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Inorganic Chemistry Article

Gallium and Gallium Dichloride, New Solid-State Reductants in Preparative Transition Metal Chemistry. New, Lower Temperature Syntheses and Convenient Isolation of Hexatantalum Tetradecachloride Octahydrate, $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4.4H_2O$, and Synthesis and Solid-State Structure of a Tetraalkylammonium Derivative, $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$, of the Reduced $[Ta_6(\mu\text{-}Cl)_{12}]^{2+}$ Cluster Core[1]

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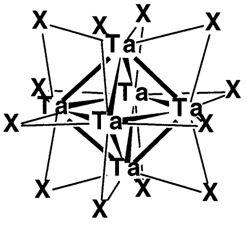
Reduction of $TaCl_5$ with either Ga or Ga_2Cl_4, in the presence of NaCl, in a sealed borosilicate glass ampule at 500 °C, followed by aqueous Soxhlet extraction and treatment with $SnCl_2$ and hydrochloric acid, yielded $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4{\cdot}4H_2O$ in 92% (Ga) or 96% (Ga_2Cl_4) yield. Ga_2Cl_4, a probable intermediate in the Ga-based reduction, is a more convenient reductant than Ga because it is readily dispersed in the reaction mixture, and these mixtures do not require homogenizations in order to afford high yields. $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4{\cdot}4H_2O$ was converted by ligand exchange to the first tetraalkylammonium derivative, $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$, of the reduced cluster core $Ta_6(\mu\text{-}Cl)_{12}^{2+}$, in 88% yield. $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$ crystallizes from 1,2-dichloroethane/toluene mixtures in two crystalline morphologies, a nonsolvated cubic form and a solvated needle form. The solid-state molecular structures of both crystalline morphologies of $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$ consist of octahedral, 16 VEC hexatantalum cluster anions with an average Ta–Ta distance of 2.900[2] Å, a Ta–Cl(bridge) distance of 2.463[2] Å, a Ta–Cl(terminal) distance of 2.567[5] Å, and a Ta–Cl–Ta angle of 72.1[1]° for the cubic form, and for the solvated needle morphology, an average Ta–Ta distance of 2.900[1] Å, a Ta–Cl(bridge) distance of 2.461[1]Å, a Ta–Cl(terminal) distance of 2.567[3] Å, and a Ta–Cl–Ta angle of 72.19[7]°.

Introduction

Octahedral, hexanuclear cluster halides of the mid-valent second- and third-row early transition metals are found in two distinct structural types[2] as either discrete molecular clusters or as clusters linked in extended arrays by halide bridges. Group 5 hexanuclear clusters usually possess one bridging halide (X) along each of the twelve octahedral edges (**1**), and a halide or other ligand in a terminal position (not depicted) on each metal. Typical Group 6 hexanuclear halide clusters differ by having face-bridging μ_3-halides in addition to terminal halides or other ligands.



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Hexatantalum tetradecachloride, Ta_6Cl_{14}, was first prepared[3] in 1907 by reduction of $TaCl_5$ with sodium amalgam and structurally characterized[4] in 1950. The $Ta_6(\mu\text{-}Cl)_{12}^{n+}$

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[1] Facile Reduction of Early Transition Metal Halides with Nonconventional, Mild Reductants. Part 5.

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cluster core unit has been isolated[5] in a variety of cluster oxidation states, with $n = 2-4$. Published synthetic approaches[6] rely on high-temperature solid-state reduction in quartz ampules (in one case,[7] by chemical transport) via either furnace or microwave[8] methods. The discrete, hydrated cluster derivative[9] $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ is obtained after lengthy aqueous extraction/reduction of the solid-state product. The most commonly used approach[10] to $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ involves reduction of $TaCl_5$ with a 4-fold excess of Ta powder at 700 °C, exhaustive extraction with substantial quantities of water (6 L for a ~40 g product scale reaction), filtration to remove finely divided Ta powder, addition of hydrochloric acid (6 L), and filtration of the resultant large volume to recover $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ (in 85% yield).

While anhydrous tetraalkylammonium salts of the discrete anion $Nb_6(\mu\text{-Cl})_{12}Cl_6^{4-}$ have been reported, no Ta analogues have been described. Tetraalkylammonium salts of $Ta_6(\mu\text{-Cl})_{12}Cl_6^{4-}$ would be potentially anhydrous and soluble in organic solvents, which would broaden the types of derivatives (e.g., alkyl complexes) that could be accessed in nonprotic solvents.

We recently reported several convenient, lower temperature, high-yield syntheses of the hexatungsten cluster compounds W_6Cl_{12} and $(H_3O)_2[W_6(\mu_3\text{-Cl})_8Cl_6](H_2O)_x$ by solid-state reduction of WCl_6 with the nonconventional reductants bismuth, antimony, and mercury.[11] This simple approach has been implemented in a local undergraduate inorganic synthesis lab course.[12] The known lower tungsten chloride[13] $(WCl_4)_x$, the new tungsten chloride clusters[14] W_3Cl_{10} and $Na_3W_3Cl_{13}$, and the known hexamolybdenum clusters Mo_6Cl_{12} and $(H_3O)_2[Mo_6(\mu_3\text{-Cl})_8Cl_6](H_2O)_x$[15] have been prepared by this lower temperature methodology. We therefore examined its utility in Group 5 cluster chemistry for the synthesis of Ta_6X_{14} derivatives, in part because of their potential as diagnostic medical X-ray contrast agents.[16,17] This new reduction method has been successfully applied[18] to the low-temperature synthesis and convenient isolation of $Ta_6(\mu\text{-Br})_{12}Br_2(OH_2)_4 \cdot 4H_2O$, a frequently used[19] high-electron-density cluster for phase determination by isomorphous replacement in biomacromolecular crystallography.

