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Synthesis and Structures of Hexanuclear Tantalum Clusters with the $[Ta_6Cl_{12}(CH_3OH)_6]^{3+}$ Unit

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Methods for the preparation of the new methanol-solvated cluster $[Ta_6Cl_{12}(CH_3OH)_6]^{3+}$ have been devised and conditions established for obtaining the crystalline compounds $[Ta_6Cl_{12}(CH_3OH)_6]X_3$, $[Ta_6Cl_{12}(CH_3OH)_6]X_3 \cdot 4H_2O$, and $[Ta_6Cl_{12}]X_3 \cdot 2H_2O \cdot 4CH_3OH$, where X = Cl or Br. Usually the three compounds cocrystallized, and the conditions were chosen to enhance one of the compounds. X-ray crystal structure determinations were completed for $[Ta_6Cl_{12}(CH_3OH)_6]Br_3$ (I) and $[Ta_6Cl_{12}(CH_3OH)_6]Br_3 \cdot 4H_2O$ (II). Crystal data for I: rhombohedral (hexagonal), space group $R\bar{3}$, $a_H = 19.127$ (4) Å, $c_H = 8.565$ (1) Å, $V = 2713.6$ (2) Å^3, $Z = 3$, $d_c = 3.567$ g cm^{-3}, $R = 0.030$ ($R_W = 0.036$) for 1898 unique reflections with $I > 2\sigma(I)$. Crystal data for II: monoclinic, space group $C2/m$, $a = 12.187$ (14) Å, $b = 15.793$ (4) Å, $c = 9.182$ (6) Å, $\beta = 99.05$ (3)°, $V = 1745.3$ (1) Å^3, $Z = 2$, $d_c = 3.835$ g cm^{-3}, $R = 0.065$ ($R_w = 0.074$) for 1566 unique reflections with $I > 2\sigma(I)$. Both I and II contain the $[Ta_6Cl_{12}(CH_3OH)_6]^{3+}$ cluster cation and Br^- anions; in the case of II, H_2O is hydrogen bonded in the lattice to both the coordinated CH_3OH molecules and Br^- anions. The average Ta–Ta bond distances for I, 2.9048 (1) Å, and for II, 2.898 (1) Å, are in good agreement with that previously reported for $[Ta_6Cl_{12}(H_2O)_6]^{3+}$, 2.906 (1) Å, but about 0.04 Å shorter than those in complexes ligated in the terminal positions with chloride or R_3P. The average Ta–Cl (bridging) bond distance, 2.439 (5) Å in both I and II, is about the same as that reported for other $[Ta_6Cl_{12}]^{3+}$ cluster compounds.

Introduction

The octahedral cluster units of niobium and tantalum $[M_6X_{12}]^{n+}$, where X = edge-bridging halogen Cl, Br, or I, may exist in three different oxidation states with $n = 2$, 3, or 4. The usual preparative procedures require starting with $[M_6X_{12}]^{2+}$ derivatives and performing one- or two-electron oxidations with various oxidizing agents; e.g., note the recent use of $NOBF_4$[1] to obtain compounds with $n = 3$ or 4. A need exists for clean preparations of $[Ta_6X_{12}]^{3+}$ derivatives, as reflected by the small number of reports of structure determinations, which are limited to the four compounds $[Ta_6Cl_{12}]Cl_3$,[2] $Me_4N[Ta_6Cl_{12}(H_2O)_6]Br_4$,[3] and *cis*- and *trans*-$[(Ta_6Cl_{12})Cl_2\{P(C_2H_5)_3\}_4](BF_4)$.[1] Our earlier-discovered method[3] for the selective preparation of $[Ta_6Cl_{12}]^{3+}$ clusters without introducing any oxidizing agent, other than oxygen in the air, has been used here to prepare for the first time crystalline compounds containing the methanol-solvated cluster cations $[Ta_6Cl_{12}(CH_3OH)_6]^{3+}$. Structural studies have shown that several different phases may coexist under the same experimental conditions or be formed selectively with small changes in the procedure.

Experimental Section

Materials. Methanol with a water content of 0.01%, concentrated aqueous HCl or HBr (ca. 12 M), and NaOH were reagent grade and were used as received. Methanolic solutions of NaOH were always freshly prepared. The cluster compounds $[(M_6Cl_{12})(H_2O)_4Cl_2] \cdot 4H_2O$ used as starting materials were prepared according to the literature method.[4]

