in this copper CVD reaction is 9,10-dihydrofulvalene comes from work on the related compound (pentamethylcyclopentadienyl)carbonylcopper(I), which decomposes to give decamethyl-9,10-dihydrofulvalene.[11]

From the data presented by Cotton and Marks[7] in their study of $(C_5H_5)CuL$ complexes, Table I was constructed. The order of stability appears to correlate strongly with the σ-donor abilities of the two-electron-donor ligand.[12] This implies that the rate-limiting step in the decomposition of all of these compounds is the dissociation of the two-electron-donor ligand, followed by the rapid decomposition of the 16-electron C_5H_5Cu fragment. This stability trend, the apparent low activation energy for film growth, and the evidence that dihydrofulvalene is the organic product of decomposition strongly suggest that the mechanism for the decomposition of the (alkylphosphine)cyclopentadienylcopper complexes of our CVD study is the surface adsorption and dissociation of the molecules to give free alkylphosphine and unstable adsorbed cyclopentadienyl copper. This is followed by coupling of the organic radical fragments which then desorb, leaving a pure copper film.

Acknowledgment. We thank Drs. Joseph M. Jasinski and Bruce A. Scott for several useful comments and suggestions.

---

[11] Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 5325.

[12] Beach, D. B.; Jolly, W. L. *Inorg. Chem.* **1985**, *24*, 567.

Hydrothermal Synthesis of Sodium Tungstates

Kenneth P. Reis, A. Ramanan, and
M. Stanley Whittingham*

Chemistry Department and
Materials Research Center
SUNY at Binghamton, Binghamton, New York 13901

Received December 28, 1989

The tungsten trioxides and their alkali-metal-intercalated products $M_xWO_{3+\delta}$ have attracted considerable attention over the years because of the variety of crystalline structures they can take up and their electrochemical and electronic properties, which make them attractive as active electrodes in electrochromic displays and as catalysts.[1,2] These structure come from joining the corner-shared WO_6 octahedral building blocks in a variety of arrangements. Through recent developments in low-temperature synthesis two metastable forms, a hexagonal[3,4] and a cubic phase,[5-7] of tungsten trioxide have been reported in addition to the well-known ReO_3-related phase. Both phases possess a rigid tungsten-oxygen framework built up of layers containing distorted corner-shared WO_6 octahedra and arranged to form six-membered rings. In hexagonal WO_3, the layers are stacked along [001] axis, giving one-dimensional tunnels. In cubic pyrochlore WO_3, the layers are linked along the [111] direction to form interconnected three-dimensional tunnels. These three tungsten oxides provide an interesting set to study the effect of structure on chemical reactivity and physical properties. In addition, it allows one to determine the impact of the openness of the structure on its behavior. As indicated in Figure 1 the pyrochlore structure has expanded about 26% above that of the simple structure which is itself relatively open, being a distorted perovskite, ABO_3, with all the A sites vacant; WO_3 is not unique in this behavior, TiO_2 showing an even larger number of structures. Here, we report the synthesis and characterization of two novel sodium tungstates with the cubic pyrochlore and a hexagonal structure.

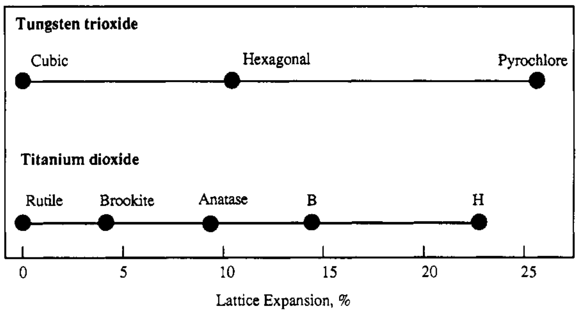

Figure 1. Lattice expansion of different structural forms of WO_3 and TiO_2; data from ref 1.

