{Ti}_{12}\text{Ta}_6\text{O}_{44}]^{10-}$ are reported as tetramethylammonium salts after synthesis at hydrothermal conditions in aqueous solution. These Ti-substituted polyoxotantalate clusters have analogues among recently discovered niobates, but are slightly larger and more persistent in solution. Most importantly, they exhibit a much wider range of pH stability than the familiar hexatantalate cluster, which is the only other tantalate known to be stable at highly basic pH conditions. These molecules are kinetically stable to near-neutral pH, making them excellent synthons for further development into materials and catalysts, and a significant advance in adapting tantalates for use in aqueous solutions.

Among the Group 5 and 6 polyoxometalates, the synthesis and characterization of polyoxotantalate clusters remains particularly underdeveloped, in part because of famously slow reaction kinetics. Thus, there exists a rich set of V-, Mo-, and W-based polyoxometalates, with highly diverse structures, and these have been exploited for many decades as catalysts and reagents.^[1] Less well developed are the niobates, yet there are still dozens of niobate clusters that are stable in solution, including substituted polyoxoniobates discovered during the last decade.^[2] In contrast, among the polyoxotantalates, only the hexatantalate^[3] ion (Ta_6) and transition-metal coordinated (capped) Ta_6 are known,^[4] in addition to the recently reported decatantalate (Ta_{10}) through condensation of Ta_6 in non-aqueous solution.^[5] The chemistries of polyoxoniobate and polyoxotantalate ions are expected to be broadly similar, but differences in the properties of hexaniobate and hexatantalate ions have been recently demonstrated.^[6]

In light of the synthetic success of Ti-substituted polyoxoniobates,^[7] we envisioned that a similar strategy for Ti-substitution in polyoxotantalate ions may be possible. Here, we report the first synthesis and characterization of substituted polyoxotantalate as Ti^{IV} -disubstituted decatantalate-type structure, $\text{TMA}_8\text{Ti}_2\text{Ta}_8\text{O}_{28}\cdot 21\text{H}_2\text{O}$ (Ti_2Ta_8) and superoctahedral cluster of $\text{TMA}_{10}\text{Ti}_{12}\text{Ta}_6\text{O}_{44}\cdot 39\text{H}_2\text{O}$ ($\text{Ti}_{12}\text{Ta}_6$), as soluble tetramethylammonium (TMA) salts (Figure 1). Similar structures have only been previously reported in the polyoxoniobate system as $\text{Ti}_2\text{Nb}_8\text{O}_{28}^{8-}$ (Ti_2Nb_8) and $\text{Ti}_{12}\text{Nb}_6\text{O}_{44}^{10-}$ ($\text{Ti}_{12}\text{Nb}_6$), and are apparently a new class of polyoxometalate ions.^[7]

The titanium-disubstituted polyoxotantalate (Ti_2Ta_8) was synthesized by hydrothermal reaction of TMAOH, titanium isopropoxide and hydrous tantalum oxide, which was prepared in a similar way to the preparation of hydrous niobium oxide (see the Supporting Information).^[8] The resultant solution was washed with isopropanol and the remaining product was extracted with ethanol. Crystalline material formed during the evaporation of the ethanol at ambient conditions or at an elevated temperature in an oven. Finally, the crystalline product was finally washed with hot isopropanol.

The structure of the substituted polyoxotantalate was identified by using single-crystal X-ray crystallography. The crystal-structure refinement of Ti_2Ta_8 shows that the cluster is Ti-disubstituted decatantalate, with two Ti sites at the center, as has also been found for decaniobates substituted with other transition metals (Figure 1).^[7a, 9] The isostructural Ti-disubstituted decaniobate (Ti_2Nb_8) ion also has two Ti sites occupying the center position. The $\text{Ti}-\mu_2\text{-O}$ bonds in Ti_2Ta_8 are 1.807(3) and 1.812(3) Å, which are slightly shorter than $\text{Ti}-\mu_2\text{-O}$ bonds in Ti_2Nb_8 (1.817(2) and 1.824(2) Å) but are comparable. The $\text{Ti}-\mu_3\text{-O}$ bonds (2.010(4) and 2.016(3) Å) and the $\text{Ti}-\mu_6\text{-O}$ bonds (2.188(3) and 2.193(3) Å) in Ti_2Ta_8 are slightly longer than those

