Chapter One

TRANSITION METAL HALIDE COMPOUNDS

1. OCTAHEDRAL HEXATANTALUM HALIDE CLUSTERS

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Octahedral hexatantalum halide clusters usually exist as extended structures of the form $Ta_6(\mu\text{-}X)_{12}X_2$ with terminal (outer) and bridging (inner) halogen atoms shared between clusters, or as discrete clusters such as $Ta_6(\mu\text{-}X)_{12}X_2 \cdot 8H_2O$ that are better formulated as $Ta_6(\mu\text{-}X)_{12}X_2(OH_2)_4 \cdot 4H_2O$. These clusters consist of six tantalums linked through Ta−Ta bonding to form a Ta_6 octahedron with a halide bridge along each of the 12 octahedral edges and one terminal ligand (halide, water, etc.) located apically on each tantalum.[1] A range of cluster oxidation states have been reported.[2]

Ta_6Cl_{14} was first reported in 1907 from the reduction of Ta_2Cl_{10} (denoted as $TaCl_5$ hereafter) with sodium amalgam,[3] and its structure was determined in 1950.[4] It is prepared typically by high-temperature, solid-state reduction of $TaCl_5$ in vacuum-sealed quartz ampules.[5] Microwave heating has also been employed.[6] Extraction with large volumes of water gives good yields of the discrete cluster[7] $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ after aqueous reduction of oxidized cluster contaminants with $SnCl_2$. The most commonly used approach is that developed by Koknat et al., involving reduction at 700°C of $TaCl_5$ with a four-fold excess of Ta powder.[8]

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Inorganic Syntheses, Volume 36, First Edition. Edited by Gregory S. Girolami and Alfred P. Sattelberger.

Ta_6Br_{14} was first prepared in 1910 by sodium amalgam reduction of $TaBr_5$.[3b] It has since been prepared by using the reductants aluminum[5a] and excess tantalum[8a] and can be isolated by aqueous extraction as the discrete cluster $Ta_6(\mu\text{-}Br)_{12}Br_2(OH_2)_4 \cdot 4H_2O$.[2a,b] A sample was structurally characterized as $[Ta_6(\mu\text{-}Br)_{12}(OH_2)_6](OH)Br \cdot 4H_2O$,[9] and another structure of the hexaaquo ion $[Ta_6(\mu\text{-}Br)_{12}(OH_2)_6]^{2+}$ was recently reported.[10]

There is considerable interest in the coordination[11] and catalytic[12] chemistries of these discrete clusters. Because of its high electron count, the hexaaquo ion $[Ta_6(\mu\text{-}Br)_{12}(OH_2)_6]^{2+}$ has been used frequently for phase determination[9,13] of isomorphous protein derivatives by SIR, MIR, SIRAS/MIRAS, and SAD/MAD methods in biomacromolecular crystallography. This use is growing as larger biomacromolecular structures and assemblies (e.g., membrane proteins, ribosomes, proteasomes) are studied.

We have found that the main group metal and metalloid reductants mercury, bismuth, and antimony are highly effective[14] in reducing WCl_6 or $MoCl_5$ at surprisingly lower temperatures than commonly used in the solid-state synthesis of early transition metal cluster halides. Borosilicate ampules can be substituted for the more expensive and less easily sealed quartz ampules at these lower temperatures, and the metals and metalloids are not as impacted by oxide coatings that inhibit solid-state reactions with more active metals. These lower temperatures may allow access to kinetic products, such as trinuclear clusters, instead of thermodynamic products.

We report here an extension of this reduction methodology to the convenient preparation[15] of $Ta_6(\mu\text{-}X)_{12}X_2(OH_2)_4 \cdot 4H_2O$ by reduction of TaX_5 with gallium dichloride, $Ga^+GaCl_4^-$ (for $X = Cl$), or gallium (for $X = Br$). Gallium dichloride has not been used as a preparative-scale reductant in transition metal chemistry. Gallium is an effective reductant, but because of its tendency to agglomerate and to adhere to glass, reductions employing Ga need to be agitated several times during the course of the reaction in order to optimize yields by homogenization of reactants. We have not yet tested the use of gallium dibromide as a reductant for $TaBr_5$, but expect that it would eliminate the need to homogenize reactants in gallium-based reductions and might improve the yield. The aquated hexatantalum clusters are liberated from the solid-state products by Soxhlet extraction with water, which greatly simplifies the isolation procedure. We also describe the straightforward preparation of a tetraalkylammonium derivative of the $[Ta_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$ anion that has solubility in a broader array of organic solvents than the aquated clusters.

General Procedures

TaX_5 ($X = Cl$, Br; Materion Advanced Chemicals, Milwaukee, WI), hydrochloric acid (12 M, Fisher Scientific), Ga (99.99%, Atlantic Equipment Engineers, Bergenfield, NJ), NaCl (Fisher), KBr (Aldrich Chemical), $SnCl_2 \cdot 2H_2O$ (Fisher), $SnBr_2$ (99.5%, Alfa Aesar), HBr (48%, Fisher), and diethyl ether (anhydrous, Fisher) are used as received. $Ga^+GaCl_4^-$ is purchased and used as received from

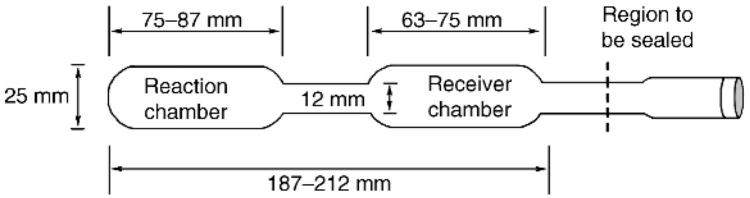

Figure 1. Ampule design for solid-state syntheses.

Alfa Aesar or is prepared by a literature method.[16] Powder X-ray diffraction is performed on samples protected from moisture by a 5 μm polyethylene film. Reactants and solid-state products are handled in a glove box under a dinitrogen atmosphere. A tube furnace with a positionable thermocouple is used in conjunction with a temperature controller in order to maintain and ramp temperatures. Syntheses are performed in dual-chamber, 25 mm OD borosilicate glass ampules with 30–40 mL total chamber volume, a 14/20 ground glass joint at one end, and constrictions between the end reaction chamber and middle receiver chamber (for volatile by-products) and between the middle receiver chamber and ground joint (Fig. 1). Ampules are oven dried at 130°C overnight and brought directly while hot into the glove box and cooled under vacuum or dinitrogen. Reactants are thoroughly mixed (employing a vortex mixer to agitate the reactants in a 20 mL glass scintillation vial) and added to the end reaction chamber via a long-stem funnel that minimizes contamination of the constriction surfaces. A gas inlet adapter* is used to seal the ampule, which is then evacuated on a Schlenk line and flame sealed between the joint and receiver chamber.

Tantalum is determined gravimetrically as the metal oxide Ta_2O_5. Samples are decomposed in tared borosilicate test tubes using concentrated nitric acid and hydrogen peroxide. The samples are dried and ignited. Other analyses are performed by Desert Analytics, Tucson, AZ.

A. TETRADECACHLOROHEXATANTALUM OCTAHYDRATE

$$6TaCl_5 + 8Ga^+GaCl_4^- + 20NaCl \rightarrow Na_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6] + 16NaGaCl_4$$

$$Na_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6] + 8H_2O \rightarrow Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O + 4NaCl$$

Procedure

A vacuum-sealed 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 is placed

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*The checkers recommend that a quick-fit be used here to simplify the procedure.

in the center of a 45° inclined tube furnace. The furnace is slowly heated to 500°C over 4 h and kept at 500°C for 24 h. After being cooled, the ampule is opened in air and the dark solid is ground to a green powder with a mortar and pestle. The hygroscopic green powder is transferred to a coarse fritted glass Soxhlet thimble (25 mm × 50 mm), containing a layer of borosilicate wool, the end packed with borosilicate wool, and the thimble is placed in a Soxhlet extractor. The apparatus is evacuated and backfilled with argon three times, and the powder is extracted (under argon to minimize air oxidation) for 17 h with argon-degassed distilled water (120 mL). The dark green solution is filtered through a medium-porosity fritted glass funnel in air, in order to remove insoluble white GaO(OH) powder (identified by powder X-ray diffractometry, matching PDF Card Number 06-0180). A solution of $SnCl_2 \cdot 2H_2O$ (1.0 g, 4.5 mmol) in 12 M hydrochloric acid (150 mL) is filtered to remove insoluble material, and a portion of this solution is added to the dark green filtrate, which is stirred and heated to near boiling, then cooled, and the remaining stannous chloride solution added. This step reduces any oxidized cluster contaminants to $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O$. The mixture is cooled in an ice bath, and the dark emerald green solid product is collected on a medium-porosity fritted glass funnel. The solid is washed with hydrochloric acid (20 mL), diethyl ether (30 mL), and dried in vacuum. Yield: 0.75 g (95%).

Anal. Calcd. for $H_{16}Cl_{14}O_8Ta_6$: Ta, 62.90; Cl, 28.75; Ga, 0.0. Found: Ta, 62.74; Cl, 28.70; Ga, <0.01.

