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Facile reduction of early transition metal halides with nonconventional, mild reductants. 6. A new, lower-temperature, solid-state synthesis of the cluster hexamolybdenum dodecachloride Mo_6Cl_{12} from $MoCl_5$, via chloromolybdic acid, $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6] \cdot 6H_2O$

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Abstract

Reduction of $MoCl_5$ with Bi in a sealed borosilicate ampule at 350 °C, followed by sublimation of by-product $BiCl_3$ and addition of aqueous hydrochloric acid, yielded chloromolybdic acid, $(H_3O)_2Mo_6(\mu_3\text{-}Cl)_8Cl_6 \cdot 6H_2O$, in 80% yield (unoptimized) after double recrystallization. Chloromolybdic acid was thermolyzed to Mo_6Cl_{12} in 95% yield.

Keywords: Molybdenum dichloride; Hexamolybdenum dodecachloride; Molybdenum pentachloride reduction; Bismuth; Chloromolybdic acid

1. Introduction

There are two principal structure types for octahedral, hexanuclear cluster halides of mid-valent second- and third-row early transition metals. Group 5 hexanuclear clusters possess terminal and octahedral edge–bridging halides, whereas Group 6 hexanuclear clusters have terminal and octahedral face–bridging halides. An alternate description of the Group 6 cluster core is a cubic array of μ_3-halides with metal atoms at the centers of each face. Both cluster types are found as discrete molecular clusters or as clusters linked in extended arrays by sharing of halides [1,2].

Molybdenum dichloride (hexamolybdenum dodecachloride, Mo_6Cl_{12}) was one of the first metal cluster compounds to be synthesized (in 1859) [3], although the actual structure was determined far later [4]. A large body of octahedral Mo_6 cluster coordination chemistry has been reported [5–17] over the past four decades. Mo_6Cl_{12}, discrete cluster derivatives, and related materials have attracted considerable photochemical interest [18–32] because of their phosphorescence, luminescence, and electrogenerated chemiluminescence. The structures and interesting photochemistry have led to considerable theoretical effort [33–41] in order to understand cluster bonding and excited states. The chemistry of chalcogenide derivatives has been explored [42–46], in part as a possible molecular precursor route to Chevrel phases. Mo_6Cl_{12} and its derivatives have been used in catalysis [47–49], intercalation chemistry [50], radiochemistry [51], and electrochemical, sensor, and conductor research [52–61].

Many synthetic routes to Mo_6Cl_{12} and chloromolybdic acid ($(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6] \cdot 6H_2O$, the discrete,

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molecular cluster chloro acid derivative) have been reported [62–72], and one has been developed for undergraduate laboratory instruction in high temperature, solid-state inorganic synthesis [73]. The most commonly used methods, usually refinements of earlier methods are: (1) conproportionation of $MoCl_5$ and Mo metal at 650 °C to $MoCl_3$, followed by disproportionation at 650 °C to Mo_6Cl_{12} and $MoCl_4$ and recycling/conproportionation of $MoCl_4$ with Mo metal, for an overall yield of 85–91% [68], (2) reduction, with concomitant mechanical shaking, of $MoCl_5$ with Al in a chloroaluminate melt at 200 °C for 6 h and then at 450 °C for 48 h, for a 98% yield of chloromolybdic acid [71], and (3) high temperature (720 °C) conproportionation of $MoCl_5$ and Mo in the presence of NaCl for a Mo_6Cl_{12} yield of 70–80% [72]. Two of these methods require substantial labor or quartz tubing because of the elevated temperatures.

Chloromolybdic acid [63,68,71,74,75] is easily prepared from Mo_6Cl_{12} via dissolution in and recrystallization from concentrated hydrochloric acid, and can be thermolyzed in vacuo back to Mo_6Cl_{12}. The chloro acid is often used as an intermediate in the purification of Mo_6Cl_{12}.

We recently reported several convenient, lower temperature, and high yield solid-state 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 reduction of WCl_6 with the nonconventional reductants bismuth, antimony, and mercury [76]. This simple approach has been implemented in a local undergraduate inorganic synthesis lab course [77]. We have extended this versatile, lower-temperature methodology to the preparation of the known lower tungsten chloride $(WCl_4)_x$ [78], the new tungsten chloride clusters W_3Cl_{10} and $Na_3W_3Cl_{13}$ [79], and the known hexatantalum clusters Ta_6X_{14} (X = Cl, Br) [80,81]. This success led us to examine the applicability of this approach [77] to the synthesis of Mo_6Cl_{12}.