Herein, we describe (1) new lower temperature (500 °C), solid-state approaches to $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ via reduction of $TaCl_5$ with gallium or gallium dichloride (correctly formulated as $Ga^+(GaCl_4)^-$), (2) a simple isolation procedure for $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ based on Soxhlet extraction, (3) the first tetraalkylammonium salt of $Ta_6(\mu\text{-Cl})_{12}Cl_6^{4-}$, and (4) the solid-state structure of $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-Cl})_{12}Cl_6]$. The only previous mention of the use of Ga in hexatantalum chemistry was the unsuccessful attempt to isolate $Ga_4[Ta_6Cl_{18}]$ (other product(s), if any, were not identified) from reduction of $TaCl_5$ with a mixture of Ta powder and Ga at 550 °C or 750−800 °C.[20] While Ga_2Cl_4 has been used in kinetic studies[21] to reduce a variety of inorganic substrates in dilute solution, to our knowledge it has not been employed as a reductant in preparative-scale transition metal compound synthesis or early transition metal chemistry.

Experimental Section

General Methods. $TaCl_5$ (Cerac), Ga_2Cl_4 (Alfa/Aesar), $SnCl_2(OH_2)_2$ (Fisher Scientific), $N(CH_2Ph)Bu_3Cl$ (Fluka), hydrochloric acid (12 M, Fisher), HNO_3 (69.8%, Fisher), hydrogen peroxide (30%, Fisher), ethanol (100%, AAPER Alcohol), benzene (Fisher), DMSO (Omnisolv, EM Scientific), and diethyl ether (anhydrous, Fisher) were used as received. Dichloromethane (Fisher) and 1,2-dichloroethane (Fisher) were degassed and distilled from P_2O_5. Toluene (Fisher) was degassed and distilled from sodium/benzophenone. Gallium (99.999%, Atlantic Equipment Engineers, Bergenfield, NJ; phone 800-486-2436; cost \$0.95/g for 100 g) was converted into 1−2 mm diameter pellets by dropping small portions of molten Ga onto a cold glass surface and cooling the pellets overnight (in our case, at −40 °C, although 0 °C would be adequate; liquid gallium supercools readily and solidifies slowly with cooling). Ga_2Cl_4 was also prepared according to the method[22] of Schmidt et al. by reduction of $GaCl_3$ (Alfa/Aesar) with Et_3SiH (Aldrich). NaCl (Fisher) was dried at 200 °C overnight.

Air- and moisture-sensitive precursors were manipulated in a Vacuum Atmospheres glovebox under a N_2/He atmosphere. Solid-state syntheses were performed in Thermolyne model 21100 (≤1200 °C) with positionable thermocouple or Thermolyne model 79500 (≤1200 °C) tube furnaces, employing dual chamber 25 mm OD borosilicate glass ampules of 30−40 mL total chamber volume, with a 14/20 or 19/22 ground glass joint at one end and constriction between the end reaction chamber and receiver chamber and between the receiver chamber and ground joint. Ampules were oven dried at 130 °C overnight and then evacuated in the glovebox antechamber while cooling. Ga pellets were added to the ampule, and $TaCl_5$ and NaCl were mixed and then introduced into the ampule's end reaction chamber with use of a long stem funnel to minimize contamination of the constriction surface. In reductions employing Ga_2Cl_4, the $TaCl_5$, NaCl, and Ga_2Cl_4 were ground with a mortar and pestle prior to adding to the ampule. The ampule was capped with a gas inlet adapter, evacuated with a vacuum pump, and flame sealed under vacuum. The reactants were homogenized by shaking prior to heating.

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Unless otherwise stated, standard Schlenk techniques were employed. UV/vis spectra were recorded on aqueous or DMSO solutions with a Hewlett-Packard model 8452A diode array spectrophotometer. Powder X-ray diffraction was performed on a Siemens D5000 diffractometer. Single-crystal X-ray diffractometry was performed on a Nonius KappaCCD diffractometer with an Oxford Cryosystems model 7000 low-temperature unit. Analyses for C, H, N, Ta, and Cl were performed by Desert Analytics, Tucson, AZ, and Ta analyses were also performed as described below.

Preparation of $Ta_6Cl_{14}\cdot 8H_2O$ via Reduction of $TaCl_5$ with Gallium in the Presence of NaCl. A vacuum-sealed ampule with $TaCl_5$ (2.29 g, 6.41 mmol), Ga (0.40 g, 5.7 mmol), and NaCl (0.58 g, 10 mmol) in the end reaction chamber was placed in the center of a horizontal tube furnace at 100 °C for 15 min. The ampule was cooled, the mixture gently shaken (to disperse the gallium without causing agglomeration), and the ampule heated at 100 °C for 15 min. The ampule was removed and allowed to cool, and the contents homogenized by vigorous shaking. This 15-min heating/cooling/homogenization cycle was repeated an additional three times to give a dark granular mixture. The ampule was placed in a furnace inclined at a 45° angle and heated to 250 °C over 4 h and at 250 °C for 12 h. After cooling, the mixture was homogenized by shaking and the ampule heated to 500 °C over 4 h and at 500 °C for 24 h.