Properties

$Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ is soluble in water, DMSO, and methanol. The solutions are an intense emerald green. UV–vis (water): 330, 400, 470 (sh), 638, 750 nm. Solid $[Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4] \cdot 4H_2O$ and its aqueous solutions are slowly oxidized by air to hexatantalum clusters with higher oxidation states. Stannous chloride is a convenient solution reductant, as it quickly reduces contaminant levels of $[Ta_6(\mu\text{-}Cl)_{12}(OH_2)_6]^{3+}$ and $[Ta_6(\mu\text{-}Cl)_{12}(OH_2)_6]^{4+}$ back to $[Ta_6(\mu\text{-}Cl)_{12}(OH_2)_6]^{2+}$.

B. TETRADECABROMOHEXATANTALUM OCTAHYDRATE

$$18TaBr_5 + 16Ga + 28KBr \rightarrow 3K_4[Ta_6(\mu\text{-}Br)_{12}Br_6] + 16KGaBr_4$$

$$K_4[Ta_6(\mu\text{-}Br)_{12}Br_6] + 8H_2O \rightarrow Ta_6(\mu\text{-}Br)_{12}Br_2(OH_2)_4 \cdot 4H_2O + 4KBr$$

Procedure

A vacuum-sealed ampule with $TaBr_5$ (7.5 g, 12.9 mmol), Ga (0.80 g, 11.4 mmol), and KBr (2.39 g, 19.9 mmol) in the end reaction chamber is placed in the center of a

270°C preheated horizontal tube furnace and heated for 20 min. After being cooled to room temperature, the reactants/products are homogenized by gentle shaking, and this heating and homogenization cycle is repeated two times in order to disperse the molten gallium throughout the reaction mixture. The ampule is then placed in a tube furnace inclined to 45° and heated to 300°C over 1 h and held at that temperature for 12 h. The furnace is turned off and allowed to cool to room temperature. The ampule is removed from the furnace and the products are homogenized by vigorous shaking to give a dark green granular powder. The ampule is returned to the inclined furnace, heated to 400°C in 1 h, and held at that temperature for 24 h. The ampule is removed from the furnace, allowed to cool to room temperature, and opened in air. The dark solid is ground with a mortar and pestle to a dark green powder. The green powder is extracted by Soxhlet extraction with degassed water (170 mL) under argon for 24 h, as described above for $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O$. The resulting dark green solution is filtered through a medium-porosity fritted glass funnel in order to remove insoluble white GaO(OH) (as confirmed by powder X-ray diffractometry) powder. The dark green filtrate is treated with a filtered solution of $SnBr_2$ (3.1 g) dissolved in 48% hydrobromic acid (200 mL) to convert any oxidized species to $Ta_6(\mu\text{-}Br)_{12}Br_2(OH_2)_4 \cdot 4H_2O$, as described above for $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O$. The mixture is cooled in an ice bath and filtered through a medium-porosity fritted glass funnel. The dark green solid is washed with 48% hydrobromic acid (30 mL) followed by diethyl ether (30 mL). Yield: 4.15 g (86%).

Anal. Calcd. for $H_8Br_{14}O_8Ta_6$: Ta, 46.23; Br, 47.63. Found: Ta, 46.8; Br, 48.22.

Properties

$Ta_6(\mu\text{-}Br)_{12}Br_2(OH_2)_4 \cdot 4H_2O$ has solubility characteristics similar to the chloride analog. Solutions are an intense emerald green. UV–vis (water): 350, 420, 496 (sh), 638, 748 nm.

C. TETRAKIS(BENZYLTRIBUTYLAMMONIUM) OCTADECACHLOROHEXATANTALATE

$$Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O + 4[N(CH_2Ph)Bu_3]Cl$$
$$\rightarrow [N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6] + 8H_2O$$

Procedure

The synthesis of this tetraalkylammonium salt of $[Ta_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$ is adapted from the method developed by McCarley[17] for the synthesis of

$(NMe_4)_4[Nb_6Cl_{18}]$.[*] In a glove box (a glove bag would be sufficient), $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ (0.50 g, 0.29 mmol) is placed into a coarse porosity fritted glass Soxhlet thimble in a Soxhlet extractor. A condenser with gas inlet and small empty flask are added and the apparatus is attached to a Schlenk line. In a 100 mL Schlenk flask containing a stir bar, a solution of $[N(CH_2Ph)Bu_3]Cl$ (0.36 g, 1.1 mmol) in 100% ethanol (50 mL) is degassed with argon with the help of a gas dispersion tube. The Soxhlet apparatus is joined to the Schlenk flask (with PTFE sleeves) under argon and the $Ta_6(\mu\text{-}Cl)_{12}Cl_2(OH_2)_4 \cdot 4H_2O$ is extracted under argon into the stirring $[N(CH_2Ph)Bu_3]Cl$/ethanol solution for 1 h, resulting in a dark green solution. After the Soxhlet apparatus is detached, the ethanol is removed under vacuum at 30°C. Degassed benzene (70 mL) is added to the dark forest green solid by cannula. A Dean–Stark trap is attached to the Schlenk flask and the solid is dried by means of azeotropic distillation for ~21 h under argon. The remaining benzene is then removed under vacuum. The dark forest green solid is dissolved in a minimum of cold (−40°C) CH_2Cl_2 in the glove box, and the resulting mixture is filtered through Celite® in order to remove a small amount of brown residue. The volume of the filtrate is reduced on a rotary evaporator until a small amount of brown residue forms. The solution is cooled to −40 °C and the brown solid is removed by filtration. The green filtrate is treated dropwise with toluene (~25% of the solution volume) and the volume is reduced by rotary evaporation until a small amount of brown precipitate is noted. The solution is filtered and the volume reduced by rotary evaporation until a clear supernatant is observed over a green solid. The supernatant is decanted and the solid is washed with toluene (3 × 2 mL) and dried in vacuum. Yield: 0.72 g (88%).

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.

Properties

Green $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$ is soluble in dichloromethane and 1,2-dichloroethane, but is insoluble in ether, benzene, and toluene. This tetraalkylammonium cation imparts higher solubility to the salt, compared to the NMe_4^+ salt, and the benzyl group reduces cation crystallographic disorder compared to NBu_4^+ salts. Single-crystal X-ray diffractometry on $[N(CH_2Ph)Bu_3]_4[Ta_6(\mu\text{-}Cl)_{12}Cl_6]$ showed a $[Ta_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$ core in each of two crystalline forms (one a solvate), with similar metrics to $[Ta_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$ salts with inorganic cations.[15a]

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[*] The checkers report that the Me_4N^+ salt of the $Ta_6Cl_{18}{}^{4-}$ anion is easily prepared, without Soxhlet extraction, by simple addition of NMe_4Cl to the $Ta_6Cl_{18}{}^{4-}$ solution.

Acknowledgments

This research was supported in part with funds from the National Science Foundation (CHE-0078701), the National Cancer Institute (1 R21 RR14062-01), the Roy J. Carver Charitable Trust (grant 01-93), a pilot grant funded by NIH/NIDDK (P30 DK 54759) and the Cystic Fibrosis Foundation (ENGELH98S0), and the Department of Energy's Energy-Related Laboratory Equipment Program (tube furnace). The Siemens D5000 automated powder diffractometer and Nonius Kappa CCD diffractometer were purchased with support from the Roy J. Carver Charitable Trust (grants 96-36 and 00-192).

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2. OCTAHEDRAL HEXAMOLYBDENUM HALIDE CLUSTERS

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Molybdenum halides in lower oxidation states typically adopt dinuclear or polynuclear structures. One of the oldest known (1859) polynuclear clusters is Mo_6X_{12},[1] whose solid-state structure consists of octahedral Mo_6 units bearing eight μ_3-halides (inner chlorides), one over each of the eight octahedral faces, and six terminal (outer) halides in apical positions on the octahedral framework. Mo_6Cl_{12}, also known by its empirical formula $MoCl_2$, has an extended structure in which some of the chlorine atoms are shared between clusters. Although it can be made by direct reduction of higher molybdenum halides, the product obtained is often impure. Much purer material can be obtained by addition of concentrated hydrochloric acid to the crude material, which affords discrete dianionic clusters of stoichiometry $[Mo_6(\mu_3\text{-}Cl)_8Cl_6]^{2-}$. The resulting chloromolybdic acid, $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6] \cdot 6H_2O$, is sparingly soluble in water and can be recrystallized from hydrochloric acid. This material can be converted in near-quantitative yield to pure Mo_6Cl_{12} by thermolysis in vacuum.[2]

Mo_6Cl_{12}, its discrete halide and chalcogenide derivatives, and its coordination complexes[3] have attracted considerable attention because of their interesting photochemical properties/lifetimes (phosphorescence, luminescence, and electrogenerated chemiluminescence),[4] utility in catalysis,[5] radiochemistry,[6] sensor and conductor research,[7] intercalation chemistry,[8] and possible use as molecular precursors to chalcogenide-based Chevrel-phase materials.[9] There has also been considerable theoretical effort to understand cluster bonding and photochemical lifetimes.[10]

There are a number of published procedures for the synthesis of Mo_6Cl_{12}.[11] The most common are based on (1) comproportionation of $MoCl_5$ and Mo at 650°C to

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$MoCl_3$, subsequent disproportionation of $MoCl_3$ to Mo_6Cl_{12} and $MoCl_4$ at the same temperature, and recycling/comproportionation of the $MoCl_4$ with Mo to give additional Mo_6Cl_{12} for an overall 85–91% yield,[11g] (2) reduction of $MoCl_5$ with Al in a chloroaluminate melt at 200–450°C to give a 98% yield of chloromolybdic acid,[11i] and (3) comproportionation at 720°C of $MoCl_5$ and Mo in the presence of NaCl to give a 70–80% yield of Mo_6Cl_{12}.[11j] Two of these approaches require quartz tubing and/or considerable labor.