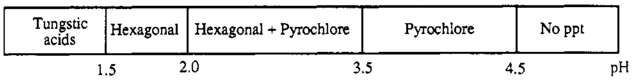

Figure 2. Effect of initial pH on structure formed on acid hydrolysis of sodium tungstate.

Günter et al.[7] recently reported the formation of the pyrochlore WO_3 by a simple hydrothermal acid hydrolysis of sodium tungstate. We followed that technique in this study and found that by careful control of the pH of the solution one could prepare tungsten trioxides in either the hexagonal or pyrochlore structures. In every case we found that these structures contained sodium ions. In a typical experiment, 20 mL of 1 M $Na_2WO_4{\cdot}2H_2O$ solution was acidified at room temperature with the required amounts of 1 M HCl so as to give a pH in the range 4.5-1.5. The solution was sealed in 1-mm wall Pyrex tubes and heated in an oven at 155 °C and autogenous pressures (about 5 atm.) for 3 days. *Care must be taken as these tubes occassionally exploded at this temperature*; thus, we are now using Parr 4745 stainless steel acid digestion bombs. At the lower pH values, prolonged standing of the acidified solution led to precipitation, so the solutions were sealed and heated within an hour of preparation. While pH values above 4.5 did not yield any precipitate after hydrothermal treatment, pH's of less than 1.5 resulted in a mixture of unidentified phases believed to be tungstic acids. After cooling to room temperature, the resulting microcrystalline product was filtered, washed with water, and dried in air; the yield was about 20%.

Powder X-ray diffraction studies of the samples showed that two distinct white phases were formed depending on the initial pH of the acidified solution. For pH's of 3.5-4.5, the patterns could be completely indexed on a cubic pyrochlore-type lattice with $a \sim 10.30$ (2) Å. A hexagonal phase appeared for pH's of less than 2.5 with cell parameters of $a \sim 7.319$ (4) and $c \sim 7.788$ (2) Å; these values are typical of a hexagonal tungsten bronze type phase. No additional lines were found in either set of patterns. For intermediate pH ranges, however, a mixture of cubic and hexagonal phase was obtained. The best yields obtained

---

* Author to whom all correspondence should be sent.

[1] Whittingham, M. S. *Mater. Res. Soc. Bull.* **1989**, *14*(Sept), 31.

[2] Murphy, D. W.; Christian, P. A. *Science* **1979**, *205*, 651.

[3] Gerand, B.; Nowogrocki, G.; Guenot, J.; Figlarz, M. *J. Solid State Chem.* **1979**, *29*, 429.

[4] Cheng, K. H.; Jacobson, A. J.; Whittingham, M. S. *Solid State Ionics* **1981**, *5*, 355.

[5] Nedjar, R.; Borel, M. M.; Hervieu, M.; Raveau, B. *Mater. Res. Bull.* **1988**, *23*, 91.

[6] Coucou, A.; Figlarz, M. *Solid State Ionics* **1989**, 28-30, 1762.

[7] Günter, J. R.; Amberg, M.; Schmalle, H. *Mater. Res. Bull.* **1989**, *24*, 289.

