

## An Improved High Yield Synthesis Procedure and Reactivity of $W_6S_8(4\text{-}tert\text{-butylpyridine})_6$

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### Introduction

Octahedral clusters of molybdenum that are face-capped by sulfur ( $Mo_6S_8$  units) form intercluster metal–sulfur interactions in an important class of solid-state compounds called “Chevrel Phases”.<sup>1</sup> These compounds possess exciting electronic properties such as superconductivity<sup>2</sup> and are known to be catalysts in the hydrodesulfurization reaction.<sup>3–7</sup> Although the Chevrel phases are generally synthesized using conventional solid-state techniques, in recent years it has been shown that the constituent  $Mo_6S_8$  clusters can be synthesized as isolated units in solution.<sup>8,9</sup> Similar chromium and tungsten chalcogenide cluster units have also been synthesized even though their corresponding Chevrel phases are unknown.<sup>10–14</sup> Based on the gamut of properties that the Chevrel phases exhibit, these soluble isolated cluster units offer an opportunity to synthesize new materials from these building blocks.

Of particular interest to our group is the electronic structure of the face-capped octahedral group 6 chalcogenide clusters. Based on the symmetry of their frontier orbitals<sup>15</sup> and from theoretical studies,<sup>16</sup> we expect extended structures that are built using the cluster and ditopic ligands with extended  $\pi$  systems to have interesting electronic properties. To study such systems, it is imperative to synthesize the isolated cluster in substantial amounts. However, the cluster units can be prepared only in

low yields and quantities using the synthetic routes that have been reported thus far.

We report in this paper an improved high-yield procedure for the synthesis of isolated  $W_6S_8$  cluster units from *isolated* chloride cluster units. This procedure has considerable advantages in purity and yield over those previously reported and can also be extended to synthesis of corresponding molybdenum clusters. We also show that the 4-*tert*-butylpyridine ligands that coordinate to the tungsten atoms in the cluster (to complete the coordination sphere of the tungsten) can be readily exchanged with ligands such as piperidine and triethylphosphine.

### Experimental Section

**General.** Potassium *tert*-butoxide, triethylphosphine, piperidine, and 4-*tert*-butylpyridine were purchased from Aldrich. *N,N*-Dimethylformamide (DMF), tetrahydrofuran (THF), acetonitrile, benzonitrile, diethyl ether, and benzene were purchased from Fischer. Benzonitrile, DMF, and 4-*tert*-butylpyridine were dried with 4 Å molecular sieves and distilled under reduced pressure before use. Piperidine was dried with solid KOH and distilled under reduced pressure; all others were used as received. Tungsten metal and tungsten hexachloride were a generous gift from Osrsm-Sylvania (Towanda, PA) and were purified according to previously reported procedures.<sup>10</sup> KSH was synthesized according to the literature and was shown to be  $\geq 95\%$  pure by iodometric titration.<sup>17,18</sup>  $(H_3O)_2W_6Cl_8/Cl_6^a$  was synthesized according to a recently reported method with high yields<sup>19</sup> and was converted to  $(Bu_4N)_2W_6Cl_8/Cl_6$  using conditions similar to that reported by McCarley.<sup>20</sup> The details of the synthesis and crystallography are provided in the Supporting Information. Potassium *tert*-butoxide, triethylphosphine, piperidine, KSH, DMF, and 4-*tert*-butylpyridine were stored under argon atmosphere in a glovebox. <sup>1</sup>H NMR spectra were obtained on an IBM/Bruker AF-300 or Varian 500 instruments. Single-crystal X-ray diffraction data were collected on a Siemens P4 or Bruker SMART system with a CCD detector, and the structures were solved using SHELXS and refined with SHELXL 97 software packages. Elemental analysis by EDAX (energy dispersive analysis by X-rays) was performed on a JEOL 733 Superprobe using the vendor-supplied SQ package for standardless semiquantitative elemental analysis.