We have found that nonconventional, mild main group metal and metalloid reductants such as mercury, bismuth, antimony, gallium, and $Ga^+GaCl_4^-$ are highly effective[12] in reducing WCl_6 and TaX_5 ($X = Cl, Br$) at surprisingly lower temperatures than commonly used in the solid-state synthesis of early transition metal cluster halides. Borosilicate ampules can be substituted for the more expensive and less easily sealed quartz ampules at these lower temperatures, and the metals and metalloids are not as impacted by oxide coatings that inhibit solid-state reactions of more active metals. Bismuth is a particularly ideal reductant because it is nontoxic, inexpensive, not impeded by a surface oxide coating, does not readily reduce Mo_6Cl_{12}, and forms a volatile $BiCl_3$ by-product that does not exert significant pressure within a closed ampule. Bismuth also dissolves in molten $BiCl_3$, and this may improve dispersal of the reductant within the reaction mixture.

We report here an extension of this reduction methodology to the convenient preparation[13] of chloromolybdic acid and Mo_6Cl_{12}.

General Procedures

$MoCl_5$ (Materion Advanced Chemicals, Milwaukee, WI), Bi (325 mesh powder, Materion), hydrochloric acid (12 M, Fisher Scientific), and 8-hydroxyquinoline (Fisher) are used as received. Powder X-ray diffraction is performed on samples protected from moisture via a 5 μm polyethylene film. $MoCl_5$ and solid-state products are handled in either a glove box or a well-purged glove bag under a dinitrogen atmosphere. The molybdenum content of the products is determined gravimetrically as $MoO_2(C_9H_6ON)_2$ (C_9H_6ON = 8-hydroxyquinolinate).[14]

A tube furnace with a positionable thermocouple is used in conjunction with a temperature controller in order to maintain and ramp temperatures. Syntheses are performed in dual-chamber, 25 mm OD borosilicate glass ampules with 30–60 mL total chamber volume, a 14/20 or 19/22 ground glass joint at one end, and constrictions between the end reaction chamber and middle receiver chamber (for volatile by-products) and between the middle receiver chamber and ground joint (Fig. 1).[*]

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[*] The checker used a 2.5 cm OD double-chamber ampule with a 15 cm length reaction chamber, a 10 cm receiver chamber, and a 0.95 cm OD end tube to which a greaseless vacuum valve was attached via a Cajon fitting. The ampule was flame sealed under vacuum between the receiver chamber and the Cajon fitting.

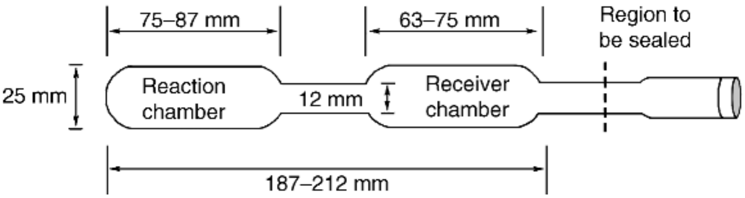

Figure 1. Ampule design for Mo_6Cl_{12} synthesis.

A. TETRADECACHLOROHEXAMOLYBDATE HEXAHYDRATE (CHLOROMOLYBDIC ACID)

$$6MoCl_5 + 6Bi \rightarrow Mo_6Cl_{12} + 6BiCl_3$$

$$Mo_6Cl_{12} + 2HCl(aq) \rightarrow (H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6] \cdot 6H_2O$$

Procedure

An ampule as described above is oven dried at 130°C overnight and brought directly while hot into a glove box or glove bag and cooled under vacuum in the antechamber or under dinitrogen, respectively. The reactants, Bi (3.825 g, 18.3 mmol) and ground $MoCl_5$ (5.00 g, 18.3 mmol), are thoroughly mixed and added to the end reaction chamber of the ampule via a long-stem funnel that minimizes contamination of the constriction surfaces. A gas inlet adapter is used to seal the ampule and prevent contamination with air. The ampule is then evacuated on a Schlenk line and flame sealed between the joint and receiver chamber.

The sealed ampule is placed in the center of a horizontal tube furnace. The temperature is ramped up to 230°C over 2 h and then to 350°C over 2 h, and the ampule is heated for 2.5 days (a shorter reaction time leads to yields in the 40–50% range). By sliding the tube, the receiver chamber is then moved out of the furnace and the $BiCl_3$ by-product is removed from the reaction chamber by sublimation over 12 h; the reaction products in the reaction chamber are converted into a free-flowing material by this step. The yellow brown non-volatile material is homogenized by shaking the cooled ampule, and then the ampule is returned to the center of the furnace and heated to 350°C for 3 h.* The receiver chamber is again moved out of the furnace, the furnace is reoriented to a slight angle (~15°) from the horizontal so that the receiver chamber is higher

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*The checker is unsure whether the actions in this sentence are necessary for the success of the preparation.

than the reaction chamber, and the ampule is heated at 350°C for 24 h. The ampule is allowed to cool, the constriction between the receiver and reaction chambers is sealed with a torch, and the reaction chamber is opened in a glove box (a glove bag would be more than adequate for this step). The homogeneous, crystalline, olive green/brown material is collected. Yield of crude material: 4.066 g (theory for Mo_6Cl_{12}, 3.056 g, consistent with appreciable Bi content).

A portion of this solid (2.00 g) is treated in air with HCl (25 mL of 12 M aqueous solution) in a 250 mL Erlenmeyer flask (attached to a water bubbler for trapping HCl vapor) and the mixture heated over a flame with vigorous agitation.[*] Gray-black (presumably Bi-containing) insoluble impurities are removed by hot filtration through a medium-porosity fritted glass funnel. The insoluble material on the frit is washed with hot concentrated aqueous HCl in order to extract chloromolybdic acid that crystallized during filtration. The yellow filtrate is allowed to cool, resulting in the deposition of orange-yellow crystals. The crystalline product is filtered and returned to the Erlenmeyer flask, HCl (25 mL of 12 M aqueous solution) is added, the product redissolved by heating, and then collected by filtration after slow cooling to room temperature to obtain orange-yellow needles of chloromolybdic acid, $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6] \cdot xH_2O$. Yield: 1.40 g (77%,[†] for $x = 6$, based on $MoCl_5$).[‡]

Analysis of the product is unreliable because of its slow evolution of HCl.[11e] The material can be converted to an air-stable tetraalkylammonium salt if analysis is needed.

Properties

Chloromolybdic acid is insoluble in and slowly reactive with water,[§] but soluble in methanol and ethanol.[¶] The solid gradually oxidizes in air to a white solid with loss

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[*] The checker reports that this procedure works well as long as the crude material is not exposed to air for more than 1 day.

[†] The checker reports yields for $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6] \cdot 6H_2O$ of 81–89% at the same scale and ≥77% at four times the reaction scale via a 6-day procedure involving (a) heating the sealed ampule from 20 to 230°C over 2 h, (b) heating to 350°C over 2 h, (c) heating at 350°C for 2.5 days with nine ampule rotations separated by a minimum of 2 h during this period, (d) sublimation of $BiCl_3$ over 5 h by positioning the receiver chamber outside the tube furnace, (e) melting of $BiCl_3$ and remixing with nonvolatile material, (f) resublimation of $BiCl_3$ over 5 h, (g) melting of $BiCl_3$ and remixing with nonvolatile material, (h) cooling to 20°C overnight, (i) shaking the ampule contents to remix, (j) heating to 35°C over 3 h, and (k) resubliming $BiCl_3$ to the receiver chamber.

[‡] The checker reports that a singly recrystallized sample of $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6] \cdot 6H_2O$ contained 750 ppb Bi impurities and ≤100 ppb for a triply recrystallized sample. XRD of a triply recrystallized sample matched literature data.

[§] The checker reports that, after being mixed with water, chloromolybdic acid forms an insoluble precipitate that converts to a pale yellow solid upon exposure to air.

[¶] The checker reports that chloromolybdic acid is soluble in acetonitrile.

of HCl. It can be converted into air-stable tetraalkylammonium derivatives by metathesis in hydrochloric acid with tetralkylammonium chlorides.[4c]

B. HEXAMOLYBDENUM DODECACHLORIDE

$$(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6]\cdot 6H_2O \rightarrow Mo_6Cl_{12} + 2HCl + 8H_2O$$

Procedure

A recrystallized sample of chloromolybdic acid (0.809 g, 0.66 mmol) is heated in vacuum using the method of Michel and McCarley.[2] Slowly (2.5 h) raising the temperature to 350°C and heating for 24 h affords an orange-yellow solid. Yield: 0.632 g (95% recovery based on chloromolybdic acid).[*]

Anal. Calcd. for Cl_2Mo: Mo, 57.50. Found (average of two trials): Mo, 57.64.[†]

Properties

Anhydrous Mo_6Cl_{12} changes to a paler yellow solid upon short exposure to air (10–15 min), due to absorption of water. The Mo analysis of an air-exposed sample is consistent with the formation of the neutral dihydrate $Mo_6(\mu_3\text{-}Cl)_8Cl_4(H_2O)_2$.

