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Novel Tantalum Chalcogenide Halides: The First Ta_3 Clusters in the Solid State

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Tantalum halide cluster chemistry is dominated by the highly stable octahedral $[Ta_6X_{12}]^{n+}$ clusters (X = Cl, Br, I) found in reduced binaries with compositions Ta_6X_{14} and Ta_6X_{15}[1] and by dinuclear species like TaX_4 (also formulated $Ta_2X_6X_{4/2}$)[2] and the abundant $Ta_2Cl_6L_3$ complexes and their derivatives.[3] Known tantalum chalcogenide halides are limited to one-dimensional compounds of the type $(TaQ_4)_nX$ (Q = Se, Te; n = 1, 2, 4; X = Br, I)[4] and to the structurally uncharacterized solids $TaSCl_3$ and TaS_2Cl_2.[5] Trinuclear tantalum clusters containing metal−metal bonds are exceedingly rare: to the best of our knowledge, only one has been unambiguously characterized, the $[Ta_3Cl_{10}(PEt_3)_3]^-$ anion reported in 1988, which was obtained by solution methods.[6] Another, $[(Me_6C_6)_3Ta_3Cl_6][BPh_4]$, containing an eight-electron Ta_3 cluster with one three center-two electron bond, has been claimed,[7] but the evidence remains equivocal; no clear structural information is known. In addition, μ-oxo trinuclear clusters of Ta(V) have been synthesized,[8] but the d^0 Ta atoms are linked by di- and tribridging oxygen atoms, not by direct Ta−Ta bonds. Considering the well-known closely parallel chemistry of Nb and Ta, this scarcity of Ta−Ta bonded trinuclear clusters presents a puzzling contrast with the solid state and solution chemistry of niobium, in which several trinuclear examples are known as well as many octahedral and dinuclear clusters isostructural to the Ta examples.[9] Most relevant to this communication are the halides Nb_3X_8 (X = Cl, Br, I), known for some 30 years,[10] and their recently discovered chalcogen-substituted derivatives, Nb_3QX_7 (Q = S, Se, Te; X = Cl, Br, I).[11] Nb_3X_8 have a defect-CdI_2 structure, consisting of close-packed halide layers with $^3/_4$ of all octahedral interstices in every alternate layer filled by Nb atoms. The Nb atoms fill these holes in an ordered fashion, clustering together to form Nb−Nb bonded triangles. In the Nb_3QX_7 family, the chalcogen atom substitutes a halide in alternating anion layers, occupying a cluster capping position directly above the Nb_3 triangle.

To date, no analogous Ta compounds have been reported: Ta_3X_8, whose existence is occasionally alluded to in the literature,[12] are still unknown. In an effort to extend the Nb examples to Ta chemistry, synthesis of Ta_3QX_7 was undertaken. We now report the first results from this work, the synthesis of two new ternary tantalum chalcogenide iodides containing triangular clusters of Ta atoms.

Ta_3QI_7 (Q = Se, Te) were prepared by stoichiometric reaction of Ta foil, chalcogen, and iodine in evacuated fused silica ampoules at 450 °C for ca. 1 week, followed by rapid quenching to room temperature. Products were identified by comparing observed Guinier powder X-ray diffraction patterns for the Ta compounds to those obtained from analogous Nb compounds. Ta_3QI_7 are the major products, but we have been unable to find conditions providing Ta_3QI_7 as the sole product. Invariably, TaI_5, Ta_6I_{14}, and Ta metal are also observed in the powder patterns, regardless of reaction duration. Interestingly, Nb_3SeI_7 and Nb_3TeI_7 reactions readily produce the pure, single phase material. The formation and temperature stability range of Ta_3QI_7 indicate a lesser thermodynamic stability with respect to the Nb analogues, which are stable up to ca. 950 °C. Guinier powder X-ray diffraction of products from reactions conducted at several temperatures in the range 350−900 °C indicates an upper temperature stability limit of ca. 550 °C. At higher temperatures, only TaI_5 can be identified; the rest of the product is amorphous. Crystals of Ta_3SeI_7 and Ta_3TeI_7 both form as shining black hexagonal columns, with a micaceous morphology. They are stable in air, water, and nonoxidizing acids indefinitely but rapidly decompose in dilute HNO_3. Small hexagonal plates suitable for X-ray diffraction cleave easily and cleanly from the longer columns—the larger, intact crystals usually are of poor quality for single crystal diffraction experiments.

Ta_3SeI_7 and Ta_3TeI_7 are isostructural with Nb_3SeI_7 (and Nb_3TeI_7).[13] From an extended solid point of view, the structure consists of ordered, close-packed layers of iodine and chalcogen interleaved in every other layer by Ta atoms. The Ta atoms order in $^3/_4$ of all octahedral sites, forming Ta_3 clusters. These Ta_3 triangles are situated in the layers directly beneath, and thus are capped by, the chalcogen atom (Figure 1A).