2. Experimental

Moisture-sensitive precursors and products were manipulated in a Vacuum Atmosphere glovebox under a N_2/He atmosphere. Thermolyne Model 21100 (⩽1200 °C) and Marshall Model 1046 single-zone (⩽2000 °C) tube furnaces equipped with positionable thermocouples were used in solid-state syntheses. All syntheses employed dual-chamber borosilicate glass ampules of 25 mm OD and 30–60 ml total chamber volume, with a 14/20 or 19/22 ground glass joint at one end and constrictions between the end reaction chamber and receiver chamber and between the receiver chamber and joint. Ampules were oven dried at 130 °C overnight and then cooled under evacuation in the glove box antechamber. Reactants were homogenized in a 20 ml scintillation vial with a vortex mixer prior to introduction into the ampule's end receiver chamber using a long stem funnel in order to minimize contamination of the constriction surfaces. The ground-jointed end was closed with a gas inlet adapter, the ampule evacuated using a Schlenk line, and the ampule flame-sealed under vacuum.

$MoCl_5$ (Cerac Inc., Milwaukee, WI), Bi (325 mesh, Cerac), hydrochloric acid (12 M, Fisher), 8-hydroxyquinoline (Fisher), NaOH (pellets, EM Science), acetic acid (glacial, EM Science), and ethanol (95%, Pharmaco) were used as received. Powder X-ray diffraction was performed on a Siemens D5000 diffractometer, with moisture-sensitive samples protected by a 5 μm film of polyethylene.

2.1. Preparation of Mo_6Cl_{12} via reduction of $MoCl_5$ with bismuth

An ampule with $MoCl_5$ (5.00 g, 18.3 mmol) and Bi (3.825 g, 18.3 mmol) in the end reaction chamber was placed in the center of a horizontal tube furnace and the temperature slowly raised to 230 °C over 2 h and then to 350 °C over 2 h. The ampule was repositioned with part of the receiver chamber out of the furnace in order to remove $BiCl_3$ by sublimation. Heating was continued at 350 °C for 24 h. After cooling, the ampule was opened in the glovebox. The crystalline, inhomogeneous nonvolatiles, dark brown with areas of yellow, weighed 4.065 g. This weight was consistent with appreciable bismuth content since the theoretical yield of Mo_6Cl_{12} was 3.053 g.

A portion of the product (2.587 g) was treated with 25 ml of 12 M HCl with agitation, resulting in a slight exotherm. The mixture was dissolved with heating and recrystallized as described below, resulting in 1.025 g of orange-yellow needles of $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ (58% yield, for $x = 6$, based on $MoCl_5$).

In a somewhat more labor-intensive procedure resulting in improved yield, $MoCl_5$ (5.00 g, 18.3 mmol) and Bi (3.825 g, 18.3 mmol) were sealed in the receiver chamber of an ampule. The ampule was placed in the center of a horizontal tube furnace, the temperature slowly raised to 230 °C over 2 h and then to 350 °C over 2 h. The ampule was heated at 350 °C for 2.5 days. After cooling to 100 °C, the end of the receiver chamber was moved out of the furnace. The furnace was heated to 350 °C over 2 h and then at 350 °C for 12 h. The ampule was allowed to cool and then removed from the furnace. The yellow-brown nonvolatile material was homogenized by shaking, the ampule returned to the center of the furnace, and the ampule heated to 350 °C over 3 h. The end of the receiver chamber was moved out of the furnace, the furnace reoriented to a slight angle (10°–15°) from the horizontal, and the ampule heated at 350 °C for 24 h. The ampule was allowed to cool and opened in the glovebox. The homogeneous, crystalline, olive green/brown nonvolatiles weighed 4.066 g (theory for Mo_6Cl_{12}, 3.053 g).

A portion of this solid (2.000 g) was treated with 12 M HCl as described below and recrystallized to yield 1.456 g of orange-yellow chloromolybdic acid, $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ (80% yield, for $x = 6$, based on $MoCl_5$).

X-ray diffraction patterns for chloromolybdic acid from both procedures were empirically identical.

A recrystallized sample of chloromolybdic acid (0.8095 g) was thermolyzed in vacuo using the method of Michel and McCarley [43] by slowly (2.5 h) raising the temperature to 350 °C and heating for 24 h. The Mo analysis of the resulting 0.632 g (95.0% recovery based on chloromolybdic acid) orange-yellow material was consistent with approximately anhydrous Mo_6Cl_{12} (*Anal.* Calc. for Cl_2Mo: Mo, 57.50. Found (average of two trials): Mo, 57.64%). The anhydrous Mo_6Cl_{12} changed to a paler color upon short exposure to air (10–15 min), characteristic of water absorption by the sample. Mo analysis of an air-exposed sample was consistent with the neutral dihydrate $Mo_6(\mu_3\text{-}Cl)_8Cl_4(OH_2)_2$ (*Anal.* Calc.: Mo 55.50. Found (average of three trials): 55.28%).