Anal. Calcd. for $H_4Cl_{12}O_2Mo_6$: Mo, 55.50. Found (average of three trials): 55.28.

Acknowledgments

This research was supported in part with funds from the National Science Foundation (CHE-0078701), the National Cancer Institute (1 R21 RR14062-01), the Roy J. Carver Charitable Trust (grant 01–93), and the Department of Energy's Energy-Related Laboratory Equipment Program (tube furnace). The Siemens D5000 automated powder diffractometer was purchased with support from the Roy J. Carver Charitable Trust.[‡]

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[*] The checker reports that the method of Mussel and Nocera,[15] heating chloromolybdic acid in vacuum at 150°C for 2 h and then overnight at 210°C, gives consistently yellow Mo_6Cl_{12} in yields of 90–93%.

[†] The checker finds Mo analyses for Mo_6Cl_{12} of 55.46% (average of two trials), 54.07% (three trials), and 54.40% (three trials) for products from three different syntheses.

[‡] D.J.O. acknowledges support (grant #452) from the 21st Century Jobs Trust Fund through the SEIC Board from the State of Michigan.

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3. ETHER COMPLEXES OF MOLYBDENUM(III) AND MOLYBDENUM(IV) CHLORIDES

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Checked by KIMBERLEY J. GALLAGHER,[†] ADAM S. HOCK,[†] and MARC J. A. JOHNSON[†]

Trichlorotris(tetrahydrofuran)molybdenum(III), $MoCl_3(THF)_3$, is a widely used starting material for the synthesis of a broad range of molybdenum compounds. It was first prepared by a carbonyl route,[1] but later the compound was obtained by a reductive procedure in three steps starting from $MoCl_5$, as initially reported by the Chatt group.[2] This synthetic method, which was later improved by several minor modifications,[3–6] has since remained the most widely employed route to this compound. In the first step in the three-step procedure, $MoCl_5$ is dissolved in acetonitrile, which causes a spontaneous reduction to $MoCl_4(MeCN)_2$. Tetrahydrofuran cannot be used in this step, because the powerful Lewis acidic properties of $MoCl_5$ lead to the ring-opening polymerization of this solvent. In two subsequent steps, the nitrile ligands in $MoCl_4(MeCN)_2$ are replaced with THF to give $MoCl_4(THF)_2$, and the synthesis is then completed by a chemical reduction with tin. In spite of the various incremental improvements, this three-step procedure remains rather long and requires, in our hands, isolation of both the $MoCl_4(MeCN)_2$ and $MoCl_4(THF)_2$ intermediates in order to obtain product of sufficient quality. With individual step yields of 63–86%, the overall yield from $MoCl_5$ is 46% at best, with a time investment of ≥ 2 days.

Unlike THF, diethyl ether is not susceptible to acid-catalyzed polymerization and, unlike acetonitrile, it is not susceptible to oxidation. Ethereal solutions of $MoCl_5$ are stable and their conversion to $MoCl_4(OEt_2)_2$ by reducing agents such as norbornene[7] or allyltrimethylsilane[8] has been previously reported. As it turns out, this reduction can also be conveniently carried out by metallic tin. The reduction reaction of $MoCl_5$ by tin in diethyl ether is fast but controlled at room temperature, without an excessive exothermicity. Therefore, this reaction does not require any special precautions except exclusion of air and moisture. In addition, the tin chloride coproduct is ether soluble, whereas $MoCl_4(OEt_2)_2$ is only sparingly soluble. Therefore, the Mo(IV) product is easily purified by ether washings with only minimal product loss. When $MoCl_4(OEt_2)_2$ is dissolved in THF in the presence of metallic tin, smooth conversion to $MoCl_3(THF)_3$ occurs. This

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transformation is the combined result of two reactions: ligand exchange to give $MoCl_4(THF)_2$ and reduction of the latter to $MoCl_3(THF)_3$ by tin as previously reported.[5] This reaction gives excellent results without the need to isolate the $MoCl_4(OEt_2)_2$ product after its generation from $MoCl_5$, nor the need to isolate the second $MoCl_4(THF)_2$ intermediate. Thus, it suffices to use enough tin reagent to reduce Mo(V) to Mo(III) and to replace the solvent after completion of the first reduction step, in order to achieve a convenient high-yield synthesis of $MoCl_3(THF)_3$ in one half day from $MoCl_5$. This contribution describes both the synthesis and isolation of the $MoCl_4(OEt_2)_2$ complex and the direct, two-step, single-flask synthesis of $MoCl_3(THF)_3$ from $MoCl_5$.

General Procedures

Solvents (diethyl ether, tetrahydrofuran) are distilled from sodium benzophenone ketyl under argon.[*] The tin granules were activated by heating in an oven at 120° C for several hours.[†]

A. TETRACHLOROBIS(DIETHYL ETHER)MOLYBDENUM(IV)

$$2MoCl_5 + 4Et_2O + Sn \rightarrow 2MoCl_4(OEt_2)_2 + SnCl_2$$

Procedure

A 100 mL Schlenk tube equipped with a magnetic stir bar is connected to a vacuum/argon line through the sidearm with ground glass stopcock.[‡] After the tube is evacuated and filled with argon three times, pentachloromolybdenum(V) (1.20 g, 4.39 mmol) and activated tin granules (20 mesh;[§] 1.04 g, 8.76 mmol) are added. Freshly distilled ether (30 mL) is added, and the suspension is then stirred at room temperature until it yields a suspension of an orange solid in an orange solution (about 30 min).[¶] The orange solid is mechanically separated from the excess tin by taking advantage of the large difference in density between the two solids, as follows. Under gentle magnetic stirring that stirs up the finely divided orange product but

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[*] The checkers report that one can also use solvents purified with the column method described in Ref. 9.

[†] The checkers activated the tin granules by drying them under vacuum on a Schlenk line overnight. Using tin that is not activated may result in longer reaction times, but can give satisfactory yields of the product.

[‡] The checkers carried out the synthesis in an inert atmosphere glove box, and note that dinitrogen can be used instead of argon as an inert gas.

[§] Subsequent separation of the tin is made much easier by using granules or shot (20 mesh) rather than powder.

[¶] The checkers note that a more typical time for this step is 60 min. The formation of an orange solid suspended in an orange solution indicates that consumption of the $MoCl_5$ is complete.

leaves the tin at the bottom of the Schlenk tube, the supernatant suspension of the $MoCl_4(Et_2O)_2$ product is transferred into a new Schlenk tube through a medium-sized (G15) cannula, taking care not to transfer any of the metallic tin. The product is then collected by filtration on a glass frit,* washed with Et_2O (5×5 mL), and finally dried under vacuum at −20° C, the low temperature being used in order to avoid the loss of diethyl ether. Yield: 1.36 g (80%).

Anal. Calcd. for $C_8H_{20}Cl_4MoO_2$: C, 24.89; H, 5.22. Found: C, 25.31; H, 5.23.

Properties

Tetrachlorobis(diethyl ether)molybdenum(IV) is an orange, air-sensitive crystalline powder. It is paramagnetic, with a triplet ground state ($\mu_{eff} = 2.33\mu_B$). The IR spectrum is reported.[8] The ^1H NMR spectrum in C_6D_6 shows two broad resonances for the methyl and the methylene protons of the ether ligands, at positions that are not significantly contact shifted from those of the free ether (δ 1.1, 3.5). These resonances are not due to the coordinated ether molecules, but instead are due to *free* ether molecules resulting from dissociation equilibria. The compound has a marked tendency to lose diethyl ether, and samples dried without special precautions systematically give low carbon and hydrogen microanalyses. Heating the compound at 80° C under vacuum affords a reactive form of $MoCl_4$, which can be transformed easily and in high yields into a variety of other useful compounds such as $MoCl_4(THF)_2$, $MoCl_3(THF)_3$, $MoCl_3(PMe_3)_3$, and $Mo(O\text{-}t\text{-}Bu)_4$.[10] It is often convenient to generate $MoCl_4(OEt_2)_2$ in situ, and to use it in subsequent reactions. This strategy is employed for the synthesis of $MoCl_3(THF)_3$ in the next section.

B. TRICHLOROTRIS(TETRAHYDROFURAN)MOLYBDENUM(III)

$$2MoCl_5 + 4Et_2O + Sn \rightarrow 2MoCl_4(OEt_2)_2 + SnCl_2$$

$$2MoCl_4(OEt_2)_2 + 6THF + Sn \rightarrow 2MoCl_3(THF)_3 + 4Et_2O + SnCl_2$$

Procedure

An orange suspension of $MoCl_4(OEt_2)_2$ and excess tin in diethyl ether is prepared according to the procedure detailed in the previous section, starting from

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*The additional cannula transfer step to an intermediate container makes it possible to evaluate whether any metallic tin has inadvertently been transferred together with the product. The checkers note that the reaction solution can be transferred directly to the glass frit (and the intermediate transfer step omitted) by using a smaller gauge cannula, through which the desired product but not the tin powder can pass.