Synthesis of $[Ta_6Cl_{12}](OCH_3)_4 \cdot 4CH_3OH$. A 0.5-g (0.290-mmol) amount of $[(Ta_6Cl_{12})(H_2O)_4Cl_2] \cdot 4H_2O$ was dissolved in 20 mL of methanol at room temperature. This solution was titrated slowly with 0.2 M methanolic NaOH solution. After addition of 2 mol of NaOH/mol of cluster, a precipitate of $[Ta_6Cl_{12}](OCH_3)_2 \cdot 4CH_3OH$ appeared, but this was dissolved with further NaOH addition. At this point, under the influence of oxygen in the air, the emerald-green color of the solution slowly changed to olive-green, and after addition of 6 mol of NaOH/mol of cluster (pH ~10), the solution became dark-red, indicating that the oxidation of the cluster units to $[Ta_6Cl_{12}]^{4+}$ had occurred. The alkaline solution was left for approximately 30 min in air at room temperature to ensure complete oxidation and was then filtered through a fine frit in order to remove traces of tantalum(V) oxide. Next, the solution was treated with slow addition of concentrated HCl or HBr dissolved in methanol. $[Ta_6Cl_{12}](OCH_3)_4 \cdot 4CH_3OH$ began to precipitate after addition of the first drops of acid. Continued addition of acid up to 2 mol/mol of cluster resulted in quantitative precipitation of this compound and a colorless solution. The precipitate was filtered off, washed with methanol, and dried in a desiccator over P_2O_5. Anal. Calcd for $[Ta_6Cl_{12}](OCH_3)_4 \cdot 4CH_3OH$: Ta, 61.57; Cl, 24.13; C, 5.44; H, 1.60. Found: Ta, 61.47; Cl, 24.09; C, 5.39; H, 1.56. X-ray powder diffraction *d*, Å ($100I/I_0$): 8.95 (100), 8.08 (56), 6.49 (4), 6.21 (7), 3.509 (6), 3.321 (6), 2.764 (4), 2.717 (4), 2.599 (9), 2.453 (6), 2.379 (7), 2.316 (7), 1.998 (3), 1.933 (3), 1.787 (3).

$[Ta_6Cl_{12}(CH_3OH)_6]X_3$ (X = Cl, Br; Rhombohedral Phases). To a suspension of $[Ta_6Cl_{12}](OCH_3)_4 \cdot 4CH_3OH$ (0.5 g) in 10 mL of methanol was added a methanolic solution of concentrated HCl (2.5 mL) or HBr (2.0 mL). With addition of these acids, the insoluble cluster methoxide $[Ta_6Cl_{12}](OCH_3)_4 \cdot 4CH_3OH$ was slowly dissolved and completely clear solutions were obtained. Subsequently, the color of the brown solution suddenly changed to olive-green. The volume of the solution was reduced to 5 mL in air, and the completely clear solutions were left to crystallize in a refrigerator. Over several days needlelike rhombohedral crystals appeared, often mixed with some rodlike crystals belonging to the monoclinic system, and also with some crystals in the shape of octahedra. X-ray powder diffractometry of these three differently shaped crystals revealed three different crystalline phases for both the chloride and bromide compounds. Anal. Calcd for $[Ta_6Cl_{12}(CH_3OH)_6]Cl_3$: Ta, 59.99; Cl, 29.38; C, 3.98; H, 1.34. Found: Ta, 60.15; Cl, 29.51; C, 4.05; H, 1.49. Calcd for $[Ta_6Cl_{12}(CH_3OH)_6]Br_3$: Ta, 55.87; Cl, 21.88; Br, 12.33; C, 3.71; H, 1.24. Found: Ta, 55.98; Cl, 21.92; Br, 11.98; C, 3.63, H, 1.47, $\mu_{eff} = 1.52\ \mu_B$. IR spectra are the same for X = Cl and X = Br, cm^{-1}: 3150 (w), 1640 (vw), 1130 (m), 985 (s), 480 (w), 420 (w), 328 (s) [ν(Ta–Cl)], 245 (m).

$[Ta_6Cl_{12}(CH_3OH)_6]X_3 \cdot 4H_2O$ (X = Cl, Br; Monoclinic Phases). The rodlike single crystals (monoclinic) were prepared by using the same procedure as described for the rhombohedral crystalline phases except 1.2 or 1.0 mL of concentrated HCl or HBr, respectively, was used in the acid-addition step. Anal. Calcd for $[Ta_6Cl_{12}(CH_3OH)_6]Cl_3 \cdot 4H_2O$: Ta, 57.69; Cl, 28.26; C, 3.83; H, 1.71. Found: Ta, 57.76; Cl, 28.31; C, 3.91; H, 1.78. Calcd for $[Ta_6Cl_{12}(CH_3OH)_6]Br_3 \cdot 4H_2O$: Ta, 53.87; Cl, 21.11;

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Table I. Crystallographic Data for Compounds I and II

	I	II
formula	$C_6H_{24}Br_3Cl_{12}O_6Ta_6$	$C_6H_{32}Br_3Cl_{12}O_{10}Ta_6$
fw	1943.10	2015.16
space group	$R\bar{3}$	$C2/m$
a, Å	19.127 (4)	12.187 (14)
b, Å		15.793 (4)
c, Å	8.565 (1)	9.182 (6)
α, deg	90	90
β, deg	90	99.05 (3)
γ, deg	120	90
V, Å^3	2713.6 (2)	1745.3 (1)
Z	3	2
d_{calc}, g cm^{-3}	3.567	3.835
μ, cm^{-1}	221.49	229.86
λ(Mo Kα), Å	0.710 73	0.710 73
temp, K	103 (3)	103 (3)
R^a	0.030	0.065
$R_w{}^b$	0.036	0.074

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(w|F_o| - |F_c|)^2]w/|F_o|^2]^{1/2}$, $w = x/[\sigma^2(F_o - 0.001F_o{}^2)]$, with $x = 1.647$ for I and 3.410 for II.