After cooling, the ampule was opened in air and the dark solid ground with a mortar and pestle to yield a forest-green powder that became tacky upon atmospheric water absorption. The powder was transferred to a coarse fritted glass Soxhlet thimble (25 mm × 85 mm) containing a layer of borosilicate glass wool, the end packed with borosilicate glass wool, and the thimble placed in a Soxhlet extractor. The apparatus was evacuated and backfilled with argon three times, and then the powder was extracted under argon (to minimize air oxidation) with ~125 mL of argon-degassed distilled H_2O for ~1 day. The green-black solution was filtered through Celite on a medium porosity fritted glass funnel to remove a white insoluble powder, identified as GaO_2H (a monohydrate of gallium oxide with the aluminum diaspore structure)[23,24] by powder X-ray diffraction with comparison to PDF Card Number 06-0180.

The green filtrate was converted to $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4\cdot 4H_2O$ by using an adaptation of a literature method.[10] A stannous chloride solution was prepared by dissolving $SnCl_2(OH_2)_2$ (1.24 g, 5.50 mmol, ~5-fold excess) in hydrochloric acid and then filtering to remove minor insolubles. The green filtrate was treated with ~200 mL of hydrochloric acid and approximately two-thirds of the $SnCl_2$ solution. The mixture was stirred and heated to near boiling, then cooled, and the remaining $SnCl_2$ solution and ~25 mL of hydrochloric acid were added. The mixture was cooled in an ice bath, then filtered to isolate the dark forest green precipitate, which was washed with ~60 mL of hydrochloric acid and ~60 mL of Et_2O. The solid was then dried in vacuo over P_2O_5 to yield 1.69 g of dark green $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4\cdot 4H_2O$ (92% yield based on $TaCl_5$). Anal. Calcd: Ta, 62.90; Cl, 28.75; Ga, 0.0. Found: Ta, 62.74; Cl, 28.70; Ga, <0.01. UV/vis (nm, water): 328, 398, 470 (sh ≡ shoulder), 636, 750. UV/vis (nm, DMSO): 336, 406, 648, 764. Literature (aqueous): 330, 398, 638, 748 nm;[8] 329, 398, 470 (sh), 637, 755 nm.[6]

Preparation of $Ta_6Cl_{14}\cdot 8H_2O$ via Reduction of $TaCl_5$ with Ga_2Cl_4 in the Presence of NaCl. An ampule with $TaCl_5$ (0.96 g, 2.7 mmol), Ga_2Cl_4 (1.00 g, 3.56 mmol), and NaCl (0.52 g, 8.9 mmol) in the end reaction chamber was placed in the center of a 45° inclined tube furnace and heated to 500 °C over 5 h and at 500 °C for 24 h. After cooling, the ampule was opened in air. The contents were ground, transferred to a coarse fritted glass Soxhlet thimble, and extracted as described above with degassed H_2O under argon for ~1 day (extraction is essentially complete in 5 h). The black-green extract was filtered through Celite to remove a fine white solid that was identified as GaO_2H by X-ray diffraction.

The dark black-green filtrate was converted to $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4\cdot 4H_2O$ as described above by using three equal, prefiltered portions of $SnCl_2(H_2O)_2$ (0.51 g total, 2.3 mmol, ~5-fold excess) dissolved in hydrochloric acid. The black-green filtrate was first treated with a portion of the $SnCl_2(H_2O)_2$ in ~10 mL hydrochloric acid and stirred. To this stirring mixture was added a second portion of $SnCl_2(H_2O)_2$ in ~150 mL of hydrochloric acid. The mixture was brought to a boil, cooled, and stirred while adding the final portion of $SnCl_2(H_2O)_2$ and ~25 mL of hydrochloric acid. The mixture was cooled in an ice bath and a dark forest green solid was recovered by filtration through a medium porosity fritted glass funnel. The solid was washed with ~50 mL of hydrochloric acid, ~50 mL of Et_2O, ~30 mL of hydrochloric acid, and ~30 mL of Et_2O and then dried in vacuo over P_2O_5 to yield 0.74 g of black $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4\cdot 4H_2O$ (96% yield based on $TaCl_5$). UV/vis (aqueous): 330, 400, 470 (sh), 638, 750 nm.

Preparation of $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-Cl})_{12}Cl_6]$. Synthesis of this tetraalkylammonium salt of $Ta_6(\mu\text{-Cl})_{12}Cl_6{}^{4-}$ was adapted from the method developed by McCarley[28] for the synthesis of $(NMe_4)_4[Nb_6Cl_{18}]$. In the glovebox, $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4\cdot 4H_2O$ (0.50 g, 0.29 mmol) was placed into a coarse fritted glass Soxhlet thimble in a Soxhlet extractor. A condenser with gas inlet and small empty flask were added and the apparatus was attached to the Schlenk line. In a 100 mL Schlenk flask, a solution of $N(CH_2Ph)Bu_3Cl$ (0.36 g, 1.1 mmol) in ~50 mL of 100% ethanol was degassed with argon via a gas dispersion tube for ~30 min. The Soxhlet apparatus was joined to the Schlenk flask (with PTFE sleeves) under argon and the $Ta_6(\mu\text{-Cl})_{12}Cl_2(OH_2)_4\cdot 4H_2O$ extracted under argon into the stirring $N(CH_2Ph)Bu_3Cl$/ethanol solution for ~17 h (the extraction was essentially complete after ~1 h), resulting in a dark green solution. The ethanol was removed under vacuum at 30 °C, and degassed benzene (~70 mL) was added to the dark forest green solid via cannula. A Dean-Stark trap was attached to the Schlenk flask and the solid dried via azeotropic distillation for ~21 h under argon. The remaining benzene was then removed under vacuum. The dark forest green solid was dissolved in a minimum of cold (−40 °C) CH_2Cl_2 in the glovebox and the resulting mixture filtered through Celite to remove a small amount of brown residue. The volume of the resulting green solution was reduced on a rotary evaporator and the solution cooled to −40 °C. On cooling, more of the brown residue was observed and removed by filtration. The green filtrate was treated dropwise with toluene (~25% of the solution volume) and the volume reduced by rotary evaporation until a brown precipitate was noted. The solution was filtered and the volume reduced by rotary evaporation until a clear supernatant was observed over a green solid. The supernatant was decanted and the solid washed with three 2-mL portions of toluene and dried