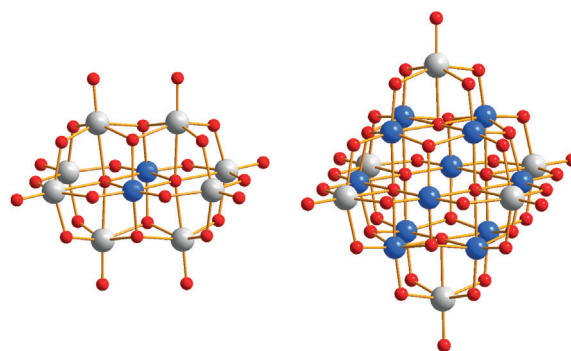


Figure 1. Ball-and-stick representation of the $[\text{Ti}_2\text{Ta}_8\text{O}_{28}]^{8-}$ (left) and $[\text{Ti}_{12}\text{Ta}_6\text{O}_{44}]^{10-}$ (right) ions (red: O, blue: Ti, gray: Ta).

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Supporting information for this article, including synthesis of hydrous tantalum oxide, instrumental details, bond lengths in the clusters, FT-IR, and pH-dependent ESI-MS spectra is available on the WWW under <http://dx.doi.org/10.1002/chem.201603335>.

of Ti_2Nb_8 (2.000(2) and 2.155(2) Å). The differences in Ta–O and Nb–O bond lengths in Ti_2Ta_8 and Ti_2Nb_8 are small, and they are summarized in Table S1 in the Supporting Information. The electrospray-ionization mass spectrometry (ESI-MS) analysis of the solution (Figure 2) and elemental analysis (see the Experimental Section) also support the stoichiometry of the Ti_2Ta_8 cluster. We note that both mono- or di-titanium-substituted decaniobates (TiNb_9 and Ti_2Nb_8) have been synthesized in the polyoxoniobates class of compounds,^[7,9a] but only the Ti_2Ta_8 was observable from our polyoxotantalate syntheses. When the Ti/Ta stoichiometry of starting material was smaller than 1:4, we observed a mixture of Ti_2Ta_8 and Ta_6 in ESI-MS, instead of TiTa_9 ion. This result indicates that Ti-disubstitution is preferred to Ti-monosubstitution in the decatantalate structure, and it also denotes a departure from niobate chemistry. Additionally, we note that the decatantalate ion was undetectable by ESI-MS in the synthesis attempts without Ti sources, suggesting that decatantalate could only be isolated in non-aqueous solution, as previously synthesized by Yagasaki et al.^[5] However, the aqueous synthesis of Ti_2Ta_8 in our study suggests that Ti substitution engenders stability to the decatantalate-type structure in aqueous solution.

We also isolated a larger titanium–tantalate cluster with different structure and stoichiometry, $[\text{Ti}_{12}\text{Ta}_6\text{O}_{44}]^{10-}$ (Figure 1). This superoctahedral ion had only previously been synthesized as a niobate,^[7b] but in many of our Ti_2Ta_8 syntheses, we detected a small amount of $\text{Ti}_{12}\text{Ta}_6$ by ESI-MS. The ESI-MS peaks of $\text{Ti}_{12}\text{Ta}_6$ are considerably broader than those of Ti_2Ta_8 due to a wider array of Ti isotopes in the cluster (Figure 2). The $\text{Ti}_{12}\text{Ta}_6$ could be separated from Ti_2Ta_8 because of its slightly lower solubility, but the amount of $\text{Ti}_{12}\text{Ta}_6$ in the product was typically much smaller than Ti_2Ta_8 . We observed that Ti_2Ta_8 can transform to $\text{Ti}_{12}\text{Ta}_6$ under hydrothermal conditions when an excess Ti^{IV} source was added in the solution. In addition, the $\text{Ti}_{12}\text{Ta}_6$ cluster can also be converted to Ti_2Ta_8 by raising the pH with TMAOH, followed by hydrothermal treatment.