Br, 11.90; C, 3.58; H, 1.60. Found: Ta, 54.04; Cl, 21.16; Br, 11.87; C, 3.69; H, 1.78. $\mu_{eff} = 1.51\ \mu_B$. IR spectra are the same for X = Cl and X = Br, cm^{-1}: 3350 (w), 3150 (vw), 1630 (w), 1140 (w), 985 (s), 428 (vw), 328 (s) [ν(Ta–Cl)], 240 (w).

$[Ta_6Cl_{12}]X_3{\cdot}2H_2O{\cdot}4CH_3OH$ (X = Cl, Br; Octahedra-like Crystals). It was possible to prepare octahedral crystals, selectively, by using the above procedure and 1.0 or 0.8 mL of concentrated HCl or HBr, respectively. Anal. Calcd for $[Ta_6Cl_{12}]Cl_3{\cdot}2H_2O{\cdot}4CH_3OH$: Ta, 60.93; Cl, 29.84; C, 2.70; H, 1.13. Found: Ta, 60.98; Cl, 29.93; C, 2.66; H, 1.19. Calcd for $[Ta_6Cl_{12}]Br_3{\cdot}2H_2O{\cdot}4CH_3OH$: Ta, 56.69; Cl, 22.21; Br, 12.52; C, 2.51; H, 1.05. Found: Ta, 56.96; Cl, 22.32; Br, 12.61; C, 2.56; H, 0.98. IR spectra are the same for X = Cl and X = Br, cm^{-1}: 3400 (w), 3150 (w), 1625 (w), 1135 (w), 985 (s), 410 (w), 328 (s) [ν(Ta–Cl)], 245 (m). X-ray powder diffraction d, Å ($100I/I_0$): for X = Cl, 8.88 (75), 8.31 (100), 6.09 (38), 4.24 (8), 3.883 (12), 3.173 (10), 3.129 (8), 2.976 (9), 2.791 (12), 2.642 (15), 2.587 (38), 2.245 (18), 2.169 (29), 2.133 (26); for X = Br, 9.02 (43), 8.42 (100), 6.19 (40), 4.53 (3), 4.31 (12), 4.0 (3), 3.86 (3), 3.338 (6), 3.209 (10), 3.015 (8), 2.855 (15), 2.619 (39), 2.453 (5), 2.359 (10), 2.279 (15), 2.199 (21), 2.154 (20), 2.098 (12), 1.901 (9).

Analysis. In all compounds, tantalum was determined by the "H-tube" method[5] and also from the amount of Ta_2O_5 obtained after thermal decomposition of samples on the thermobalance. Halogens were determined by potentiometric titration with standard silver nitrate solution after decomposition of the clusters with KOH and H_2O_2. Carbon and hydrogen analyses were performed by the Rudjer Bošković Institute Analytical Service.

Physical Measurements. A Perkin-Elmer 580B spectrophotometer was used to record the infrared spectra. Magnetic susceptibilities were measured by the Gouy method at 22 °C for the starting substances and all complexes. Magnetic moments were calculated from the formula $\mu_{eff} = (\chi_m T)^{1/2}$, where χ_m is the molar susceptibility corrected for diamagnetic core contributions. Thermogravimetric measurements were carried out on a Cahn RG microanalytical balance with a heating rate of 2 °C/min. The X-ray diffraction patterns were recorded on a Philips X-ray diffractometer using graphite-monochromatized Cu Kα radiation.

X-ray Structure Determinations. Needlelike crystals of $[Ta_6Cl_{12}(CH_3OH)_6]Br_3$ (I) and rodlike crystals of $[Ta_6Cl_{12}(CH_3OH)_6]Br_3{\cdot}4H_2O$ (II) were subjected to X-ray structure analysis. The crystalline phases with octahedrally shaped crystals did not give good diffraction patterns, and the crystal quality was inadequate for X-ray structure analysis. A summary of crystal data for both I and II is presented in Table I. The crystals of these compounds were separated from the mother solution, coated with a viscous, high molecular weight hydrocarbon oil, and secured on a glass fiber by cooling to 103 K in a cold N_2 stream on the diffractometer. The intensities of three standard reflections were measured every hour of X-ray exposure time during data collection. Decays of 1.2% and 4.5% were noted for I and II, respectively. The data were scaled to account for the degradation and corrected for Lorentz, polarization, and background effects. The experimental absorption corrections were made on the basis of a ψ-scan of reflections $\bar{1}\bar{2}1$, $\bar{1}\bar{1}3$, $\bar{1}\bar{2}4$, $\bar{1}\bar{1}6$, $\bar{1}\bar{2}7$, $\bar{1}\bar{1}9$, and $\bar{1},\bar{2},10$ for I and reflections $20\bar{4}$, $20\bar{5}$, $20\bar{6}$, $20\bar{3}$, and $20\bar{2}$ for II. Average transmissions were 0.969 (I) and 0.834 (II). Data reductions were performed by the Enraf-Nonius SDPVAX package.[6] The structures were solved by the Patterson method using SHELXS-86.[7] Tantalum scattering factors and anomalous dispersion values were taken from ref 8. For other atoms, the scattering factors were those included in the SHELXS-77 program.[9] In the structure of $[Ta_6Cl_{12}(CH_3OH)_6]{\cdot}Br_3$, all atoms occupied the general position 18(f) of the space group $R\bar{3}$. Because the charge on the cluster, $[Ta_6Cl_{12}(CH_3OH)_6]^{3+}$, was known to be 3+, hence requiring only nine Br atoms in the unit cell, the occupancy of Br sites in the structure of I had to be reduced to 0.5.