**Typical Synthesis of  $W_6S_8(4\text{-}tert\text{-butylpyridine})_6$  (1).** In an argon-filled glovebox, a 50 mL Schlenk flask containing a Teflon stir bar was charged with  $(Bu_4N)_2W_6Cl_8/Cl_6^a$  (0.802 g, 0.385 mmol), DMF (6 g), and 4-*tert*-butylpyridine (0.62 g, 4.6 mmol) to form a light yellow solution. To this solution was added KSH (0.233 g, 3.22 mmol), resulting in a yellow-green slurry. Upon addition of potassium *tert*-butoxide (0.172 g, 1.53 mmol), a slightly exothermic reaction occurred and the reaction mixture turned red-brown in color. The flask was sealed with a greased ground glass stopper and taken out of the glovebox, and the reaction mixture was stirred at 90 °C in an oil bath for 4 days. The reaction mixture was then cooled to room temperature and filtered through a glass frit (ACE, “E”). The residue on the frit was washed with acetonitrile until the solvent passing through was colorless. This was followed by washing with deoxygenated water (to remove KCl) until the filtrate gave no precipitate with  $AgNO_3$  solution. The residue was further washed with acetonitrile to remove water and then washed with THF (5 mL), which had been chilled in an ice bath, until the solvent passing through was light orange. A final wash was done with  $Et_2O$  (5 mL). After the residue was dried, the product was a brick-red powder (0.592 g, 71%). The crystals were grown either by the diffusion of DMSO into a solution of the cluster in benzene or by the slow cooling of a hot solution of the cluster in 4-*tert*-butylpyridine. The unit cell

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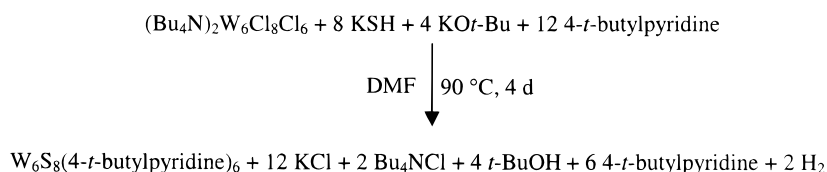
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## Scheme 1



dimensions obtained from single-crystal X-ray diffraction and  $^1\text{H}$  NMR of the cluster were similar to those previously reported.<sup>10</sup> We also obtained two more polymorphs for  $\text{W}_6\text{S}_8(4\text{-}t\text{-butylpyridine})_6$  from these crystallization conditions. Due to the poor quality of the X-ray data, we have not been able to solve the structures to acceptable  $R$  values. For polymorph 1: space group  $C2/c$  with  $a = 24.318 \text{ \AA}$ ,  $b = 26.896 \text{ \AA}$ ,  $c = 15.740 \text{ \AA}$  and  $\beta = 123.3^\circ$ . For polymorph 2: space group  $P1$  with  $a = 13.938 \text{ \AA}$ ,  $b = 15.774 \text{ \AA}$ ,  $c = 20.737 \text{ \AA}$ ,  $\alpha = 89.43^\circ$ ,  $\beta = 82.09^\circ$ , and  $\gamma = 66.48^\circ$ . A quantitative  $^1\text{H}$  NMR study was done in  $\text{C}_6\text{D}_6$  using pentamethylbenzene as an internal standard to estimate the number of ligands on the cluster (see Supporting Information).

**Exchange of 4-*tert*-Butylpyridine in  $\text{W}_6\text{S}_8(4\text{-}t\text{-butylpyridine})_6$  with piperidine.** In an argon-filled glovebox, a thick-walled glass vessel with a Chemglass joint equipped with a Teflon stir bar was charged with  $\text{W}_6\text{S}_8(4\text{-}t\text{-butylpyridine})_6$  (0.325 g, 0.150 mmol) and piperidine (1.52 g, 17.85 mmol). The reaction mixture was taken out of the box and heated to  $100^\circ\text{C}$  for 14 h. The reaction mixture was slow-cooled to room temperature over 4 h after which dark brown crystals appeared. The crystals were then filtered out of the solution using a glass frit (ACE, "E") and were washed first with piperidine and then with *n*-heptane to obtain  $\text{W}_6\text{S}_8(\text{piperidine})_6 \cdot 7\text{piperidine}$  (yield = 60%). The cell constants are similar to those reported for  $\text{Mo}_6\text{S}_8(\text{piperidine})_6 \cdot 7\text{piperidine}$ , and the crystallographic details are presented in the Supporting Information.<sup>8</sup>