$MoCl_5$ (3.18 g, 11.64 mmol) and Sn granules (5–20 mesh; 2.77 g, 23.33 mmol) in diethyl ether (30 mL). Once the orange solid has settled well at the bottom of the Schlenk tube, the supernatant liquid is removed by using a thin cannula,[*] and freshly distilled THF (30 mL) is added to the remaining solid. The resulting mixture is then stirred at room temperature until a beige solid forms in a dark purple solution (~4 h).[†] The product is separated mechanically from the excess tin by taking advantage of the large difference in density between the two solids. Under gentle magnetic stirring that stirs up the finely divided product but leaves the tin at the bottom of the Schlenk tube, the supernatant suspension of $MoCl_3(THF)_3$ is transferred into a new Schlenk tube through a medium-sized (G15) cannula, taking care not to transfer any of the metallic tin. The product is then collected by filtration on a glass frit, washed with Et_2O (3 × 15 mL),[‡] and finally dried under vacuum. The complex is stored under dry argon. Yield: 3.99 g (82%).[§]

Anal. Calcd. for $C_{12}H_{24}Cl_3MoO_3$: C, 34.43; H, 5.78. Found: C, 34.04; H, 5.51.

Properties

Trichlorotris(tetrahydrofuran)molybdenum(III) is a beige[¶] crystalline product that deteriorates upon exposure to the laboratory atmosphere. When dissolved or suspended in solvents other than THF, it progressively loses THF and transforms to darker dinuclear complexes such as $Mo_2Cl_6(THF)_4$ or $Mo_2Cl_6(THF)_3$.[11] It also decomposes slowly in THF, especially upon warming, with formation of 1,4-dichlorobutane and more soluble molybdenum oxo derivatives whose precise nature is unknown. Therefore, when $MoCl_3(THF)_3$ is used as a starting material, it is important to use its solutions in THF promptly.

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[*] The checkers removed the solution with a cannula filter. As mentioned above, subsequent separation of the tin is made much easier by using granules or shot (20 mesh) rather than powder.

[†] In the checker's hands, this step is typically more rapid and is usually complete in about 2.5 h. The appearance of the purple color in the supernatant signals the proper time for filtration.

[‡] The checkers prefer to wash first with small quantities of THF until the washings are orange with no hint of red or purple, and then with Et_2O as described.

[§] The checkers obtained a yield of 72%.

[¶] The color of the solid may have orange or pink overtones.

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4. OCTAHEDRAL HEXATUNGSTEN HALIDE CLUSTERS

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Tungsten dichloride or, more correctly, hexatungsten dodecachloride, W_6Cl_{12}, has an octahedral hexanuclear cluster structure with μ_3-chlorines over each of the eight octahedral faces and six terminal chlorines, some of which are shared between clusters in an extended array. Treatment of W_6Cl_{12} with concentrated hydrochloric acid yields the discrete cluster dianion $[W_6(\mu_3\text{-Cl})_8Cl_6]^{2-}$ as the H_3O^+ salt. The $[W_6(\mu_3\text{-Cl})_8Cl_6]^{2-}$ cluster, with a variety of cations, has attracted considerable interest because of its long photo-excited state lifetimes and photochemical, electrochemical, and spectroscopic properties.[1]

W_6Cl_{12} and $[W_6(\mu_3\text{-Cl})_8Cl_6]^{2-}$ have been used in the synthesis of hexatungsten chalcogenide molecular precursors for tungsten analogs of Chevrel phases,[2] organotungsten compounds,[3] alkene polymerization and metathesis catalysts,[4] and tungsten thiochlorides.[5]

The principal routes to W_6Cl_{12} have involved reduction of WCl_6, with yields of 35–60%. Reductants have included Na/Hg,[6] Al,[1f,7] Al in molten $NaAlCl_4$,[8] Mg,[7b] Zn,[7b] Pb,[7b] W,[2c,9] and WO_2.[10] Tungsten tetrachloride has also been used as a precursor to W_6Cl_{12} by either thermal disproportionation[11] or reduction with Fe.[2b] Disadvantages of many of these preparative routes include low yields, slow reactions, high temperatures necessitating the use of quartz vessels, contamination by reductant or intermediate reduction products, and violent explosions during the opening of sealed tubes.[1f] Some procedures require (1) small scales, (2) careful control of ampule position within a furnace, (3) careful control of thermal gradients, (4) tungsten powder pre-purification in H_2 at 1000° C, or (4) rocking furnaces. W_6Cl_{12} is usually purified by crystallization from hot concentrated hydrochloric acid, forming the chloro acid $(H_3O)_2[W_6(\mu_3\text{-Cl})_8Cl_6]\cdot 7H_2O$, followed by thermolysis to brown to pale yellow W_6Cl_{12}.

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We have reported that mild main group metal reductants such as mercury, bismuth, antimony, gallium, and $Ga^+GaCl_4^-$ are highly effective solid-state reductants[12] for reducing WCl_6, $MoCl_5$, and TaX_5 ($X = Cl$, Br) at considerably lower temperatures than those used in other syntheses of early transition metal cluster halides. These lower temperatures allow the use of borosilicate glass ampules in place of more expensive, harder-to-seal quartz ampules.

Bismuth is an ideal reductant for WCl_6 because it is nontoxic, inexpensive, not impeded by a surface oxide, does not readily reduce W_6Cl_{12}, and forms volatile but low vapor pressure $BiCl_3$ for greatly improved safety in sealed tube reactions. Bismuth is also easily dispersed in reaction mixtures because it dissolves in molten $BiCl_3$.

We report here an extension of this approach to the convenient preparation of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6] \cdot 6H_2O$ and thus W_6Cl_{12} at significantly lower temperatures and greater yield than other published procedures.[13] The procedure is simple enough for use in undergraduate inorganic synthesis laboratory courses, particularly when combined with instruction in basic glassblowing.

General Procedures

WCl_6 (Materion Advanced Chemicals, Milwaukee, WI), Bi (325 mesh powder, Materion), and hydrochloric acid (12 M, Fisher Scientific) are used as received. Powder X-ray diffraction is performed on samples protected from moisture by a 5 μm polyethylene film. WCl_6 and solid-state products are handled in either a glove box or a well-purged glove bag under a dinitrogen atmosphere. A tube furnace with a positionable thermocouple and temperature controller for ramping temperatures is employed for the solid-state reduction. Syntheses are performed in dual-chamber, 25 mm OD borosilicate glass ampules with 60–70 mL total chamber volume, a 19/22 ground glass joint at one end, and constrictions between the end reaction chamber and middle receiver chamber (for volatile by-products) and between the middle receiver chamber and ground joint (Fig. 1). The ampule is oven dried at 130° C overnight and brought directly while hot into the glove box or glove bag and cooled under vacuum (in the antechamber) or dinitrogen, respectively. Reactants are thoroughly mixed and added to the end reaction chamber via a long-stem funnel that minimizes contamination of the constriction surfaces. A gas inlet adapter is used to seal the ampule, which is then evacuated on a Schlenk line and flame sealed between the joint and receiver chamber. Recrystallizations involving concentrated aqueous HCl are performed in stoppered filter flasks with the outlet connection attached by rubber tubing to a water trap in order to absorb HCl gas released from the heated HCl solution. Tungsten analyses are based on gravimetric determination of WO_3 after oxidation with HNO_3 and ignition.

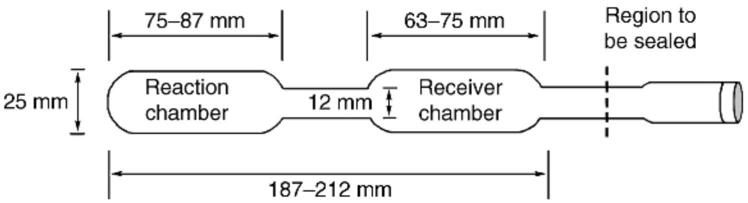

Figure 1. Ampule employed in the synthesis of W_6Cl_{12}.

A. BIS(HYDROXONIUM) TETRADECACHLOROHEXATUNGSTATE HEPTAHYDRATE (CHLOROTUNGSTIC ACID)

$$6WCl_6 + 8Bi \rightarrow W_6Cl_{12} + 8BiCl_3$$

$$W_6Cl_{12} + 2HCl(aq) \rightarrow (H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6] \cdot 7H_2O$$

Procedure

WCl_6 (15.00 g, 37.8 mmol) and Bi (10.54 g, 50.4 mmol) are mixed in the glove box and sealed in an ampule under vacuum. The ampule is positioned at the tube furnace center and the temperature slowly raised to 230° C over 2 h,* and then to 355° C over 2 h. The ampule is then positioned with the receiver chamber in a cooler area of the furnace and heated at the reaction chamber end at 350–355° C for 24 h. After being cooled to room temperature, the ampule is opened in the glove box, taking care not to mix any nonvolatile material and $BiCl_3$ from their respective chambers. Alternatively, before opening the ampule, the two chambers can be separated with a torch in order to separate/store the sublimed $BiCl_3$. The chocolate brown nonvolatile material weighs 18.28 g, consistent with appreciable bismuth content because the theoretical yield of W_6Cl_{12} is 9.64 g.