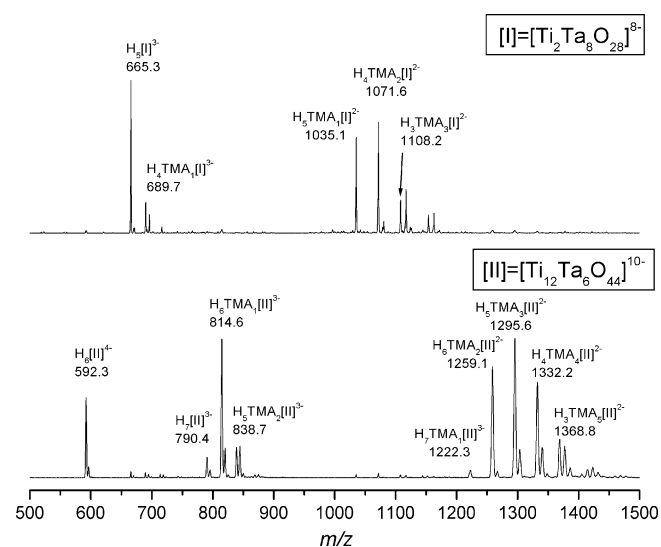


Figure 2. ESI-MS spectra of solutions of Ti_2Ta_8 and $\text{Ti}_{12}\text{Ta}_6$ showing the m/z values of ions assignable to the tantalate ions $[\text{Ti}_2\text{Ta}_8\text{O}_{28}]^{8-}$ and $[\text{Ti}_{12}\text{Ta}_6\text{O}_{44}]^{10-}$.

The structure of superoctahedral $\text{Ti}_{12}\text{Ta}_6$ is, unsurprisingly, very similar to the previously reported titanoniobate analogue, $[\text{Ti}_{12}\text{Nb}_6\text{O}_{44}]^{10-}$.^[7b] The structure can be described as $[\text{Ti}_{12}\text{O}_{38}]^{28-}$ core capped with six Ta=O groups. Ta=O bonds (1.797(7) Å) are slightly longer than Nb=O bonds (1.767(5) Å) and Ta- μ_5 -O bonds (2.285(6) Å) are slightly shorter than Nb- μ_5 -O bonds (2.304(5) Å) in $\text{Ti}_{12}\text{Nb}_6$. The Ti–O bonds in both structures of $\text{Ti}_{12}\text{Nb}_6$ and $\text{Ti}_{12}\text{Ta}_6$ are very similar. The six oxo groups in the cluster are bonded to six Ta^V sites at the corners of the superoctahedral $\text{Ti}_{12}\text{Ta}_6$ structure. The structure shows that six capping tantanyl groups are stabilizing the otherwise hydrolytically unstable $[\text{Ti}_{12}\text{O}_{38}]^{28-}$ cluster. Bare titanium-oxide cluster ions are generally unstable and prone to condensation because of their high charge, however many kinds of alkoxy-coordinated titanium oxide cluster ions exist.^[10] Similar to the $\text{Ti}_{12}\text{Nb}_6$ cluster, there is a void site at the center of the $\text{Ti}_{12}\text{Ta}_6$ cluster surrounded by six oxygen ligands. The isolation of both Ti_2Ta_8 and $\text{Ti}_{12}\text{Ta}_6$ clusters confirms the homology between the Nb^V and Ta^V substituent chemistry; substitution in a polyoxotantalate ion can occur when a similarly substituted polyoxoniobate cluster is known, which leads us to wonder if a vanadium-substituted version exists.