**Exchange of 4-*tert*-Butylpyridine in  $\text{W}_6\text{S}_8(4\text{-}t\text{-butylpyridine})_6$  with Triethylphosphine.** In an argon-filled glovebox, a thick-walled glass vessel with a Chemglass joint equipped with a Teflon stir bar was charged with  $\text{W}_6\text{S}_8(4\text{-}t\text{-butylpyridine})_6$  (0.200 g, 0.092 mmol), THF (5 mL), and triethylphosphine (0.6 mL, 1M in THF, 0.6 mmol). The reaction mixture was taken out of the box and heated to  $100^\circ\text{C}$  for 24 h, after which it was pumped to dryness to quantitatively obtain dark brown crystals of  $\text{W}_6\text{S}_8(\text{triethylphosphine})_6$ . We have obtained a rhombohedral modification of the reported  $\text{W}_6\text{S}_8(\text{PEt}_3)_6$  by evaporation of a solution of the cluster in benzene. The details of the crystallographic information are provided in the Supporting Information.

**Thermogravimetric Analysis.** The thermogravimetric analyses (TGA) of the cluster complexes were done on a Seiko thermal analyzer. The samples were loaded on to an aluminum pan and were heated from room temperature to  $550^\circ\text{C}$  at the rate of  $20^\circ\text{C}/\text{min}$  under a flow of nitrogen (60 mL/min).

**Electrochemical Study.** A three-electrode cell consisting of a Pt disk (0.9 mm in diameter) as working electrode and a platinum wire as the counter electrode was used to study the electrochemical properties of the clusters. The reference electrode was  $\text{Ag}/\text{AgCl}$ , and the supporting electrolyte was  $\text{Bu}_4\text{NClO}_4$ . Typically, a 1 mM solution of the cluster complex in benzonitrile was used. The cyclic voltammograms were run between  $-0.5$  and  $1.0 \text{ V}$  with a scan rate of  $100 \text{ mV/s}$ .

## Results and Discussion

**Synthesis.** There are two older routes to synthesize the isolated cluster units with organic ligands. In the first route, reported by Saito and co-workers,<sup>9,13</sup> trimeric clusters are reductively dimerized to form the octahedral hexanuclear clusters. Triethylphosphine is the ligand of choice in this route. The second route, developed by McCarley and co-workers, involves the substitution of chlorides in  $\text{MoCl}_2$  or  $\text{WCl}_2$  by sulfides.<sup>8,14</sup> This latter method has been used for the synthesis of the molybdenum and tungsten chalcogenide clusters with

ligands such as propylamine, pyridine, piperidine, and triethylphosphine. Our group reported earlier a modified McCarley procedure for the synthesis of tungsten clusters with 4-*tert*-butylpyridine as the ligand.<sup>10</sup> A major drawback in these three synthetic routes is the low yield. Unfortunately, since the byproducts that result from these reactions are amorphous and cannot be characterized, it is difficult to pinpoint the source of the low yield. In addition, the procedures reported by our group and by McCarley's group require the use of reagents in excess of the required stoichiometric ratios.

We identified at least two sources in our synthesis procedure that might contribute to the low yield: the starting materials  $\text{WCl}_2$  and KSH. Since both are moisture-sensitive and are synthesized as amorphous powders, it was difficult to estimate their purity. It was also found by  $^1\text{H}$  NMR that in the synthesis of  $\text{WCl}_2$ , the conversion of  $(\text{H}_3\text{O})_2\text{W}_6\text{Cl}_8\text{Cl}_6$  to  $\text{WCl}_2$  by heating the hydrate to  $300^\circ\text{C}$  for 2 h was generally incomplete, especially at larger scales. By IR spectroscopy, varied amounts of  $\text{OH}^-$  were detected in the samples of KSH.