The close-packed mixed anion layers in Ta_3QI_7 stack in a ...*ABAC*..., or ...*hc*..., manner, with the clustered metal atoms inserted into alternating AB and the AC bilayers. Thus, there are two identical Ta_3QI_7 slabs per unit cell, with one related to the other by a 6_3 screw axis. The ...*hc*... variant is one of five different stacking variants discovered so far in the Nb_3X_8 and

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[13] (a) Crystal data (23 °C, Mo Kα radiation): Ta_3SeI_7: space group $P6_3mc$ (no. 186), a = 7.541(1) Å, c = 13.590(3) Å, V = 669.90(20) Å^3, Z = 2; 3259 data collected, 710 unique; no. of variables, 24; final R = 0.053, R_w = 0.046; goodness-of-fit, 1.11. Ta_3TeI_7: space group $P6_3mc$ (no. 186), a = 7.591(2) Å, c = 13.907(3) Å, V = 694.03(26) Å^3, Z = 2; 1031 data collected, 303 unique; no. of variables, 24; final R = 0.030, R_w = 0.031; goodness-of-fit, 1.30. Both structures solved by direct methods using SHELXS-86[13b] and refined with the TEXSAN[13c] package of crystallographic programs. An empirical ψ-scan absorption correction was applied to both data sets, followed by a DIFABS[13d] correction to the isotropically refined atoms (unnormalized transmission ranges: Ta_3SeI_7, 0.8−1.1; Ta_3TeI_7, 0.9−1.1). All positions were then refined anisotropically. (b) Sheldrick, G. M. In *Crystallographic Computing* 3, Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175−189. (c) TEXSAN: Single Crystal Structure Analysis Software, Version 5.0; Molecular Structure Corporation: The Woodlands, TX 77381, 1989. (d) Walker, N.; Stuart, D. *Acta Crystallogr.* **1986**, *A39*, 158.

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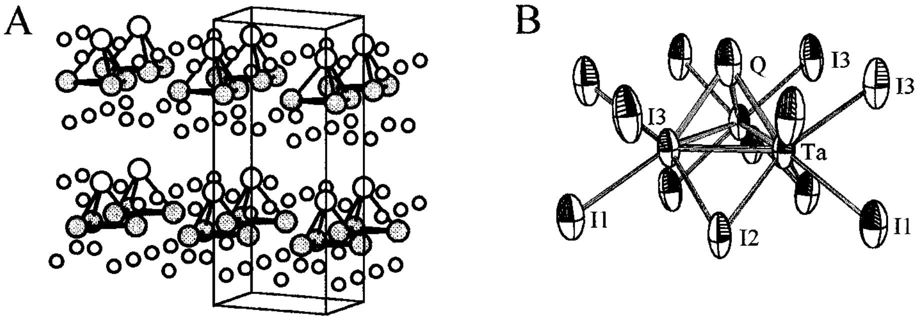

Figure 1. (A) Approximate [100] view of two layers of the extended structure of Ta_3QI_7 (Q = Se, Te): small white circles, I; large white circles, Se or Te; dark circles, Ta. (B) Ta_3QI_{12} cluster unit. Some atom labels omitted for clarity. Selected bond distances (Å) and angles (deg): Ta_3SeI_7: Ta−Ta, 2.957(3); Ta−Se, 2.537(8); Ta−I(1), 3.010(4), Ta−I(2), 2.725(3); Ta−I(3), 2.905(3); Ta−Ta−Ta, 60.00(1); Ta−Se−Ta, 71.2(2); Ta−I(2)−Ta, 66.8(1). Ta_3TeI_7: Ta−Ta, 3.004(3); Ta−Te, 2.698(4); Ta−I(1), 3.019(3); Ta−I(2), 2.736(2); Ta−I(3), 2.897(2); Ta−Ta−Ta, 60.00(1); Ta−Te−Ta, 67.7(1); Ta−I(2)−Ta, 66.59(6).

Nb_3QX_7 systems. The reason for the occurrence of the ...*hc*... modification over, for example, an ...*ABAB*... (...*h*...) anion layer stacking pattern remains unclear. There would at first appear to be no great driving force for this particular stacking situation over any of the others, and thus one might expect to observe polymorphism. (Indeed, both the ...*hc*... and the ...*h*... variants have been observed in the Nb_3TeI_7 case.[14]) However, separate Guinier powder patterns of several individual single crystals have revealed evidence for only the *hc*-Nb_3SeI_7 variant. We are currently exploring the relative magnitudes of van der Waals interactions and dipole−dipole interactions between adjacent Ta_3QI_7 layers and experimenting with the intercalation properties of these layered phases.