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in vacuo. Weight 0.72 g (88% yield). Anal. Calcd for $C_{38}H_{68}N_2Cl_9Ta_3$: C, 32.26; H, 4.84; N, 1.98; Cl, 22.55. Found: C, 32.14; H, 5.04; N, 2.04; Cl, 22.14.

Recrystallization from CH_2Cl_2 yielded mosaic crystals that were unsuitable for single-crystal X-ray diffraction. The solid (containing CH_2Cl_2 as solvate) was recrystallized by slow diffusion from 1,2-dichloroethane layered with toluene. The resulting crystals had two distinct morphologies, cubic and needlelike. By X-ray diffraction, the crystals of cubic appearance were nonsolvated and the needles were a solvate (vida infra).

Analytical Procedure for Tantalum. Tantalum was determined gravimetrically as the metal oxide Ta_2O_5. Samples were decomposed in tared borosilicate test tubes with concentrated nitric acid and hydrogen peroxide. The samples were dried and ignited.

Single-Crystal Diffractometry on $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$: Cubic Crystal Morphology. A dark green prism with a 0.42 × 0.29 × 0.23 mm^3 dimension was mounted via grease to the tip of a glass fiber (epoxied to a brass pin) and placed on the diffractometer with the long physical dimension of the crystal (corresponding to the *a* unit cell direction) approximately parallel to the diffractometer phi axis.

Data were collected on a Nonius KappaCCD diffractometer (Mo Kα radiation, graphite monochromator) at 190(2) K (cold N_2 gas stream), using standard CCD data collection techniques. Lorentz and polarization corrections were applied to the 20677 data. A correction for absorption using the multiscan technique was applied ($T_{\max} = 0.2787$, $T_{\min} = 0.1457$). Equivalent data were averaged yielding 10869 unique data ($R(\text{int}) = 0.020$, 10414, $F > 4\,\text{sig}(F)$). The space group $P\bar{1}$ was assigned on the basis of preliminary examination of the crystal. The computer programs from the HKLint package were used for data reduction, and structure refinement was performed with the SHELXTL v5.1 package.

The preliminary model of the structure was obtained with XS, a direct methods program. Least-squares refining of the model vs the data was performed with the XL program. Illustrations were made with the XP program and tables were made with the XCIF program. Thermal ellipsoids in the figures are at the 35% probability level.

All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were included with the riding model, using the XL program default values. No further restraints or constraints were imposed on the refinement model.

Single-Crystal Diffractometry on $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]\cdot(C_2H_4Cl_2)_3(CH_2Cl_2)_{0.5}(C_6H_5CH_3)_{0.5}$: Needle Crystal Morphology. A dark green prism with a 0.40 × 0.10 × 0.08 mm^3 dimension was mounted via grease to the tip of a glass fiber (epoxied to a brass pin) and placed on the diffractometer with the long physical dimension of the crystal (corresponding to the *c* unit cell direction) approximately parallel to the diffractometer phi axis.

Data were collected on a Nonius KappaCCD diffractometer (Mo Kα radiation, graphite monochromator) at 190(2) K (cold N_2 gas stream), using standard CCD data collection techniques. Lorentz and polarization corrections were applied to the 78473 data. A correction for absorption using the multiscan technique was applied ($T_{\max} = 0.6332$, $T_{\min} = 0.1876$). Equivalent data were averaged yielding 21153 unique data ($R(\text{int}) = 0.063$, 16260; $F > 4\,\text{sig}(F)$). The space group $P2_1/c$ was assigned on the basis of preliminary examination of the crystal. The same software packages as listed above were used.

All anion atoms were refined with anisotropic thermal parameters. Two cations (N3, C41−C59 and N4, C61−C79) were refined anisotropically. Two cations and three solvent sites exhibited disorder. In all cases (including disordered molecules) the H atoms were included as riding atoms. Treatment of the disorder is described in the Supporting Information.

Results and Discussion

Ga as Reductant in Tantalum Cluster Chemistry. Tantalum is a relatively difficult element to reduce from the pentavalent state, as this reduction usually requires alkali metals, aluminum, or tantalum itself. The reduction of $TaCl_5$ with Ga (eq 1) is a surprisingly facile, low-temperature route to hexatantalum chloride clusters. The 500 °C reaction temperature allows the use of borosilicate glass tubing and minimizes the reaction of tantalum chlorides with the glass. With a 45 h total reaction time, the yield of $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4\cdot 4H_2O$ after workup (vide infra) was 92%. Bismuth and antimony, which are effective in Group 6 cluster synthesis, were inadequate for $TaCl_5$ reduction under the reaction conditions (Bi, 255 °C; Sb, 180 °C) employed, and reduction with Ga at 400 °C resulted in lower yield.