Table II. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (×10^4) for $[Ta_6Cl_{12}(CH_3OH)_6]Br_3$ (I)

	x	y	z	U_{EQ},^{a} Å^2
Ta	0.9000 (1)	0.9630 (1)	0.3612 (1)	93 (2)
Cl1	0.8086 (1)	0.8388 (1)	0.4987 (2)	145 (5)
Cl2	0.9562 (1)	1.0746 (1)	0.1747 (2)	142 (5)
Br^b	0.3806 (1)	0.3597 (1)	0.5088 (2)	239 (6)
O	0.7940 (3)	0.9267 (3)	0.2115 (6)	210 (18)
C	0.7391 (5)	0.8491 (5)	0.1425 (9)	256 (29)

[a] $U_{EQ} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \vec{a}_i\vec{a}_j$. [b] Br was refined at 0.5 occupancy.

The Patterson map of II revealed two crystallographically independent Ta atoms: one in a general position [8(j)] and the other on the special position (mirror plane) [4(i)] of the space group $C2/m$. The halogen atoms Cl1 and Br1 and both atoms (C, O) of one methanol molecule also occupy position [4(i)]. The atoms Cl4 and Br2 are located on the 2-fold axes in positions [4(g)]. The other atoms are situated in general positions [8(j)]. A difference Fourier map gave evidence for half-occupancy of Br2, and it was restricted to this occupancy in the refinement. This finding is in accord with the chemical analysis and the known charge of the cluster unit. In both structures, there are three bromine ions per one cluster unit. In the unit cell of II, there are uncoordinated water molecules generated from one crystallographically independent position [8(j)]. The structures were refined with a full-matrix least-squares method. All atoms except H were refined with anisotropic thermal parameters. There are somewhat higher residual electron densities in the vicinity of Br1 (structure I) and Br2 (structure II). Partly occupied sites introduced disorder in the packing of both structures. In the crystal structure of compound II there are two short C–O distances (methanol molecules) of 1.36 (4) and 1.31 (5) Å, which did not change significantly after corrections for riding motions according to Busing and Levy.[10]

Results

Both compounds I and II were found to contain the methanol-coordinated cluster cation $[Ta_6Cl_{12}(CH_3OH)_6]^{3+}$. Positional parameters and equivalent isotropic thermal parameters are given for I in Table II and for II in Table III. Bond distances and angles are listed in Tables IV and V for compounds I and II, respectively. Information on the hydrogen-bonding interactions in compound II is given in Table VI.

Discussion

Deprotonation of Methanol at pH ≥7. In this work it has been established that when methanolic solutions of $[Ta_6X_{12}(H_2O)_4X_2]{\cdot}4H_2O$ (X = Cl, Br) are titrated with alkali metal hydroxides in methanolic solution, the deprotonation of methanol occurs at pH ≥7, and the cluster methoxides $[Ta_6X_{12}](OCH_3)_2{\cdot}4CH_3OH$ are precipitated with addition of two M′OH per cluster (M′ = Li, Na, K). Chemical analyses, infrared spectra, and X-ray powder diffraction data for these precipitates indicate that the same cluster methoxides were formed that were earlier prepared by the reaction of $[Ta_6X_{12}]X_2{\cdot}nCH_3OH{\cdot}(8-n)H_2O$ with 2 equiv of alkali metal

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Table III. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (×10⁴) for $[Ta_6Cl_{12}(CH_3OH)_6]Br_3{\cdot}4H_2O$ (II)

	x	*y*	*z*	U_{EQ},[a] Å²
Ta1	0.0615 (1)	0.0919 (0)	0.3772 (1)	247 (3)
Ta2	0.1463 (1)	0.0000	0.3560 (1)	238 (4)
Cl1	0.1433 (6)	0.0000	0.2096 (7)	336 (22)
Cl2	−0.1002 (5)	0.1071 (3)	0.1846 (5)	321 (15)
Cl3	0.2444 (4)	0.1082 (4)	0.5252 (6)	390 (17)
Cl4	0.0000	0.2165 (5)	0.5000	389 (24)
Br1	0.5294 (7)	0.0000	0.6759 (9)	1541 (44)
Br2[b]	1.0000	0.2932 (13)	0.0000	1751 (115)
C1	0.2339 (30)	0.1956 (19)	0.2018 (31)	751 (133)
C2	−0.3423 (40)	0.0000	0.0526 (45)	787 (212)
O1	0.1282 (15)	0.1897 (11)	0.2476 (20)	560 (62)
O2	−0.3076 (17)	0.0000	0.2076 (25)	457 (85)
O3	0.9962 (18)	0.3382 (10)	0.1602 (16)	594 (69)

[a] $U_{EQ} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \vec{a}_i\vec{a}_j$. [b] Br2 was refined at 0.5 occupancy.