A portion of the chocolate brown product (3.00 g) is treated with concentrated aqueous HCl (5 mL) while agitating for 10–15 min at room temperature. This step results in the formation of a fine, yellow-brown precipitate. The precipitate is separated by decanting off the liquid, and then the precipitate is washed with concentrated HCl (5 mL) and dissolved in boiling concentrated HCl (20 mL). When the solution cools to room temperature, greenish yellow needles form. The needles are collected by filtration through a coarse porosity fritted glass funnel. The

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*The checkers recommend removing the ampule with heat-resistant gloves after it reaches 230° C, thoroughly shaking the tube in order to mix the reactants, and then placing the tube in the furnace with the receiver area in a cooler region of the furnace so that $BiCl_3$ can sublime away while heating to 350° C.

product is recrystallized in the same manner three times to afford the pure product. Yield: 1.65 g (91% based on WCl_6, for workup of 3 g of the 18.28 g total impure nonvolatile product).*

Anal. Calcd. for $H_{20}O_9Cl_{14}W_6$ $\{(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6]\cdot 7H_2O\}$: W, 62.55. Found: W, 62.41.

Properties

Yellow, crystalline $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6]\cdot 7H_2O$ is insoluble in water, with which it slowly reacts, but is soluble in methanol. The crystals slowly lose HCl and water upon prolonged storage, but recrystallization from concentrated hydrochloric acid restores the material to crystalline form with a small loss of material from oxidation. For long-term storage, it can be converted to the air-stable, crystalline tetrabutylammonium salt by metathesis with Bu_4NCl in halogenated solvents such as $CHCl_3$ or CH_2Cl_2.

B. HEXATUNGSTEN DODECACHLORIDE

$$(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6]\cdot 7H_2O \rightarrow W_6Cl_{12} + 2HCl + 9H_2O$$

Procedure

A triply recrystallized chlorotungstic acid sample is thermolyzed in vacuum by slowly (over 3–3.5 h) raising the temperature under nitrogen to 325° C and heating for 1 h. Yield: 98%.

Anal. Calcd. for Cl_2W: W, 72.2. Found: W, 72.0.

Properties

Pale canary yellow W_6Cl_{12} absorbs water from the air to form the very pale yellow neutral dihydrate. The material is slowly oxidized or hydrolyzed in air to a white solid, presumed to be WO_3. W_6Cl_{12} is best stored under anhydrous conditions and under a dioxygen-free atmosphere or in vacuum.

Acknowledgments

This research was supported in part with funds from the National Science Foundation (CHE-0078701), the National Cancer Institute (1 R21 RR14062-01),

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*The checkers report consistent yields of ~90%.

the Roy J. Carver Charitable Trust (grant 01-93), Nycomed Inc., and the Department of Energy's Energy-Related Laboratory Equipment Program (tube furnace). The Siemens D5000 automated powder diffractometer was purchased with support from the Roy J. Carver Charitable Trust.

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5. TRINUCLEAR TUNGSTEN HALIDE CLUSTERS

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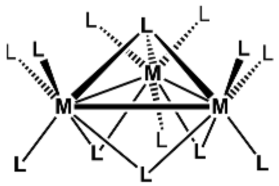
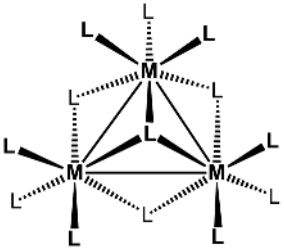
Checked by SUSAN E. LATTURNER[†] and WILLIAM AINSWORTH[†]

Triangular tritungsten compounds with one or two face-bridging chalcogenides are well known.[1] Monocapped clusters[2] with three edge-bridging ligands μ-L (e.g., μ-O) and three terminal ligands per metal can be described as three octahedra that share a common vertex (the capping μ_3-L) and edges in a pairwise fashion.





These clusters have also been described as incomplete metallacubanes, lacking only a fourth metal that would bond to the three bridging ligands μ-L. Tritungsten clusters with μ_3-halides are rare,[3] and monocapped group 6 clusters with *exclusively* halides were unknown before our research. In contrast, perhalo trinuclear clusters are more common for the nearby elements Re,[4] Nb,[5] and Ta.[6]

Mild main group metal reductants such as mercury, bismuth, antimony, gallium, and $Ga^+GaCl_4^-$ are highly effective[7] solid-state reductants for reducing WCl_6, $MoCl_5$, and TaX_5 ($X = Cl, Br$) at considerably lower temperatures than those used in traditional syntheses of group 5 and 6 metal cluster halides. Borosilicate glass ampules can thus replace more expensive, harder-to-seal quartz ampules. We have reported convenient routes to tungsten dichloride, W_6Cl_{12},[7b] and to crystalline[7a] and reactive[8] forms of tungsten tetrachloride, $(WCl_4)_x$, from reduction of WCl_6 with Hg, Sb, or Bi. Antimony is oxidized to the volatile (moderate vapor pressure) liquid $SbCl_3$, which can act as a solid-state flux. Nontoxic, inexpensive bismuth is another ideal reductant for WCl_6 because it is not impeded by a surface oxide, it forms the volatile by-product $BiCl_3$ (which has a low vapor pressure for improved safety in heated sealed tube reactions), and it is easily dispersed through dissolution in molten $BiCl_3$.

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In an attempt to extend this methodology to the preparation of tungsten trichloride, $W_6(\mu\text{-}Cl)_{12}Cl_6$,[9] we instead found a new monocapped, eight-electron binary tungsten chloride, W_3Cl_{10}, and the perchlorotritungstates, $Na_3[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]$ and $[N(CH_2Ph)Bu_3]_3[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]$.[10] The latter trianionic clusters can be oxidized in solution to salts of the seven-electron isostructural dianion, $[N(CH_2Ph)Bu_3]_2[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]$. These perchlorotritungsten clusters constitute new synthons, readily accessed from WCl_6, for the development of tritungsten chemistry. They have potential use in the synthesis of heterometallacubanes and higher nuclearity[11] clusters. Meyer has recently reported an alternative synthesis of $Na_3[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]$ from WCl_4 and its solid-state structure.[12]

General Procedures

WCl_6 (Materion Advanced Chemicals, Milwaukee, WI), Bi (325 mesh powder, Materion), Sb (100 mesh powder, Aldrich Chemical, Milwaukee, WI), and tetrahydrofuran (anhydrous, inhibitor-free, Aldrich) are used as received. Acetonitrile (Aldrich) is degassed with argon and distilled from granular P_2O_5. Hydrochloric acid (12 M, Fisher Scientific) is used as received. Benzyltrialkylammonium chloride salts (alkyl = ethyl, butyl; Aldrich) are dried by azeotropic distillation with benzene. NaCl (Fisher) is dried overnight in an oven at 130° C and then evacuated overnight in the glove box antechamber under vacuum while cooling. Powder X-ray diffractometry is performed on samples protected from moisture by a 5 μm polyethylene film. WCl_6 and solid-state products are handled in a glove box under a dinitrogen atmosphere. A tube furnace with a positionable thermocouple and temperature controller for ramping temperatures is employed for the solid-state reductions. Syntheses at scales described below are performed in dual-chamber, 25 mm OD borosilicate glass ampules with ~60 mL total chamber volume, a 19/22 ground glass joint at one end, and constrictions between the end reaction chamber and middle receiver chamber (for volatile by-products) and between the middle receiver chamber and ground joint (Fig. 1). The ampule size should be adjusted for different reaction scales.

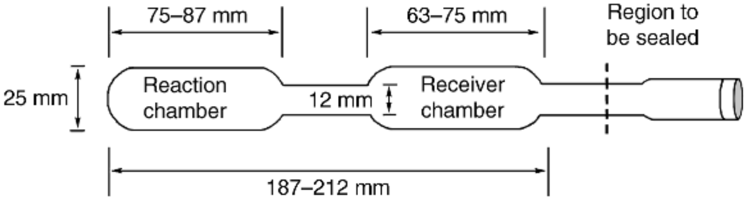

Figure 1. Ampule employed in the synthesis of trinuclear tungsten clusters.

Ampules are oven dried at 130° C overnight and cooled under vacuum in the glove box antechamber. Reactants are thoroughly mixed and ground and then added to the end reaction chamber by means of a long-stem funnel that minimizes contamination of the constriction surfaces. A gas inlet adapter is used to seal the ampule, which is then evacuated on a Schlenk line and flame sealed between the joint and receiver chamber. Tungsten analyses are based on gravimetric determination of WO_3 after oxidation with HNO_3 and ignition.