The FT-IR spectra of Ti_2Ta_8 and $\text{Ti}_{12}\text{Ta}_6$ are compared in Figure S1 in the Supporting Information. The Ti_2Ta_8 cluster clearly shows a Ta=O band at 889 cm^{-1} , a Ta-O-Ta stretching band at 800 cm^{-1} , and a Ta-O-Ta bending band at 528 cm^{-1} . The band at 683 cm^{-1} is assigned to a Ta-O-Ti band. In the spectrum of $\text{Ti}_{12}\text{Ta}_6$, a Ta=O band at 872 cm^{-1} is small compared to that of Ti_2Ta_8 , due to the relatively smaller portion of Ta=O groups in the larger $\text{Ti}_{12}\text{Ta}_6$ structure. We tentatively assign the band at 737 cm^{-1} to a Ta-O-Ti and the band at 584 cm^{-1} to a Ti-O-Ti.

The general pH-dependent stability or persistence of Ti_2Ta_8 , $\text{Ti}_{12}\text{Ta}_6$, and Ta_6 was studied by using ESI-MS (Figures S2–S4 in the Supporting Information). Their representative peak intensities at each pH were normalized and plotted to compare their trend in pH stability (Figure 3). The natural pH found by dissolving crystals of Ti_2Ta_8 is ≈ 7.8 (at 6 mM), consistent with

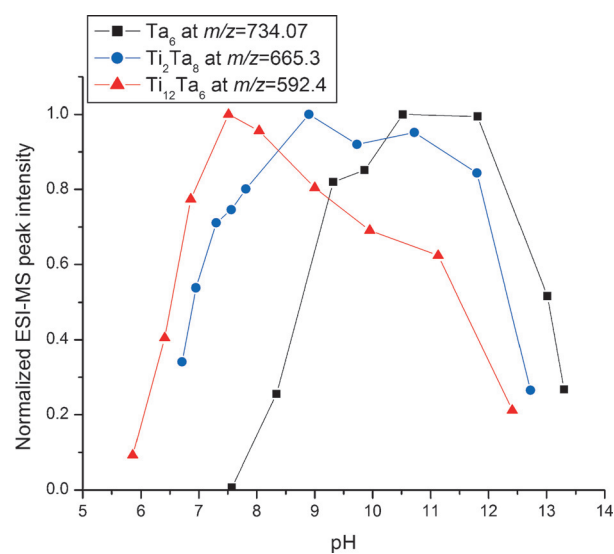


Figure 3. pH-Dependent stabilities of Ta_6 , Ti_2Ta_8 , and $\text{Ti}_{12}\text{Ta}_6$, determined by ESI-MS.

a very weak acid–base chemistry. Acid titration of this solution with dilute HCl caused immediate precipitation, accompanied of course by strong pH buffering. Thus, Ti_2Ta_8 is unstable when titrated with acid, which is commonly observed for the highly basic niobate and tantalate clusters that possess high negative charges; once this molecular charge is compensated by protons, colloids form immediately. Conversely, in base titration, we found that Ti_2Ta_8 was stable above pH 12 when titrated with TMAOH solution. The kinetic stability range of Ti_2Ta_8 ($7.5 < \text{pH} < 12$) is significantly narrower relative to Ti_2Nb_8 ($5.5 < \text{pH} < 12$),^[7c] which demonstrates more basic character of polyoxotantalate when compared to isostructural polyoxoniobate. The mechanism of instability at high pH is presumably OH^- nucleophilic attack at the metal centers. On the other hand, pH stability range of $Ti_{12}Ta_6$ was between $7 < \text{pH} < 11$, which is shifted closer to the acidic region when compared to Ti_2Ta_8 . We note that both Ti_2Ta_8 and $Ti_{12}Ta_6$ are stable in more neutral to weakly basic condition than Ta_6 , which is only stable under strongly basic conditions (Figure 3). It is possible that these narrower pH stability ranges of the polyoxotantalates when compared to polyoxoniobates may have delayed development of polyoxotantalate chemistry. Nyman et al. recently suggested that some polyoxotantalates could only be stable or isolable from non-aqueous solutions; she based her supposition on small-angle X-ray scattering data on solutions.^[6b]