Table IV. Bond Lengths (Å) and Angles (Deg) for I[a]

Ta–Cl1	2.436 (2)	O–C	1.448 (13)
Ta–Cl2	2.443 (2)	Ta–Ta(i)	2.9012 (1)
Ta–O	2.197 (5)	Ta–Ta(iv)	2.9084 (1)
Cl1–Ta–O	82.82 (17)	O–Ta–Ta(i)	135.69 (18)
Cl1–Ta–Cl2(ii)	162.92 (6)	O–Ta–Ta(iv)	134.28 (19)
Cl1–Ta–Ta(v)	53.51 (4)	Ta–Cl1–Ta(v)	73.19 (5)
Cl2–Ta–Ta(ii)	96.27 (4)	Ta–Ta(i)–Cl2	53.57 (5)
Cl2–Ta–Cl1(iv)	163.11 (7)	Ta–Ta(v)–Cl1	53.30 (5)
O–Ta–Ta(ii)	133.66 (17)	Cl1–Ta–Ta(i)	95.86 (5)
O–Ta–Cl1(iv)	81.01 (19)	Cl1–Ta–Ta(iv)	96.05 (5)
Ta–Cl2–Ta(i)	72.85 (5)	Cl2–Ta–O	82.14 (19)
Cl1–Ta–Cl2	88.23 (7)	Cl2–Ta–Cl2(ii)	89.34 (7)
Cl1–Ta–Ta(ii)	143.51 (4)	Cl2–Ta–Ta(v)	95.93 (4)
Cl1–Ta–Cl1(iv)	88.66 (8)	O–Ta–Cl2(ii)	80.09 (17)
Cl2–Ta–Ta(i)	53.58 (4)	O–Ta–Ta(v)	136.33 (17)
Cl2–Ta–Ta(iv)	132.58 (4)	Ta–O–C	130.10 (7)

[a] Symmetry operations: (i) $-y, x-y, z$; (ii) $-x+y, -x, z$; (iii) $-x, -y, -z+1$; (iv) $y, -x+y, -z+1$; (v) $x-y, x, -z+1$.

methoxide.[11] Further hydroxide addition resulted in complete dissolution of the cluster methoxides at the point of 6 mol of M′OH/mol of cluster. The change of color of the solution from emerald-green to dark-red indicated that the oxidation of $[Ta_6X_{12}]^{2+}$ to $[Ta_6X_{12}]^{4+}$ by oxygen was complete. As already described,[12] the bromotantalum cluster $[Ta_6Br_{12}]^{2+}$ is unstable in alkaline medium and decomposes with ultimate formation of $Ta(OH)_5{\cdot}nH_2O$.

In contrast, the $[Ta_6Cl_{12}]^{2+}$ cluster is oxidized to $[Ta_6Cl_{12}]^{4+}$ in alkaline methanol, and by slow evaporation in vacuo, cluster methoxide complexes $[M'_2(CH_3OH)_9][Ta_6Cl_{12}(OCH_3)_6]{\cdot}3CH_3OH$ (M′ = alkali metals) can be isolated.[11,13] In this work, we find that when methanolic solutions of the latter are treated by concentrated mineral acids, the insoluble compound $[Ta_6Cl_{12}](OCH_3)_4{\cdot}4CH_3OH$ is formed at the point of adding exactly 2 equiv of acid/equiv of cluster. Poorly crystalline, diamagnetic $[Ta_6Cl_{12}](OCH_3)_4{\cdot}4CH_3OH$ was used as a convenient starting material for the preparation of all $[Ta_6Cl_{12}(CH_3OH)_6]^{3+}$ compounds, as well as the octahedral crystals of unknown structure. Related efforts to obtain $[Nb_6Cl_{12}](OCH_3)_4{\cdot}CH_3OH$ and $[Nb_6Cl_{12}(CH_3OH)_6]^{3+}$ by similar procedures failed.

Formation of Phases with $[Ta_6Cl_{12}]^{3+}$ Units. When the suspension of $[Ta_6Cl_{12}](OCH_3)_4{\cdot}4CH_3OH$ in methanol was treated with mineral acids, the cluster methoxide dissolved and the color of the solution changed from dark-red to olive-green, indicating the reduction of $[Ta_6Cl_{12}]^{4+}$ to $[Ta_6Cl_{12}]^{3+}$ units. Simultaneously with this reduction process, some of the cluster molecules present in the solution were decomposed and oxidized to $Ta(OH)_5{\cdot}nH_2O$.