$$18TaCl_5 + 16Ga + 28NaCl \rightarrow 3Na_4Ta_6Cl_{18} + 16NaGaCl_4 \tag{1}$$

Gallium is a relatively inexpensive reductant compared to Ta powder, especially if obtained from atypical chemical suppliers ($0.95/g from Atlantic Equipment Engineers; $22/reduction equivalent; if purchased from Cerac, Inc. at 99.99% purity, $5.00/g or $117/reduction equivalent). These costs are less than that for tantalum powder ($2.04/g for Ta powder, ≤2 μm particle size, Cerac, Inc.; $159/reduction equivalent for Ta(V) reduction to Ta(+2.33)). Ga is also used in a stoichiometric amount rather than in 4-fold excess as in the case of Ta powder reduction of $TaCl_5$.[10]

The only minor complications of Ga use as a reductant are its tendencies to agglomerate and to adhere to borosilicate glass. The homogenization steps are important for maximizing yield of $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4\cdot 4H_2O$, as homogenization results in more effective dispersal of the Ga throughout the reaction mixture.

Ga_2Cl_4 as Reductant in Tantalum Cluster Chemistry. We observed that Ga metal droplets became unobservable after one or two intermediate homogenizations, yet the yield of $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4\cdot 4H_2O$ was lowered with insufficient heating, so we postulated that the Ga metal was initially oxidized to an intermediate lower valent gallium chloride that was still effective in reduction of tantalum chlorides. Since Ga_2Cl_4 (actually, $Ga^+GaCl_4^-$) was a logical candidate, we examined the reduction of $TaCl_5$ with Ga_2Cl_4 (eq 2).

$$6TaCl_5 + 8Ga_2Cl_4 + 20NaCl \rightarrow Na_4Ta_6Cl_{18} + 16NaGaCl_4 \tag{2}$$

These reductions were notably less labor-intensive: homogenization of the reaction mixture during heating was unnecessary because Ga_2Cl_4 was readily dispersed throughout the solid-state mixture. Ga_2Cl_4 is considerably more expensive than Ga if purchased directly but can be prepared readily from $GaCl_3$ and Et_3SiH. Workup (vide infra) of Ga_2Cl_4-based reductions gave $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4\cdot 4H_2O$ in a virtually quantitative 96% yield based on $TaCl_5$.

Other Synthesis and Isolation Details. Since $TaCl_5$ and Ga_2Cl_4 are moisture sensitive, and gallium is slowly oxidized by air, the ampules are best prepared under an inert atmosphere. While we employed a glovebox for the ampule loadings, a well-purged glovebag with a top-loading balance is adequate for this initial step.

Soxhlet extraction is a straightforward, easy method for isolating $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4{\cdot}4H_2O$ from the solid-state reduction product and byproduct, believed to be $Na_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$ and $NaGaCl_4$. Soxhlet extraction minimizes the labor and solution volume needed for effective extraction. A subsequent filtration removes hydrated gallium oxides that are formed by slow hydrolysis of gallium chlorides. We were unable, under the conditions employed, to sublime $GaCl_3$ from mixtures lacking NaCl, as such mixtures exhibited chemical transport of colored Ta-containing volatiles along with some $GaCl_3$. The NaCl thus serves several roles by (1) providing the added chloride ligands to form discrete hexatantalum clusters, (2) complexing $GaCl_3$, and (3) complexing to intermediate tantalum chlorides and rendering them involatile under the low-temperature reaction conditions.

Since $Ta_6(\mu\text{-}Cl)_{12}{}^{n+}$ clusters with various terminal ligands are known in a variety of oxidation states, and can be readily oxidized in solution upon exposure to air, we took precautions to exclude air during Soxhlet extraction and subsequent workup and employed stannous chloride as a solution reductant. To verify that the isolated cluster compound was the fully reduced form (i.e., with a $Ta_6(\mu\text{-}Cl)_{12}{}^{2+}$ core) by UV−vis spectrophotometry, we deliberately oxidized the emerald green cluster compound with dioxygen in acidified aqueous solution, reexamined the UV−vis spectrum to verify oxidation via spectral changes, and then rereduced the compound with $SnCl_2$. The final UV−vis spectrum matched that of the initially isolated $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4{\cdot}4H_2O$. The UV−vis spectrum in DMSO of the originally isolated $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4{\cdot}4H_2O$ also showed no change upon addition of $SnCl_2$.

Solid $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4{\cdot}4H_2O$ slowly oxidizes in air to yield a brown solid whose UV−vis spectrum in DMSO correspnds to that of oxidized cluster; the oxidized cluster can be rereduced back to emerald green $Ta_6(\mu\text{-}Cl)_{12}{}^{2+}$ in DMSO with $SnCl_2$. The oxidized cluster has very low solubility in water and can be removed by filtration combined with reduction of solutions with stannous chloride. Therefore, solid $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4{\cdot}4H_2O$ should be stored under inert atmosphere.

Synthesis of a Tetraalkylammonium Salt of the Reduced Cluster $[Ta_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$. Tetraalkylammonium salts of cluster compounds, with their potential solubility in organic solvents, are plausible synthons for new types of cluster compounds. Several organic cation salts of the oxidized clusters $[Ta_6(\mu\text{-}Cl)_{12}Cl_6]^{n-}$ ($n = 2, 3$) have been reported.[25−27] A number of inorganic cation salts of the reduced cluster $[Ta_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$ are known, but in contrast to the case of hexaniobium chloride clusters, no tetraalkylammonium salts have been reported. We therefore adapted McCarley's method[28] for tetraalkylammonium derivatives of $[Nb_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$ to $[Ta_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$. $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4{\cdot}4H_2O$ can be extracted into ethanol containing $N(CH_2Ph)Bu_3Cl$ and the water removed by azeotropic distillation, yielding $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$ in 88% yield with appropriate anaerobic technique.