For the first time, isolation of Ti-substituted polyoxotantalates from aqueous solutions is reported and a strategy outlined for further synthesis of other substituted polyoxotantalates. The substituted polyoxotantalates exhibited higher kinetic stability than unsubstituted polyoxotantalate, which means that polyoxotantalates substituted with other elements, which tunes the molecular charge, could also be stable. This aqueous route is important because it suggests that a wider library of substituted polyoxotantalates await discovery and that the library may ultimately be as large as the niobates, providing new materials and new catalysts.

Experimental Section

Synthesis of Ti_2Ta_8 : 1 g of hydrous tantalum oxide (83% w/w) was mixed with 1 g of TMAOH·5H₂O in a PTFE-lined autoclave, and 0.3 mL of titanium isopropoxide was added. The mixture was hydrothermally reacted at 140 °C for 16 h. After cooling, the solution was washed with isopropanol in a plastic centrifuge tube a few times until sticky product remained. The product was extracted with ethanol, and the ethanolic solution was evaporated in an oven at 70 °C in an Erlenmeyer flask. Crystalline material was obtained during evaporation. The product was finally washed with hot isopropanol. Yield = 0.75 g (53%). Elemental analysis calcd (%) for $C_{32}H_{138}N_8O_{49}Ta_8Ti_2$ ($M_w = 2962.77$): C 12.97, H 4.69, N 3.78, Ti 3.23, Ta 48.86; found: C 13.15, H 4.64, N 3.79, Ti 3.3, Ta 46.7.

Synthesis of $Ti_{12}Ta_6$: 1 g of hydrous tantalum oxide (83% w/w) was mixed with 1 g of TMAOH·5H₂O in a PTFE-lined autoclave, and 2 mL of titanium isopropoxide was added. The mixture was hydrothermally reacted at 150 °C for 16 h. The resultant product was extracted with methanol. The methanol extract was evaporated in air. Crystalline material formed from the oily product after a few months. Yield = 0.4 g (17%). Elemental analysis calcd (%) for

$C_{60}H_{298}N_{15}O_{125}Ta_9Ti_{18}$ ($M_w = 5721.16$): C 12.60, H 5.25, N 3.67, Ti 28.47, Ta 15.06; found: C 13.68, H 4.60, N 3.86, Ti 28.3, Ta 14.9.