Usually two or even three kinds of differently shaped single crystals were formed during slow evaporation of the acidified solutions in a refrigerator. Although the different relative proportions of concentrated HCl or HBr promoted one form in preference to the others, the relationship between the form obtained and the acid proportion is not understood. The rhombohedral and monoclinic phases were not stable under ambient conditions. According to evidence provided by X-ray powder diffraction patterns, slow transformation of both $[Ta_6Cl_{12}(CH_3OH)_6]X_3$ (rhombohedral) and $[Ta_6Cl_{12}(CH_3OH)_6]X_3{\cdot}4H_2O$ (monoclinic) to the less crystalline $[Ta_6Cl_{12}]X_3{\cdot}2H_2O{\cdot}4CH_3OH$ (X = Cl, Br) was observed within a few days. In this respect, the monoclinic crystals were less stable than the rhombohedral ones. The olive-green solutions of these $[Ta_6Cl_{12}]^{3+}$ clusters were stable only in the presence of the mineral acids. In their absence, a slow change of color to emerald-green indicated reduction of the cluster units to $[Ta_6Cl_{12}]^{2+}$. The 3+ substances described here are paramagnetic with magnetic moments close to that expected for one unpaired electron characteristic of the $[Ta_6Cl_{12}]^{3+}$ unit.[14]

Structures. The crystal structure of $[Ta_6Cl_{12}(CH_3OH)_6]Br_3$ (I) exhibits a slightly distorted octahedral cluster unit with the symmetry $\bar{3}$. Figure 1 shows the cluster unit with the atom-numbering scheme; the symmetry codes for different atoms are given at the bottom of Table IV. The two Ta–Ta distances of 2.9012 (1) and 2.9084 (1) Å are close to 2.9059 (8) Å observed in the structure of $NMe_4[Ta_6Cl_{12}(H_2O)_6]Br_4$.[3] According to the space-group symmetry there are only two different Ta–Cl distances: 2.436 (2) and 2.443 (2) Å (Table IV). These values are also in agreement with the value of 2.449 (2) Å found in the 3+ cluster unit of the above-mentioned aquo compound.[3] In I, six methanol molecules are coordinated in the terminal positions of the cluster with the Ta–O distance of 2.197 (5) Å.

In the crystal lattice, the cluster units are connected via Br···H–O hydrogen bonds, as evidenced by the Br–O distance of 2.999 (8) Å. The symmetry operations of the $R\bar{3}$ space group generate 18 Br atoms (general position 18(f)). However, both space and charge neutrality considerations dictate that the number of Br atoms be reduced to 9 Br atoms per unit cell. There is no space available to accommodate 18 Br atoms; in the case of completely occupied sites, the Br···Br distance would be 3.162 Å. The calculated van der Waals distance[15] is 3.90 Å. The population parameter of 0.5 for the Br atoms enables formation of three hydrogen bonds per cluster unit; this means that only half of the methanol molecules participate in the hydrogen-bond network.

In the structure of $[Ta_6Cl_{12}(CH_3OH)_6]Br_3{\cdot}4H_2O$ (II), the cluster unit has 2/*m* symmetry with a mirror plane perpendicular to the octahedral equatorial plane (defined by Ta1 atoms). Ta2, Cl1, and atoms of methanol molecules (C2 and O2) coordinated at the apical positions lie on this mirror plane (Figure 2). Symmetry operations of the space group *C*2/*m* generate four different Ta–Ta bonds (Table V) with a mean value of 2.898 (1) Å. As a consequence of the space group symmetry, there are four Ta1–Cl and two Ta2–Cl crystallographically different bonds (Table V). The mean value of Ta–Cl distances is 2.439 (5) Å. However, bond distance differences of crystallographically independent bonds are not significant (below three standard deviations). Two crystallographically independent methanol molecules are coordinated to the Ta atoms. Methanol with O1 (and C1) situated in a general position [8(j)] is coordinated to the Ta1 located on the equatorial plane at a Ta1–O1 distance of 2.181 (18) Å. Methanol with O2 (and C2) on the mirror plane is coordinated to Ta2 at the apical site with a Ta2–O2 distance

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Table V. Bond Lengths (Å) and Angles (Deg) for II[a]

Ta1–Ta2	2.898 (1)	Ta1–Cl1	2.439 (6)	Ta1–Cl2	2.444 (5)	Ta1–Cl3	2.435 (5)
Ta1–Cl4	2.444 (6)	Ta1–O1	2.181 (18)	Ta1–Ta1(i)	2.898 (1)	Ta1–Ta2(i)	2.895 (1)
Ta1–Ta1(iii)	2.9028 (1)	Ta2–Cl2	2.435 (5)	Ta2–O2	2.21 (2)	O1–C1	1.36 (4)