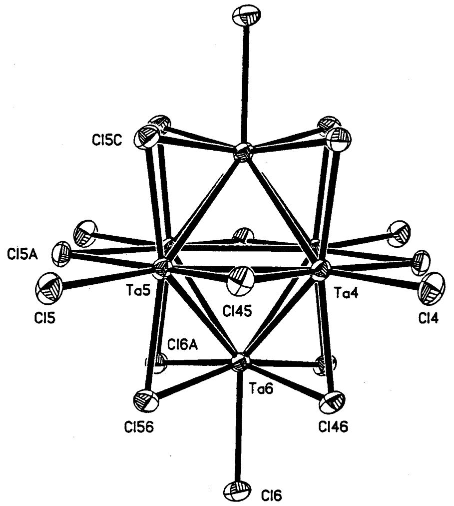

Figure 1. Thermal ellipsoid plot of the molecular structure of the cluster anion portion of nonsolvated $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$, showing the atom numbering scheme.

Table 1. Crystal Data and Refinement Results for Nonsolvated $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$ and Solvated $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]{\cdot}(C_2H_4Cl_2)_3(CH_2Cl_2)_{0.5}(C_6H_5CH_3)_{0.5}$ Crystalline Forms

form	nonsolvated	solvated
formula	$C_{76}H_{136}Cl_{18}N_4Ta_6$	$C_{86}H_{152}Cl_{25}N_4Ta_6$
fw	2829.69	3215.07
space group (no.)	$P\bar{1}$ (2)	$P2_1/c$ (14)
a (Å)	12.9703(6)	27.259(6)
b (Å)	14.0317(8)	14.319(3)
c (Å)	14.0542(8)	30.788(6)
α (deg)	69.074(3)	90
β (deg)	83.616(3)	106.26(3)
γ (deg)	82.896(3)	90
V (Å^3)	2364.5(2)	11536(4)
Z	1	4
T (K)	190(2)	190(2)
λ (Å)	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	1.987	1.851
μ (mm^{-1})	7.462	6.287
$R_1{}^a$	0.0216	0.0377
w$R_2{}^b$	0.0512	0.0834

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $I > 2\sigma(I)$. [b] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$ for $I > 2\sigma(I)$.

Solid-State Molecular Structures of $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$. Figure 1 shows the thermal ellipsoid plot for the cubic morphology, nonsolvated form of $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$. Tables 1 and 2 list data collection parameters and chemically significant bond distances and bond angles, respectively, for both crystalline morphologies. The compound crystallizes in the triclinic space group $P\bar{1}$ for the nonsolvated form, with the octahedral metal cluster on the inversion center so that half of the cluster and two tetraalkylammonium cations are generated by inversion. The cluster has the expected octahedral $Ta_6(\mu\text{-}Cl)_{12}Cl_6{}^{4-}$ cluster structure, with an average Ta−Ta distance of 2.900[2] Å (numbers in square brackets represent the standard deviation

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Nonsolvated and Solvated Crystalline Forms of $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$[a]