CCDC 1472708 (Ti_2Ta_8) and 1472709 ($Ti_{12}Ta_6$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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- a) M. T. Pope, *Heteropoly and Isopolyoxometalates*, Springer-Verlag, Berlin, 1983; b) M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* 1991, 30, 34–48; *Angew. Chem.* 1991, 103, 56–70; c) M. T. Pope, A. Müller eds. in *Polyoxometalates. From Platonic Solids to Anti-Retroviral Activity*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1994; d) C. L. Hill, *Chem. Rev.* 1998, 98, 1–390; e) C. Ritchie, A. Ferguson, H. Nojiri, H. N. Miras, Y.-F. Song, D.-L. Long, E. Burkholder, M. Murrie, P. Kögerler, E. K. Brechin, L. Cronin, *Angew. Chem. Int. Ed.* 2008, 47, 5609–5612; *Angew. Chem.* 2008, 120, 5691–5694; f) J.-D. Compain, P. Mialane, A. Dolbecq, I. Mbomekallé, J. Marrot, F. Sécherresse, E. Rivière, G. Rogez, W. Wernsdorfer, *Angew. Chem.* 2009, 121, 3123–3127.
- M. Nyman, *Dalton Trans.* 2011, 40, 8049–8058.
- a) H. Hartl, F. Pickhard, F. Emmerling, C. Röhr, *Z. Anorg. Allg. Chem.* 2001, 627, 2630–2638; b) M. Nyman, T. M. Anderson, P. P. Provencio, *Cryst. Growth Des.* 2009, 9, 1036–1040; c) F. Pickhard, H. Hartl, *Z. Anorg. Allg. Chem.* 1997, 623, 1311–1316; d) L. Shen, Y. Q. Xu, Y. Z. Gao, F. Y. Cui, C. W. Hu, *J. Mol. Struct.* 2009, 934, 37–43; e) T. M. Anderson, M. A. Rodriguez, F. Bonhomme, J. N. Bixler, T. M. Alam, M. Nyman, *Dalton Trans.* 2007, 4517–4522; f) M. Matsumoto, Y. Ozawa, A. Yagasaki, *Inorg. Chem. Commun.* 2011, 14, 115–117.
- a) A. V. Besserguenev, M. H. Dickman, M. T. Pope, *Inorg. Chem.* 2001, 40, 2582–2586; b) P. A. Abramov, M. N. Sokolov, A. V. Virovets, S. Floquet, M. Haouas, F. Taulelle, E. Cadot, C. Vicent, V. P. Fedin, *Dalton Trans.* 2015, 44, 2234–2239; c) P. A. Abramov, M. N. Sokolov, S. Floquet, V. Haouas, V. Taulelle, E. V. Peresypkina, A. V. Virovets, C. Vicent, N. B. Kompankov, A. A. Zhdanov, O. V. Shuvaeva, V. P. Fedin, *Inorg. Chem.* 2014, 53, 12791–12798.
- M. Matsumoto, Y. Ozawa, A. Yagasaki, Y. Zhe, *Inorg. Chem.* 2013, 52, 7825–7827.
- a) E. Balogh, T. M. Anderson, J. R. Rustad, M. Nyman, W. H. Casey, *Inorg. Chem.* 2007, 46, 7032; b) L. B. Fullmer, P. I. Molina, M. R. Antonio, M. Nyman, *Dalton Trans.* 2014, 43, 15295–15299; c) L. B. Fullmer, R. H. Mansergh, L. N. Zakharov, D. A. Keszler, M. Nyman, *Cryst. Growth Des.* 2015, 15, 3885–3892.
- a) M. Nyman, L. J. Criscenti, F. Bonhomme, M. A. Rodriguez, R. T. Cygana, *J. Solid State Chem.* 2003, 176, 111–119; b) C. A. Ohlin, E. M. Villa, J. C. Fettinger, W. H. Casey, *Angew. Chem. Int. Ed.* 2008, 47, 5634–5636; *Angew. Chem.* 2008, 120, 5716–5718; c) E. M. Villa, C. A. Ohlin, W. H. Casey, *J. Am. Chem. Soc.* 2010, 132, 5264–5272.
- W. G. Klemperer, K. A. Marek, *Eur. J. Inorg. Chem.* 2013, 1762–1771.
- a) C. A. Ohlin, E. M. Villa, J. C. Fettinger, W. H. Casey, *Dalton Trans.* 2009, 2677–2678; b) J.-H. Son, C. A. Ohlin, W. H. Casey, *Dalton Trans.* 2013, 42, 7529–7533; c) J.-H. Son, J. Wang, W. H. Casey, *Dalton Trans.* 2014, 43, 17928–17933; d) J.-H. Son, W. H. Casey, *Dalton Trans.* 2015, 44, 20330–20333.
- a) V. W. Day, T. A. Eberspacher, W. G. Klemperer, C. W. Park, *J. Am. Chem. Soc.* 1993, 115, 8469–8470; b) P. Coppens, Y. Chen, E. Trzop, *Chem. Rev.* 2014, 114, 9645–9661.

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