Ta2–Ta1–Cl1	95.69 (14)	Ta2–Ta1–Cl2	53.42 (12)	Ta2–Ta1–Cl3	143.50 (14)
Ta2–Ta1–Cl4	96.09 (9)	Ta2–Ta1–O1	135.60 (50)	Ta2–Ta1–Ta1(i)	59.92 (3)
Ta2–Ta1–Ta1(iii)	59.95 (3)	Cl1–Ta1–Cl2	88.00 (20)	Cl1–Ta1–Cl3	89.20 (20)
Cl1–Ta1–Cl4	162.87 (15)	Cl1–Ta1–O1	81.60 (50)	Cl1–Ta1–Ta1(i)	143.49 (10)
Cl1–Ta1–Ta1(iii)	53.49 (10)	Cl2–Ta1–Cl3	163.08 (19)	Cl2–Ta1–Cl4	89.08 (12)
Cl2–Ta1–O1	82.20 (50)	Cl2–Ta1–Ta1(i)	96.10 (14)	Cl2–Ta1–Ta2(i)	143.28 (13)
Cl2–Ta1–Ta1(iii)	95.64 (12)	Cl3–Ta1–Cl4	88.72 (14)	Cl3–Ta1–O1	80.90 (50)
Cl3–Ta1–Ta1(i)	96.08 (13)	Cl3–Ta1–Ta2(i)	53.63 (14)	Cl3–Ta1–Ta1(iii)	96.07 (15)
Cl4–Ta1–O1	81.30 (50)	Cl4–Ta1–Ta1(i)	53.64 (11)	Cl4–Ta1–Ta1(iii)	143.64 (12)
O1–Ta1–Ta1(i)	134.90 (50)	O1–Ta1–Ta2(i)	134.50 (50)	O1–Ta1–Ta1(iii)	135.10 (50)
Ta1–Ta2–Cl2	53.68 (14)	Ta1–Ta2–O2	136.50 (40)	Ta1–Ta2–Ta1(i)	60.02 (3)
Ta1–Ta2–Cl3(i)	95.95 (13)	Ta1–Ta2–Ta1(ii)	90.14 (4)	Ta1–Ta2–Cl3(ii)	143.63 (13)
Ta1–Ta2–Ta1(iii)	60.09 (3)	Ta1–Ta2–Cl2(iii)	95.92 (14)	Cl2–Ta2–O2	82.90 (50)
Cl2–Ta2–Ta1(i)	96.36 (11)	Cl2–Ta2–Cl3(i)	88.94 (18)	Cl2–Ta2–Ta1(ii)	143.82 (14)
Cl2–Ta2–Cl3(ii)	162.68 (19)	Cl2–Ta2–Ta1(iii)	95.92 (14)	Cl2–Ta2–Cl2(iii)	87.97 (16)
Ta1–Cl1–Ta1(iii)	73.02 (19)	Ta1–Cl2–Ta2	72.90 (13)	Ta1–Cl3–Ta2(i)	72.87 (15)
Ta1–Cl4–Ta1(i)	72.70 (20)	Ta1–O1–C1	130.10 (170)	Ta2–O2–C2	136.00 (300)
Ta1–Ta1(i)–Ta2	60.06 (3)	Ta1–Ta1(i)–Cl4	53.64 (11)	Ta1–Ta2(i)–Cl3	53.50 (13)
Ta1–Ta1(iii)–Ta2	59.95 (3)	Ta1–Ta1(iii)–Cl1	53.49 (10)		

[a] Symmetry operations: (i) $-x, y, -z$; (ii) $-x, y, -z + 1$; (iii) $-x, -y, -z + 1$; (iv) $x, -y, z$.

Table VI. Packing Interactions in the Crystal Structure of II

D–H···A	D···A, Å	symm operation on A
O1–H···Br2	3.03 (2)	x, y, z
O2–H···Br1	3.06 (2)	$x - 1, y, z$
O3–H1···O1	2.89 (2)	x, y, z
O3–H2···Br1	3.01 (2)	$^1/_2 + x - 1, ^1/_2 - y, z$ $^1/_2 + x - 1, ^1/_2 + y, z$
O3–H2···O3	2.96 (2)	$-x, y, -z$

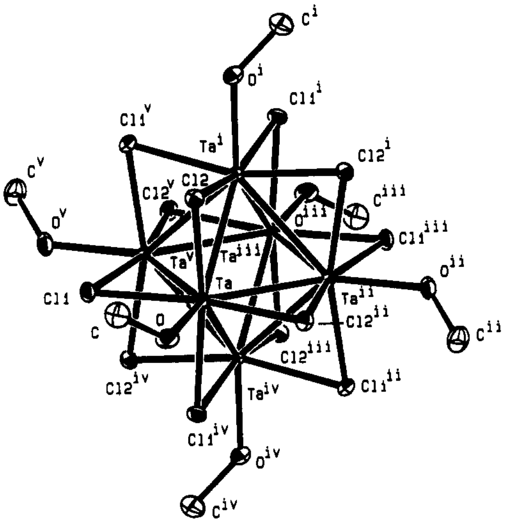

Figure 1. ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the $[Ta_6Cl_{12}(CH_3OH)_6]^{3+}$ cluster unit of compound I. The cluster unit is centered at a crystallographic site with $\bar{3}$ symmetry.