crystalline form	nonsolvated		solvated	
Ta−Ta	Ta(1)−Ta(2)	2.8968(2)	Ta(1)−Ta(2)	2.8929(6)
	Ta(2)−Ta(3)	2.9081(2)	Ta(2)−Ta(3)	2.8960(7)
	Ta(1)−Ta(3)	2.9030(2)	Ta(1)−Ta(3)	2.8946(8)
	Ta(1)−Ta(3)#1	2.8970(2)	Ta(1)−Ta(2)#1	2.9085(7)
	Ta(2)−Ta(1)#1	2.8981(2)	Ta(1)−Ta(3)#1	2.9031(6)
	Ta(2)−Ta(3)#1	2.8982(2)	Ta(2)−Ta(3)#1	2.9078(6)
			Ta(4)−Ta(5)	2.9001(6)
			Ta(4)−Ta(5)#2	2.8980(7)
			Ta(4)−Ta(6)#2	2.9001(7)
			Ta(5)−Ta(6)	2.8921(7)
			Ta(4)−Ta(6)	2.9018(7)
			Ta(5)−Ta(6)#2	2.9011(7)
Ta−Cl(terminal)	Ta(1)−Cl(1)	2.5579(7)	Ta(1)−Cl(1)	2.554(1)
	Ta(2)−Cl(2)	2.5764(8)	Ta(2)−Cl(2)	2.569(1)
	Ta(3)−Cl(3)	2.5657(8)	Ta(3)−Cl(3)	2.566(2)
			Ta(4)−Cl(4)	2.567(2)
			Ta(5)−Cl(5)	2.572(1)
			Ta(6)−Cl(6)	2.572(2)
Ta−μ-Cl	Ta(1)−Cl(12)	2.4716(7)	Ta(1)−Cl(12)	2.463(1)
	Ta(1)−Cl(13)	2.4613(7)	Ta(1)−Cl(13)	2.457(2)
	Ta(1)−Cl(3A)#1	2.4686(7)	Ta(1)−Cl(1B)	2.451(1)
	Ta(1)−Cl(2A)#1	2.4616(7)	Ta(1)−Cl(1C)	2.463(2)
	Ta(2)−Cl(12)	2.4705(7)	Ta(2)−Cl(12)	2.470(1)
	Ta(2)−Cl(23)	2.4593(7)	Ta(2)−Cl(23)	2.461(2)
	Ta(2)−Cl(2A)	2.4593(7)	Ta(2)−Cl(1B)#1	2.451(1)
	Ta(2)−Cl(2C)	2.4642(7)	Ta(2)−Cl(2C)	2.470(2)
	Ta(3)−Cl(13)	2.4553(7)	Ta(3)−Cl(13)	2.464(1)
	Ta(3)−Cl(23)	2.4527(8)	Ta(3)−Cl(23)	2.454(1)
	Ta(3)−Cl(3A)	2.4674(7)	Ta(3)−Cl(1C)#1	2.467(1)
	Ta(3)−Cl(2C)#1	2.4616(8)	Ta(3)−Cl(2C)#1	2.469(1)
			Ta(4)−Cl(45)	2.458(1)
			Ta(4)−Cl(46)	2.459(2)
			Ta(4)−Cl(5A)#2	2.459(1)
			Ta(4)−Cl(6A)#2	2.458(2)
			Ta(5)−Cl(45)	2.455(2)
			Ta(5)−Cl(56)	2.467(2)
			Ta(5)−Cl(5A)	2.459(1)
			Ta(5)−Cl(5C)	2.469(2)
			Ta(6)−Cl(46)	2.460(2)
			Ta(6)−Cl(56)	2.457(1)
			Ta(6)−Cl(5C)#2	2.465(1)
			Ta(6)−Cl(6A)	2.460(2)
Ta−Cl−Ta	Ta(1)−Cl(12)-Ta(2)	71.77(2)	Ta(1)−Cl(12)-Ta(2)	71.82(4)
	Ta(1)−Cl(13)-Ta(3)	72.38(2)	Ta(1)−Cl(13)-Ta(3)	72.06(4)
	Ta(1)#1-Cl(2A)-Ta(2)	72.16(2)	Ta(2)−Cl(23)-Ta(3)	72.21(4)
	Ta(1)#1-Cl(3A)-Ta(3)	71.88(2)	Ta(1)−Cl(1B)-Ta(2)#1	72.79(4)
	Ta(2)−Cl(23)-Ta(3)	72.60(2)	Ta(1)−Cl(1C)-Ta(3)#1	72.14(4)
	Ta(2)−Cl(2C)-Ta(3)#1	72.08(2)	Ta(2)−Cl(2C)-Ta(3)#1	72.13(4)
			Ta(4)−Cl(45)-Ta(5)	72.36(4)
			Ta(4)−Cl(46)-Ta(6)	72.31(4)
			Ta(5)−Cl(56)-Ta(6)	71.94(4)
			Ta(5)−Cl(5C)-Ta(6)#2	72.03(4)
			Ta(4)#2-Cl(5A)-Ta(5)	72.21(4)
			Ta(4)#2-Cl(6A)-Ta(6)	72.26(4)

[a] Symmetry operations used to generate equivalent atoms: #1, −*x*, −y + 1, −*z* + 1; #2, −*x* + 1, −*y* + 1, −*z* + 1.

of the mean[29]), a Ta−Cl(bridge) distance of 2.463[2] Å, a Ta−Cl(terminal) distance of 2.567[5] Å, and a Ta−Cl−Ta angle of 72.1[1]°. The solvated needle morphology, which is of the formula $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]\cdot(C_2H_4Cl_2)_3(CH_2Cl_2)_{0.5}(C_6H_5CH_3)_{0.5}$ and crystallizes in the $P2_1/c$ space group, exhibited some disorder for the solvate and cation molecules. Figures 2 and 3 show the crystallographically independent cluster anions for the solvated morphology, to illustrate the atom numbering scheme. The cluster anions, well-ordered crystallographically, exhibited nearly identical metrical parameters to those for the nonsolvated cubic crystalline form, with an average Ta−Ta distance of 2.900[1] Å, a Ta−Cl(bridge) distance of 2.461[1] Å, a Ta−Cl(terminal) distance of 2.567[3] Å, and a Ta−Cl−Ta angle of 72.19[7]°. These values for both crystalline forms are very similar to averaged parameters for other structurally characterized clusters with $Ta_6(\mu\text{-}Cl)_{12}^{2+}$ cores, such as the hydrate[30] $Ta_6Cl_{14}\cdot 7H_2O$ (Ta−Ta, range 2.63−3.27 Å, average 2.96 Å), $H_4Ta_6Cl_{12}(CN)_6\cdot 12H_2O$[31] (Ta−Ta, 2.932(1) Å; Ta-μ-Cl, 2.44(1) Å; Ta−Cl−Ta, 73.6(4)°), $Ta_6Cl_{12}Cl_2(PEt_3)_4$[32]

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[29] The value in brackets, the standard deviation of the mean, equals $[(\Sigma_m \Delta_i^2)/m(m-1)]^{1/2}$ with Δ_i defined as the deviation from the mean of the *i*th value in a set of *m* values.