2.2. Procedure for isolation and purification of crude Mo_6Cl_{12} via recrystallization and thermolysis of $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$

Concentrated aqueous HCl (12 M, 25 ml per 2.0–4.0 g of impure chloromolybdic acid) was added to the impure product (after $BiCl_3$ sublimation) in a 250 ml Erlenmeyer flask (attached to a water bubbler for trapping HCl vapor) and the mixture heated with intensive agitation to dissolve the material. An initial hot filtration through a medium porosity fritted glass funnel was necessary in order to remove gray-black (presumably Bi-containing) insoluble impurities. The solid was washed with hot concentrated aqueous HCl in order to recover any product that may have crystallized during filtration. The yellow filtrate was allowed to cool, resulting in orange-yellow crystals. The crystalline product was returned to the Erlenmeyer flask with aqueous HCl, redissolved by heating, and recovered by filtration after slow cooling. One to three recrystallizations were sufficient to obtain orange-yellow needles of $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$.

2.3. Analytical procedure for molybdenum

The molybdenum content was determined gravimetrically as $MoO_2(C_9H_6ON)_2$ (C_9H_6ON = 8-hydroxyquinolinate) [82]. All samples were handled under inert atmosphere in order to prevent exposure to moisture until sample decomposition in the procedure. In a 20 ml scintillation vial an accurately weighed sample (ca. 50 mg) was decomposed with 7 ml of aqueous 1 M NaOH, forming a brown suspension after 20 min. To this suspension 30% H_2O_2 was added dropwise (8–12 drops) until evolution of gas was observed. The mixture was allowed to stand for ~1 h, during which all solids dissolved to yield a yellow solution that bleached while standing. The nearly colorless solution was transferred to a 125 ml Erlenmeyer flask and the scintillation vial repeatedly rinsed with water to give a final volume of 40–50 ml. The Erlenmeyer flask was placed in a boiling water bath for 30 min in order to complete oxidation of molybdenum species and to destroy excess H_2O_2; during this time the solution became colorless. The flask was then removed from the bath and the pH adjusted to ~5 with acetic acid. The flask was returned to the water bath and heated for 30 min. To the heated solution 5 ml of a 0.25 M ethanolic 8-hydroxyquinoline solution was slowly added, resulting in a yellow precipitate. The mixture was stirred and returned to the water bath for 15 min. 8-Hydroxyquinoline solution was added dropwise to check for completeness of precipitation. The precipitate was filtered hot through a tared medium porosity fritted funnel, rinsed with 100–150 ml of hot water, dried overnight at ~130 °C, and weighed.

3. Results and discussion

The reduction of $MoCl_5$ with Bi (Eq. (1)) is a straightforward, low-temperature route to Mo_6Cl_{12} via the intermediate chloromolybdic acid. With a 28 h reaction time

$$6MoCl_5 + 6Bi \rightarrow Mo_6Cl_{12} + 6BiCl_3 \qquad (1)$$

the chloromolybdic acid yield was 58%. The yield improved to 80% with extra heating time (total of ~4.5 days) and homogenization steps, and decreased markedly with shorter heating times. The homogenization step can be performed by either (1) opening the ampule in a glove box, grinding the contents with a mortar and pestle, and resealing the powder in a new ampule or (2) temporarily removing the $BiCl_3$ by sublimation, which results in a free-flowing nonvolatile mixture that is easily shaken and rehomogenized. The second approach requires more time but less labor.

Bismuth is a useful reductant because it (1) is inexpensive, (2) is nontoxic, (3) is not impeded by a surface oxide coating, (4) generates a volatile by-product that does not exert significant pressures within an ampule under reaction conditions, for improved safety, and (5) does not readily overreduce Mo_6Cl_{12}. The dissolution of bismuth in molten $BiCl_3$ may also assist in the reduction.

The yields are unoptimized and, presumably, may be improved by elevated temperature, increased reaction time, or additional homogenization of reactants during the procedure. The only disadvantage of this new route is the extended time for $BiCl_3$ sublimation; however, sublimation can be performed unattended.

4. Concluding remarks

Bismuth is a convenient reductant for the direct reduction of $MoCl_5$ to Mo_6Cl_{12} at relatively low temperature as compared to other methods. Reduction of $MoCl_5$ with Bi at 350 °C over 4.5 days affords chloromolybdic acid, $(H_3O)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_6$, in 80% yield after sublimation of $BiCl_3$ and dissolution of the nonvolatiles in and recrystallization from hydrochloric acid. Chloromolybdic acid can be thermolyzed at 350 °C in vacuo to Mo_6Cl_{12} in virtually quantitative yield, based on a literature procedure.

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