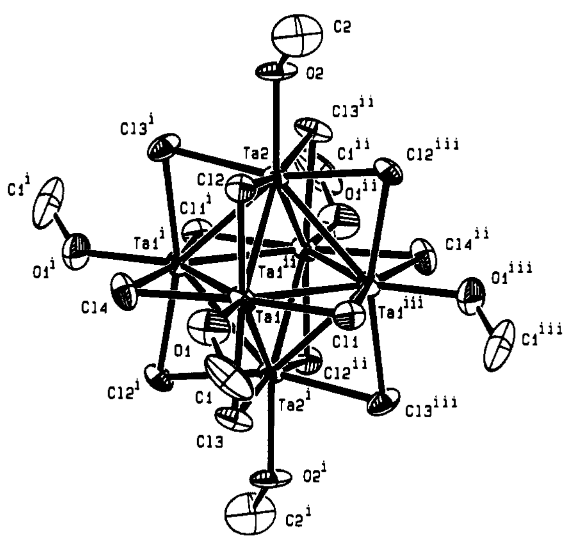

Figure 2. ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the cluster unit of compound II. The cluster unit occupies a site with $2/m$ symmetry, where the 2-fold axis passes through atoms Cl4 and Cl4^{ii}, and the mirror plane contains Ta2, Ta2^{i}, C2, O2, C2^{i}, O2^{i}, Cl1, and Cl1^{i}.

Table VII. Average Bond Distances (Å) for Compounds Containing the $[Ta_6Cl_{12}]^{3+}$ Cluster Unit

	I[a]	II[b]	III[c]	IV[d]	V[e]	VI[f]
Ta–Ta	2.9048 (1)	2.898 (1)	2.9059 (8)	2.940 (1)	2.942 (1)	2.925 (4)
Ta–Cl_b[g]	2.439 (2)	2.439 (5)	2.449 (2)	2.441 (4)	2.445 (3)	2.44 (1)
Ta–O	2.197 (5)	2.19 (2)	2.22 (2)			
Ta–Cl_t[h]				2.482 (6)	2.494 (3)	2.56 (2)
Ta–P				2.713 (5)	2.724 (3)	

[a] Compound I, this work. [b] Compound II, this work. [c] $NMe_4[Ta_6Cl_{12}(H_2O)_6]Br_4$, ref 3. [d] *cis*-$[(Ta_6Cl_{12})Cl_2(PEt_3)_4](BF_4)\cdot 3CH_2Cl_2$, ref 1. [e] *trans*-$[(Ta_6Cl_{12})Cl_2(PEt_3)_4](BF_4)\cdot CHCl_3$, ref 1. [f] $[Ta_6Cl_{12}]Cl_3$, ref 2. [g] Bridging chlorine. [h] Terminal chlorine.

of 2.21 (2) Å. The interatomic O···Br contacts were used to derive the hydrogen bonding system given in Table VI. The Br2 atoms should form bridges via O1–H···Br interactions between cluster units along $\vec{a}$, $\vec{b}$, and $\vec{c}$ directions. But because of partly occupied sites of Br2, this three-dimensional network is disconnected. The interaction O2–H···Br1 interconnects the clusters along $\vec{a}$. The water molecules included in the lattice complete the hydrogen bonding in $\vec{a}$ and $\vec{b}$ directions. One of the protons (H2) of the water molecule is involved in hydrogen bonds to three other atoms, O3(2×) and Br1(1×) (Table VI).

A comparison of average bond distances for all structures containing the $[Ta_6Cl_{12}]^{3+}$ cluster unit is given in Table VII. It is noted that the O-donor ligands in the terminal positions promote somewhat shorter Ta–Ta distances, by about 0.04 Å, than those observed when Cl- or P-donors occupy these positions. This is consistent with a weaker bonding between Ta and H_2O or CH_3OH, as reflected in the disproportionately long Ta–O distances of 2.19–2.22 Å in these cases. A radius of ca. 1.45 Å may be derived for Ta by subtracting the Pauling radius of Cl, 0.99 Å, from the nearly constant Ta–Cl_b distance of 2.44 Å in all of these compounds. Thus, to compare with the observed Ta–O distances, a distance for a Ta–O bond of normal strength may be estimated as about $r(Ta) + r(O) = 1.45$ Å + 0.66 Å = 2.11 Å. By this reasoning, the observed Ta–O distances are about 0.10 Å longer than normal, whereas the observed Ta–Cl_t distances are only

0.05 Å longer than that of a normal bond. The bulkier phosphine ligands of *cis*- and *trans*-$[(Ta_6Cl_{12})Cl_2(PEt_3)_4](BF_4)$ have Ta–P bond distances greatly elongated by about 0.16 Å. The steric effect here is enhanced by recession of the Ta atoms below the plane of the surrounding Cl_b atoms in the cluster unit. In the compound $[Ta_6Cl_{12}]Cl_3$, the bond distance Ta–Cl_t, 2.56 (2) Å, is unusually long compared to those in the phosphine complexes, 2.488 Å average, because the Cl_t atoms in the former compound are involved in bridging between cluster units, as indicated by the formula $[Ta_6Cl_{12}]Cl_{6/2}$, and this additional Ta–Cl–Ta bridge bonding causes an increase in the Ta–Cl_t distance, typically by about 0.1 Å.

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Supplementary Material Available: Listings of complete crystallographic parameters, tables of anisotropic temperature factors, and figures showing stereo illustrations of unit cells (8 pages). Ordering information is given on any current masthead page.