A. TRITUNGSTEN DECACHLORIDE

$$9WCl_6 + 8Bi \rightarrow 3W_3Cl_{10} + 8BiCl_3$$

Procedure

In the glove box, WCl_6 (10.00 g, 25.2 mmol) and Bi (4.68 g, 22.4 mmol) are thoroughly mixed, ground in a polished agate mortar, and added to a dual-chamber borosilicate glass ampule. The ampule is evacuated and flame sealed and then placed into a horizontal tube furnace and the temperature ramped to 220° C over 2 h. After 1 day, the ampule is withdrawn from the furnace and the purple-brown solid is homogenized by gentle shaking for ~1 min. This and subsequent homogenization steps increase the overall yield. The ampule is returned to the tube furnace, angled at ~45° to the vertical in order to facilitate refluxing of the $BiCl_3$ by-product, and the temperature is raised to 350° C over 8 h. After 1 day, the furnace is repositioned to horizontal and the ampule is oriented so that the empty receiving chamber is located in a cooler end of the furnace. The by-product $BiCl_3$ is removed by sublimation in order to make the nonvolatile materials free flowing. After 24 h, the ampule is removed and the nonvolatile material is homogenized by gentle shaking for 1 min. The ampule is heated at 350° C at a furnace angle of 45° for 2 days, the furnace is reoriented to horizontal, and the $BiCl_3$ is removed by sublimation at 350° C for 2 days. Once sublimation of $BiCl_3$ is judged to be complete, the ampule is cooled to room temperature, and the chamber containing the $BiCl_3$ is flame sealed at the constriction in order to separate it from the W_3Cl_{10} chamber. The W_3Cl_{10} chamber is opened under inert atmosphere. Yield: 9.0 g (92%).[*] According to X-ray powder diffractometry, the product is a single phase free from Bi, $BiCl_3$, WCl_4, and W_6Cl_{12} impurities. The purity can be further improved by washing the solid with aqueous HCl (6–12 M), which removes any residual $BiCl_3$ and trace amounts of WCl_4 and W_6Cl_{12}.

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[*] The checkers reported a yield of 6.88 g (70%) with powder XRD showing mostly single-phase material with the dominant impurity being WCl_4. The lower yield may be the result of employing different ampule dimensions.

Anal. Calcd. for $Cl_{10}W_3$: W, 60.87; Cl, 39.13. Found: W, 60.3; Cl, 39.81.

Properties

Brown, nonvolatile, microcrystalline W_3Cl_{10} appears to be indefinitely stable when stored under an inert atmosphere. The compound is insoluble in all common organic solvents and does not react with concentrated aqueous HCl or HNO_3 (facilitating its separation from WCl_4 and W_6Cl_{12}). The compound as obtained by this procedure is crystalline by powder X-ray diffraction. W_3Cl_{10} is converted into $Na_3W_3Cl_{13}$ when heated to 350° C with NaCl and $SbCl_3$ (which acts as solvent). The structure of W_3Cl_{10} is believed to be analogous to that of Nb_3Cl_8 [5a,b] and $Na_2Ti_3Cl_8$,[13] with an extended structural net of nondiscrete $W_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3Cl_9$ units that share chloride ions.

B. TRISODIUM TRIDECACHLOROTRITUNGSTATE

$$9WCl_6 + 8Sb + 9NaCl \rightarrow 3Na_3W_3Cl_{13} + 8SbCl_3$$

Procedure

WCl_6 (10.9 g, 25.4 mmol), Sb (3.0 g, 22.4 mmol), and NaCl (1.6 g, 25.4 mmol) are mixed and ground in an agate mortar in a glove box and then loaded into a double-chamber borosilicate ampule. After the ampule is evacuated and flame sealed, it is placed in a tube furnace oriented at 45° to the vertical, in order to facilitate $SbCl_3$ reflux, and the temperature is ramped to 200° C over 2 h. After 1 day at 200° C, the tube furnace is pivoted to the horizontal position and the ampule repositioned so that the receiver chamber is in a cool region of the furnace. After 1 day, the sublimation of $SbCl_3$ is complete. The nonvolatile product is homogenized through gentle ampule shaking for ~1 min (this step improves the overall yield). The ampule is returned to the tube furnace, at a 45° orientation, and the reaction mixture is heated at 240° C for 5 days. The furnace is rotated to the horizontal and the ampule is repositioned so that the receiver chamber is in a cool region of the furnace. $SbCl_3$ is removed by sublimation at 240° C for 24 h. The ampule is removed from the furnace, allowed to cool to room temperature, and opened under an inert atmosphere (taking care to prevent the sublimed by-products from falling back into the bottom chamber of the reaction vessel). Yield: 9.8 g (98%).[*]

Anal. Calcd. for $Cl_{13}Na_3W_3$: W, 51.00; Cl, 42.62. Found: W, 50.9; Cl, 42.85.

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[*] The checkers obtained 9.563 g of a dark purple powder, with powder XRD showing mostly single-phase material with weak NaCl reflections and possibly trace amounts of W_6Cl_{12}.

Properties

$Na_3W_3Cl_{13}$ is a free-flowing purple, nonvolatile, microcrystalline solid that is stable to air. It is homogeneous by powder X-ray diffractometry. The compound is insoluble in common organic solvents, including dichloromethane, and modestly soluble in degassed water and CH_3CN, producing deep purple solutions. Aqueous solutions in air slowly oxidize to an unknown, deep blue complex over the course of several months. The compound is stable in vacuum to $\leq 370°C$.

C. TRIS(BENZYLTRIBUTYLAMMONIUM) TRIDECACHLOROTRITUNGSTATE

$$Na_3W_3Cl_{13} + 3[N(CH_2Ph)Bu_3]Cl \rightarrow [N(CH_2Ph)Bu_3]_3[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9] + 3NaCl$$

Procedure

$Na_3W_3Cl_{13}$ (2.00 g, 1.85 mmol) and $[N(CH_2Ph)Bu_3]Cl$ (1.73 g, 5.55 mmol) are stirred in anhydrous acetonitrile (20 mL). After 3 days, the NaCl precipitate is removed by filtration and the solvent is removed by rotary evaporation to give a viscous oil. The oil is layered with tetrahydrofuran (15 mL) and allowed to stand undisturbed. After 4 days, the mother liquor is decanted, and the solid is washed with tetrahydrofuran (3 × 2 mL) and dried in vacuum. The dark purple crystals are washed again with tetrahydrofuran (3 mL, 10 min), the solution is decanted, and the solid is dried in vacuum for 3 h. Yield: 3.34 g (98%).*

Anal. Calcd. for $C_{57}H_{102}N_3Cl_{13}W_3$: W, 29.95; Cl, 25.02. Found: W, 29.6; Cl, 25.18.

Properties

Dark purple $[N(CH_2Ph)Bu_3]_3[W_3Cl_{13}]$ is diamagnetic (or weakly paramagnetic) at 25° C, with a low effective moment of 0.73–0.79μ_B. This tetraalkylammonium cation imparts higher solubility for the salt, compared to the NMe_4^+ salt, and the benzyl group reduces cation crystallographic disorder compared to NBu_4^+ salts. The UV–vis spectrum (λ in nm, ϵ in $M^{-1}\,cm^{-1}$) of $[N(CH_2Ph)Bu_3]_3[W_3Cl_{13}]$ in dichloromethane exhibits maxima at 555 (1010), 420 (shoulder; 1600), 350 (6630), 270 (shoulder; 25,100), and 240 (35,400). Mass spectrometry (FAB, NPOE matrix, negative ion mode, *m*/*e*, base peak of isotopic grouping): 1290 $[N(CH_2Ph)Bu_3][W_3Cl_{13}]$, 1253 (loss of Cl). The $N(CH_2Ph)Et_3$ salt can be isolated

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*The checkers stirred the initial mixture for 5 days, and after filtration, rotary evaporation, and crystallization, they obtained 0.962 g of pure phase material as shown by powder XRD.

in similar fashion, with the Et groups being less disordered than the Bu groups. Single-crystal X-ray diffractometry on $[N(CH_2Ph)Et_3]_3[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]$ shows a solid-state structure with an average W−W distance of 2.778(5) Å,[10] an average W−Cl−W angle of 70.4(1)°, and a W−Cl(terminal) distance of 2.415(3) Å. Chemical oxidation of $[N(CH_2Ph)Bu_3]_3[W_3Cl_{13}]$ with 2,4-dichlorophenyliodine dichloride in dichloromethane gives the seven-electron cluster compound $[N(CH_2Ph)Bu_3]_2[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]$ with longer W−W distances.[10]

Acknowledgments

This research was supported in part with funds from the National Science Foundation (CHE-0078701), the National Cancer Institute (1 R21 RR14062-01), the Roy J. Carver Charitable Trust (grant 01-93), Nycomed Inc., and the Department of Energy's Energy-Related Laboratory Equipment Program (tube furnace). The Siemens D5000 automated powder diffractometer was purchased with support from the Roy J. Carver Charitable Trust.

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6. CRYSTALLINE AND AMORPHOUS FORMS OF TUNGSTEN TETRACHLORIDE

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Tungsten tetrachloride is the most synthetically useful binary tungsten chloride after WCl_6 and is an important precursor in W^{IV} coordination[1] and organometallic chemistries,[2] metal–metal bonded ditungsten chemistry,[3] materials synthesis,[4] hexatungsten chloride cluster synthesis,[5] and catalysis.[6]

Of the many published procedures for the synthesis of WCl_4, the two most commonly employed methods are reduction of WCl_6 with red phosphorus in a sealed tube,[7] or reduction of WCl_6 with $W(CO)_6$ in refluxing chlorobenzene.[8] The suitability of WCl_4 for some chemical uses is dependent on its preparative route because of associated impurities. For example, tungsten phosphides and phosphorus are potential contaminants in WCl_4 that is derived from reduction with red phosphorus. Tungsten hexacarbonyl, $W(CO)_6$, is an expensive reductant, toxic CO is liberated, and chlorobenzene can be difficult to remove.