The use of  $\text{WCl}_2$  is more attractive than Saito's synthesis since the reductive coupling step is often not reproducible (at least in our hands), and  $\text{WCl}_2$  already contains the hexanuclear tungsten cluster unit that is present in the final product. To overcome the problem of moisture-sensitivity and ill-defined purity of  $\text{WCl}_2$ , we chose  $(\text{Bu}_4\text{N})_2\text{W}_6\text{Cl}_8\text{Cl}_6$  as the starting material.  $(\text{Bu}_4\text{N})_2\text{W}_6\text{Cl}_8\text{Cl}_6$  is obtained as a crystalline product and is stable to air and moisture. In addition, unlike the two-dimensionally linked clusters in  $\text{WCl}_2$  ( $\text{WCl}_8\text{Cl}_{4,2}^{a-a}\text{Cl}_2^a$ ), it contains isolated  $\text{W}_6\text{Cl}_8\text{Cl}_6$  units. We reasoned that for the synthesis of isolated  $\text{W}_6\text{S}_8$  units, it might be easier to add a sulfide to an isolated cluster rather than to clusters that are linked. To prevent the degradation of KSH to KOH, extreme care was taken to avoid moisture in the preparation of KSH. The purity of KSH was estimated by iodimetry (see Supporting Information). With these changes and by increasing the reaction temperature to  $90^\circ\text{C}$ , upon workup, the 4-*tert*-butylpyridine-ligated  $\text{W}_6\text{S}_8$  cluster was obtained as a crystalline product in 71% yield. The amount of hydrogen evolved during the reaction was measured using a Toepler pump, and it does correspond to the expected stoichiometry and the yield of  $\text{W}_6\text{S}_8(4\text{-}t\text{-butylpyridine})_6$  (Scheme 1). The reaction has been scaled up to 8.0 g of the reactant,  $(\text{Bu}_4\text{N})_2\text{W}_6\text{Cl}_8\text{Cl}_6$ , with similar yields. The reagents are used in stoichiometric amounts according to Scheme 1 rather than in excess as reported in the literature. We have also extended this synthetic route to obtain molybdenum clusters.

The  $\text{W}_6\text{S}_8(4\text{-}t\text{-butylpyridine})_6$  cluster has moderate solubility (ca. 5 mg/mL) in aromatic solvents and in solvents such as dichloromethane and THF. It is very sparingly soluble in polar solvents such as DMF and DMSO and is insoluble in water, acetonitrile, and diethyl ether. By taking advantage of the solubility properties of the  $\text{W}_6\text{S}_8(4\text{-}t\text{-butylpyridine})_6$  cluster in the workup, there is no necessity for prolonged washing or chromatography for the purification of the cluster. When exposed to light and air for 2 days, the cluster degrades, changing color from red-brown to dark brown and showing

reduced solubility in aromatic solvents. However, the cluster is found to be stable when heated with deoxygenated water at 100 °C.

**Exchange of 4-*tert*-Butylpyridine in  $W_6S_8(4\text{-}i\text{-tert-butylpyridine})_6$  with Triethylphosphine and Piperidine.** Our focus on these clusters is to use them as building blocks for extended frameworks. Conceptually, linked clusters may be obtained by exchanging monotopic ligands on the cluster with ditopic ligands, if the monotopic ligand is labile enough to be replaced.

We chose triethylphosphine and piperidine as ligands to probe the lability of the W–N bond in  $W_6S_8(4\text{-}i\text{-tert-butylpyridine})_6$ . At room temperature, the replacement of 4-*tert*-butylpyridine on the cluster with triethylphosphine and piperidine is extremely slow. Even after 5 days,  $^1\text{H}$  NMR showed the presence of multiple products. However, at 100 °C, the replacement is complete within 24 h. While a stoichiometric amount of triethylphosphine completely replaced 4-*tert*-butylpyridine, a 120-fold excess was required in the case of piperidine. It was also found that at 100 °C, a 100-fold excess of 4-*tert*-butylpyridine could not completely replace  $\text{PEt}_3$  in  $W_6S_8(\text{PEt}_3)_6$ . However, such a replacement was possible in the case of  $W_6S_8(\text{piperidine})_6$ .