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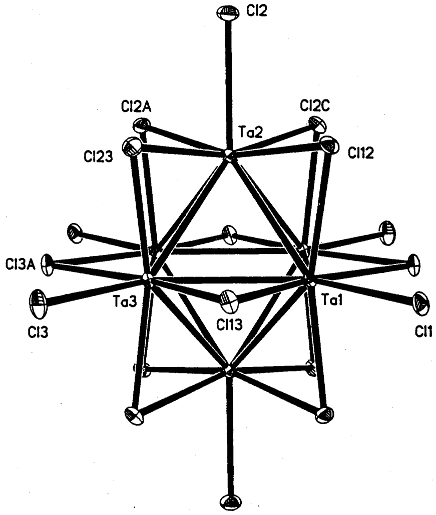

Figure 2. Thermal ellipsoid plot of the molecular structure of one of the crystallographically independent cluster anion portions of solvated $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]\cdot(C_2H_4Cl_2)_3(CH_2Cl_2)_{0.5}(C_6H_5CH_3)_{0.5}$, showing the atom numbering scheme.

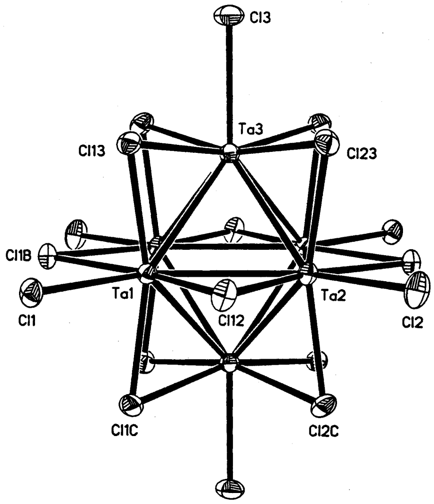

Figure 3. Thermal ellipsoid plot of the molecular structure of the other crystallographically independent cluster anion portion of solvated $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]\cdot(C_2H_4Cl_2)_3(CH_2Cl_2)_{0.5}(C_6H_5CH_3)_{0.5}$, showing the atom numbering scheme.

(Ta−Ta, 2.901 Å; Ta-μ-Cl, 2.462 Å; Ta−Cl(terminal), 2.531 Å), $Cs_2PbTa_6Cl_{18}$[33] (Ta−Ta, 2.888(1) Å; Ta-μ-Cl, 2.462(2) Å; Ta−Cl(terminal), 2.595(2) Å), $In_4Ta_6Cl_{18}$[34] (Ta−Ta, 2.889 Å; Ta-μ-Cl, 2.466 Å; Ta−Cl(terminal), 2.591 Å), $CsErTa_6Cl_{18}$[35] (Ta−Ta, 2.874 Å; Ta-μ-Cl, 2.463 Å; Ta−Cl(terminal), 2.691 Å), the cluster cation[36] in $[Ta_6Cl_{12}(PrCN)_6]^{2+}[Ta_6Cl_{12}Cl_6]^{2-}$ (Ta−Ta, 2.8700 Å; Ta-μ-Cl, 2.458 Å), and the cluster cation[37] in $[Ta_6Cl_{12}EtOH)_6]^{2+}[Mo_6Cl_8Cl_6]^{2-}$ (Ta−Ta, 2.872 Å; Ta−μ-Cl, 2.464 Å).

Neither the nonsolvated nor the solvated forms showed any close contacts between the tetraalkylammonium cations and the hexatantalum chloride anions, and the solvated form showed no close contacts between the disordered solvate molecules and either the cations or cluster anions.

Conclusion

Gallium and Ga_2Cl_4 are convenient reductants for the direct reduction of $TaCl_5$ to hexatantalum chlorides at significantly lower temperature compared to other methods, and we believe that Ga and Ga_2Cl_4 will prove to be useful reductants in preparative early transition metal chemistry. Reduction of $TaCl_5$ with Ga at 500 °C over 2 days in borosilicate glass tubing affords $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4\cdot 4H_2O$ in 92% yield after aqueous Soxhlet extraction and precipitation with hydrochloric acid; the corresponding yield starting with Ga_2Cl_4 is 96%. Ga is a less expensive reductant than the Ta powder used in other, high-temperature methods of preparation. The $GaCl_3$ byproduct, were it to be liberated during reduction instead of associated with the reaction products, has significantly lower vapor pressure than that exhibited by $AlCl_3$ in Al-based reduction methods. Ga- and Ga_2Cl_4-based routes are thus inherently safer than other approaches that can lead to ampule rupture from internal overpressure. Ga_2Cl_4, while more expensive if purchased rather than prepared from Ga and Et_3SiH or Ga and $GaCl_3$,[38] is the more convenient reductant as rehomogenizations of the solid-state mixture at intermediate reduction stages are unnecessary. Aqueous Soxhlet extraction of the solid-state reduction product is a convenient, easy workup procedure for formation and isolation of the hydrated cluster, $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4\cdot 4H_2O$. $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4\cdot 4H_2O$ can be converted to the anhydrous, chlorocarbon-soluble tetraalkylammonium derivative $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$ in 88% yield by Soxhlet-assisted ligand exchange with $N(CH_2Ph)Bu_3{}^+Cl^-$. The solid-state molecular structures of the two crystalline morphologies of $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$, which represent the first structure determinations of the reduced $Ta_6(\mu\text{-}Cl)_{12}Cl_6{}^{4-}$ cluster with an organic cation, have the expected M_6Y_{18} octahedral metal cluster structure by analogy to the Nb analogue, with average Ta−Ta distances of 2.900[2] and 2.900[1] Å that are very similar to structurally characterized salts of $Ta_6(\mu\text{-}Cl)_{12}Cl_6{}^{4-}$ with inorganic cations.

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Supporting Information Available: Crystallographic data and refinement details, alternate thermal ellipsoid plots including cations and solvate molecules, fractional coordinates, anisotropic thermal parameters, CIF files, and tables of bond lengths and angles for both crystalline forms of $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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