Main group metal and metalloid reductants such as mercury, bismuth, antimony, gallium, and $Ga^+GaCl_4^-$ are highly effective[9] in reducing WCl_6, $MoCl_5$, and TaX_5 ($X = Cl$, Br) at surprisingly lower temperatures (allowing the use of borosilicate ampules) than commonly used in the solid-state synthesis of early transition metal polynuclear halides. These metals and metalloids are not as impacted by oxide coatings that inhibit solid-state reactions of more active metal reductants such as aluminum or the alkali metals.

We report here an extension of this reduction methodology to the convenient preparations[10] of WCl_4 from WCl_6 in a crystalline, edge-sharing bioctahedral polymer form via solid-state methods (employing Sb as reductant) and a reactive

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(or more readily extracted) amorphous powder form of unknown structure via solution methods (employing Sn).

General Procedures

WCl_6 (Materion Advanced Chemicals, Milwaukee, WI), Sb (100 mesh powder, Aldrich Chemical, Milwaukee, WI), and Sn (325 mesh, Aldrich) are used as received. Methylene chloride (Fisher Scientific) and 1,2-dichloroethane (Aldrich) are degassed with argon and distilled from granular P_2O_5. Powder X-ray diffraction is performed on samples protected from moisture by a 5 μm polyethylene film. WCl_6 and solid-state products are handled in either a glove box or a well-purged glove bag under a dinitrogen atmosphere. A tube furnace with a positionable thermocouple is used in combination with a temperature controller in order to maintain and ramp temperatures. Syntheses are performed in dual-chamber, 25 mm OD borosilicate glass ampules with 30–60 mL total chamber volume, a 14/20 or 19/22 ground glass joint at one end, and constrictions between the end reaction chamber and middle receiver chamber (for volatile by-products) and between the middle receiver chamber and ground joint (Fig. 1). In order to improve temperature homogeneity and preclude cooler zones where WCl_5 could collect, the ratio of lengths of tube furnace and ampule is kept at ≥ 1.6. The ampule and all glassware are oven dried at 130° C overnight and brought directly while hot into the glove box and cooled under vacuum in the antechamber or, in the glove bag, under dinitrogen. Reactants are thoroughly mixed and added to the end reaction chamber via a long-stem funnel that minimizes contamination of the ampule constrictions. A gas inlet adapter is used to seal the ampule, which is then evacuated on a Schlenk line and flame sealed between the joint and receiver chamber.

A literature procedure is followed for gravimetric determination of tungsten as WO_3 after treatment with HNO_3 and ignition.[11] Chlorine content is determined gravimetrically (average of two determinations) as AgCl after removal of tungsten. An accurately weighed sample of WCl_4 (0.17–0.19 g) is decomposed at 20° C with aqueous 1 M KOH (5 mL). 30% Hydrogen peroxide (two drops) is added to the suspension and, after 1 h the solution is diluted to

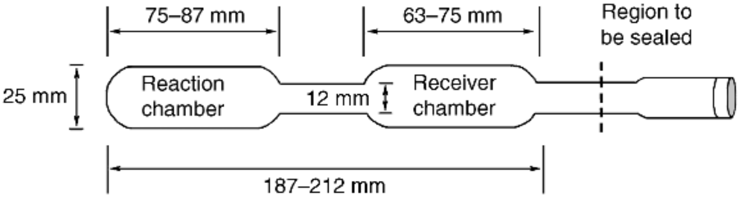

Figure 1. Ampule design for crystalline $(WCl_4)_x$ synthesis.

50 mL with water and heated at 100° C for 20 min. To the hot solution is added dropwise $Ba(NO_3)_2$ (7 mL of a 0.1 M aqueous solution) and the mixture heated at 100° C for 20 min. After settling overnight at room temperature, the $BaWO_4$ precipitate is removed by filtration through a medium-porosity fritted glass funnel and the solid is washed with distilled water. The combined filtrate and wash is diluted to 75 mL and neutralized with concentrated HNO_3 (~12 drops). $AgNO_3$ (5.5 mL of a 0.5 M aqueous solution) is added dropwise. The mixture is heated at 100° C for 20 min and then allowed to settle overnight, protected from light, at room temperature. The AgCl precipitate is recovered by filtration, washed with distilled water, oven dried for 2 h at 150° C, and weighed.

A. CRYSTALLINE TUNGSTEN TETRACHLORIDE BY SOLID-STATE REDUCTION

$$3WCl_6 + 2Sb \rightarrow 3(WCl_4)_x + 2SbCl_3$$

Procedure

WCl_6 (10.0 g, 25.2 mmol) and Sb (2.04 g, 16.7 mmol) are sealed in a glass ampule under vacuum. After the contents are mixed, the ampule is placed in the center of the tube furnace and heated at 75° C for 12 h, 105° C for 12 h, and 130° C for 12 h (the calculated vapor pressure of $SbCl_3$ at 130° C is 46 mmHg).[*] The ampule's receiver chamber is moved out of the furnace and the $SbCl_3$ is removed by distillation at 130° C.[†] Residual WCl_5 and $WOCl_4$ are removed by sublimation at 160° C for 1 day and 215° C for 1 day. The ampule is cooled and opened in a glove box. Black, nonvolatile, crystalline $(WCl_4)_x$ is removed from the end chamber. Yield: 7.99 g (97% based on WCl_6).

Anal. Calcd. for Cl_4W: W, 56.45; Cl, 43.55. Found: W, 56.5; Cl, 43.39. No Sb was detected by qualitative microanalysis.

Properties

$(WCl_4)_x$ is an air- and moisture-sensitive solid. It can be stored indefinitely under dry, oxygen-free dinitrogen or argon. This crystalline form of $(WCl_4)_x$ has solubility properties that are similar (i.e., insoluble in noncoordinating solvents)

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[*] If all of the above heating is done at 200° C, the yield of crystalline $(WCl_4)_x$ drops to 75%.

[†] To remove the $SbCl_3$, the checkers used an L-shaped ampule, similar to that used in the synthesis[7] of $(WCl_4)_x$ from red phosphorus and WCl_6. They reported a lower yield of $(WCl_4)_x$ starting from $WOCl_4$-contaminated WCl_6.

and reactivity that is similar to that of WCl_4 prepared by red phosphorus or mercury reduction.[10] The solid-state structure of $(WCl_4)_x$ from reduction of WCl_6 with mercury is an edge-shared bioctahedral linear polymer, as predicted by McCarley[11] by analogy to $(NbCl_4)_x$, with alternating short W=W (2.688(2) Å) and long (3.787(3) Å) nonbonded W−W distances. Other structural features support this bonding description.[10]

B. AMORPHOUS TUNGSTEN TETRACHLORIDE BY SOLUTION-PHASE REDUCTION

$$2WCl_6 + Sn \rightarrow 2(WCl_4)_x + SnCl_4$$

Procedure

A 50 mL Schlenk flask is loaded with WCl_6 (2.00 g, 5.04 mmol), Sn powder (0.299 g, 2.52 mmol), and 1,2-dichloroethane (10 mL) in the glove box. The mixture is stirred at room temperature for 20 h, yielding a gray suspension. A reflux condenser is attached to the flask, and the mixture is heated and stirred at 85° C for 2 days under argon. The appearance of the shiny dark suspension is unchanged during heating. After the flask is cooled and transferred to a glove box, the suspension is removed and centrifuged. The supernatant is discarded, the solid is resuspended in CH_2Cl_2 (10 mL), and the mixture is centrifuged again. The supernatant is discarded and the resuspension in CH_2Cl_2/centrifugation process is repeated four times in order to remove $SnCl_4$.* The resulting fine powder is rinsed into a 20 mL flask with CH_2Cl_2, the supernatant is decanted, and the precipitate is dried under dynamic vacuum at room temperature. Yield: 1.576 g (96% based on WCl_6).

Anal. Calcd. for Cl_4W: W, 56.45; Cl, 43.55. Found: W, 56.6; Cl, 43.27. No Sn was detected by qualitative microanalysis.

Properties

The $(WCl_4)_x$ produced by Sn reduction of WCl_6 resembles graphite in appearance. It is amorphous as shown by X-ray diffraction. It is more extractable (suspensions in organic solvents have slight color) and more reactive than WCl_4 prepared by other methods.[10] It reacts readily with tetrahydrofuran to give the known $WCl_4(THF)_2$, with acetonitrile to yield the known $WCl_4(MeCN)_2$ in 81% yield, and with methanol to yield the known $W_2Cl_4(OMe)_4(HOMe)_2$ in 73% yield.[10] It reacts with tetraalkylammonium chlorides to give the face- and edge-bridging

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*The presence of $SnCl_4$ in the washings can be detected by addition of pyridine, which causes precipitation of $SnCl_4$ in virtually quantitative yield as $SnCl_4(py)_2$.

ditungsten(IV) complexes $W_2(\mu\text{-Cl})_3Cl_6^-$ and $W_2(\mu\text{-Cl})_2Cl_8^{2-}$ with formal W=W double bonds.[3h]

Acknowledgments

This research was supported in part with funds from the National Science Foundation (CHE-0078701) and Nycomed Inc. The Siemens D5000 automated powder diffractometer was purchased with support from the Roy J. Carver Charitable Trust.

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