An explanation for the occurrence of the chalcogen exclusively in the capping position, profferred to explain the chalcogen site preference in the Nb_3QX_7 family but equally valid here, has been proposed on the basis of site electron density.[15] Mulliken population analysis of α-Nb_3Cl_8 showed the μ_3 capping position to be the least electron-rich site of the four crystallographically distinct anion positions. Consequently, one would expect the less electronegative element in a mixed system to reside at this position, leaving the more electronegative atoms in the electron-rich sites. Since the (Pauling) electronegativities of Se (2.4) and Te (2.1) are less than that of I (2.5), the chalcogens choose the μ_3 position, leaving the iodine atoms to occupy the sites of greater electron density.

From a cluster fragment point of view, the local cluster unit is the common M_3X_{13} type, written in the notation of Schäfer and von Schnering as $Ta_3(\mu_3\text{-}Q^i)(\mu_2\text{-}X_3{}^i)(\mu_3\text{-}X_{3/3}{}^a)(\mu_2\text{-}X_{6/2}{}^a)$ (Figure 1B). The perfectly equilateral triangular Ta cluster has one μ_3 capping atom, three μ_2 edge-bridging atoms, and nine atoms which bridge two or three other clusters, linking the extended layers together. The immediate environment around the Ta cluster in Ta_3QI_7 is exactly analogous to the $[Ta_3Cl_{10}(PEt_3)]^-$ anion but now condensed into a quasi-infinite two-dimensional solid.

Ta−Ta distances in Ta_3SeI_7 and Ta_3TeI_7 (2.957(3) and 3.004(3) Å, respectively) are comparable to those in Ta_6I_{14} (2.80−3.08 Å),[1] though slightly longer than in $[Ta_3Cl_{10}(PEt_3)]^-$ (2.932 Å),[6] presumably because of the latter's smaller halide. Ta−I and Ta−chalcogen distances are also typical. The Nb−Nb distances in the corresponding Nb analogues (3.02 Å for Nb_3SeI_7 and 3.04 Å for Nb_3TeI_7)[11] are slightly longer than the Ta−Ta distances, which agrees with the concept of greater d−d orbital overlap in reduced Ta compounds.[16]

Magnetic measurements on powdered samples of many handpicked small single crystals of both Ta_3SeI_7 and Ta_3TeI_7 display a weak paramagnetic signal, obeying the Curie−Weiss law (Ta_3SeI_7, 0.95 μ_B; Ta_3TeI_7, 0.60 μ_B). In contrast, Nb_3SeI_7 and Nb_3TeI_7 show the diamagnetic behavior expected from formally closed-shell six-electron metal clusters. The precise origin of this magnetic moment eludes us at present, but two possibilities readily present themselves: either there is an extrinsic paramagnetic impurity, or iodine/chalcogen mixing or substitution is taking place, especially in the form of substitution of Se and Te by I on the cluster capping site. Such a substitution would create local paramagnetic "Ta_3I_8" regions, with seven-electron Ta_3 clusters. An estimate of the concentration of such regions in the Ta_3QI_7 framework (using a spin-only moment of 1.73 μ_B and diluting a pure Ta_3I_8 sample with diamagnetic Ta_3QI_7) yields a "Ta_3I_8 fraction" necessary to give rise to the observed moment. A hypothetical iodine-substituted Ta_3SeI_7 sample would require a Ta_3I_8 mole fraction of 0.55 (i.e., $Ta_3Se_{0.45}I_{7.55}$). For Ta_3TeI_7, the required mole fraction is 0.65 ($Ta_3Te_{0.35}I_{7.65}$). To address this possibility, electron microprobe quantitative analysis was performed on several crystals of both compounds. The microprobe results confirmed the 3-1-7 stoichiometry in both cases. Also, at least in the case of the selenide, a dramatic effect in the μ_3-Q^i atom thermal parameter should result from such mixing, but this is not observed.

Ta_3SeI_7 and Ta_3TeI_7 are the first solid-state examples of the well-known trinuclear clustering observed frequently in niobium halide and chalcogenide halide compounds. While the structural analogues reported here may seem to be further examples of the often indistinguishable behavior of these two elements, subtle differences are also suggested by the inevitable presence of side products, the lesser temperature stability range, and the continued absence of any trinuclear clusters of binary halides in the Ta system.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates with isotropic thermal parameters, and anisotropic displacement parameters for Ta_3SeI_7 and Ta_3TeI_7 (6 pages). See any current masthead page for ordering and Internet access instructions.

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