**Thermal De-Ligation and Electrochemical Properties of  $W_6S_8(4\text{-}i\text{-tert-butylpyridine})_6$ ,  $W_6S_8(\text{triethylphosphine})_6$ , and  $W_6S_8(\text{piperidine})_6$ .** Thermogravimetric analysis (TGA) was used to probe the decomposition temperature of the cluster complexes. From the TGA, the decomposition temperatures (indicated by the onset of the weight loss) obtained for  $W_6S_8(\text{piperidine})_6$ ,  $W_6S_8(4\text{-}i\text{-tert-butylpyridine})_6$ , and  $W_6S_8(\text{triethylphosphine})_6$  are 150, 190, and 250 °C, respectively. These data indicate that the W–ligand bond in the piperidine-ligated cluster may be weaker or more labile than in triethylphosphine and 4-*tert*-butylpyridine ligated clusters. We have not yet characterized the products that result after the ligand loss in the TGA.

The redox behavior of the cluster complexes was studied by cyclic voltammetry. Since the  $W_6S_8(\text{piperidine})_6$  is obtained as a microcrystalline material and contains piperidine as a solvent of crystallization, we have not yet deconvoluted the redox behavior of the cluster complex from the unbound ligand. The redox behaviors of  $W_6S_8(4\text{-}i\text{-tert-butylpyridine})_6$  and  $W_6S_8(\text{triethylphosphine})_6$  are similar, indicating that the electrochemical changes occur on the cluster core. The clusters can be reversibly reduced and oxidized by one electron.<sup>13</sup> In benzonitrile, the first oxidation of  $W_6S_8(4\text{-}i\text{-tert-butylpyridine})_6$  and  $W_6S_8(\text{triethylphosphine})_6$  occurs at 0.13 and 0.11 V (vs Ag/AgCl),

respectively. A second oxidation of the cluster occurs around 0.8 V (vs Ag/AgCl) and is irreversible. A large current is associated with this peak, and on the basis of the electrochemical data, we believe that an internal cluster chemical reaction follows the electrochemical oxidation.<sup>21</sup> This process is insensitive to the identity of the ligand or solvent. We have not yet been able to chemically characterize the product of the second oxidation.

## Conclusions

We have reported an improved high-yield procedure for the synthesis of isolated  $W_6S_8$  cluster units from *isolated* chloride cluster units. This procedure avoids the use of moisture-sensitive  $\text{WCl}_2$  and has considerable advantages in purity, yield, and workup over those previously reported. We have also shown that the 4-*tert*-butylpyridine in  $W_6S_8(4\text{-}i\text{-tert-butylpyridine})_6$  is labile at 100 °C and can be readily exchanged with ligands such as piperidine and triethylphosphine. Work is in progress in exchanging the 4-*tert*-butylpyridine with nitrogen-based ditopic ligands for the construction of electronically interesting framework structures.

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**Supporting Information Available:** Details of synthesis and crystal structure of  $(\text{Bu}_4\text{N})_2\text{W}_6\text{Cl}_8\text{Cl}_6$ , crystal structure solution of  $W_6S_8(\text{piperidine})_6$ , thermogravimetric traces of  $W_6S_8(4\text{-}i\text{-tert-butylpyridine})_6$ ,  $W_6S_8(\text{piperidine})_6$ , and  $W_6S_8(\text{triethylphosphine})_6$ ,  $^1\text{H}$  NMR of  $W_6S_8(4\text{-}i\text{-tert-butylpyridine})_6$ ,  $W_6S_8(\text{piperidine})_6$ , and  $W_6S_8(\text{triethylphosphine})_6$ , quantitative estimation of the 4-*tert*-butylpyridine ligands around the cluster by  $^1\text{H}$  NMR, cyclic voltammogram of  $W_6S_8(\text{triethylphosphine})_6$ , and titration of KSH using iodimetry. X-ray crystallographic files, in CIF format, for the structure determinations of  $(\text{Bu}_4\text{N})_2\text{W}_6\text{Cl}_8\text{Cl}_6$ ,  $W_6S_8(\text{piperidine})_6 \cdot 7\text{piperidine}$  and  $W_6S_8(\text{PEt}_3) \cdot 2\text{C}_6\text{H}_6$  are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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