0897-4756/90/2802-0219$02.50/0

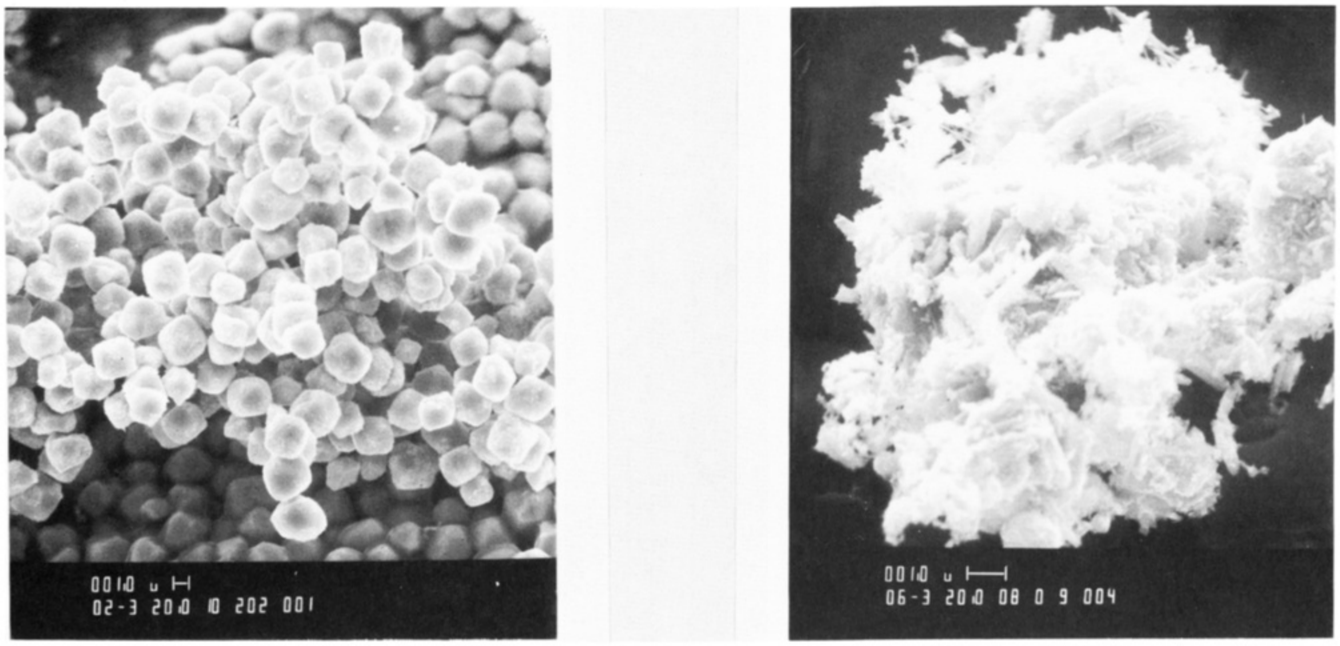

Figure 3. Scanning electron micrographs of the two tungstate phases, pyrochlore (left) and hexagonal (right).

were around pH 3.5 and 1.5, respectively, for the cubic and hexagonal phases. These ranges are shown in Figure 2. Using lithium tungstate we formed a hexagonal phase at pH = 1.7 with a = 7.313 (3) Å and c = 7.747 (4) Å; experiments at higher pH are now underway.

A scanning electron microscopic examination of the samples (Figure 3) revealed that the cubic phase showed uniform particles with a cubic habit; the hexagonal phases were needle aggregates similar to the morphology of $WO_3\cdot{}^1/_3H_2O$ as reported by Gerand et al.[3] Electron microprobe results indicated the absence of chlorine, but the presence of sodium could not be quantified. Thus, chemical analysis was carried out using TGA for water content and atomic absorption spectrometry for sodium on samples dissolved in 0.3 M $K_3Fe(CN)_6$ in 4% KOH solution. These gave the compositions $Na_{1.10}W_2O_{6.55}\cdot1.4H_2O$ and $Na_{0.3}WO_{3.15}\cdot0.55H_2O$ for the cubic and hexagonal phases, respectively.

Ammonium and potassium ions were readily exchanged for sodium with 1 M MNO_3 ($M = K^+, NH_4^+$) at 80 °C for a few hours. The cell parameters of the potassium and ammonium ion-exchanged pyrochlores are 10.317 (5) Å and 10.344 (5) Å, respectively; sodium was not detectable in these samples. The ammonium was detected in the structure by IR spectroscopy. Cubic $WO_3\cdot xH_2O$ could be prepared by repeatedly exchanging with 1 M HNO_3 at 80 °C for 1 h following the literature;[6,8] longer heating and higher temperatures always led to decomposition of the product. In contrast to the facile ion exchange in the cubic phase we have not successfully completely ion-exchanged the hexagonal phase. This is presumably due to blockages and restricted diffusion in the one-dimensional tunnels in the latter.

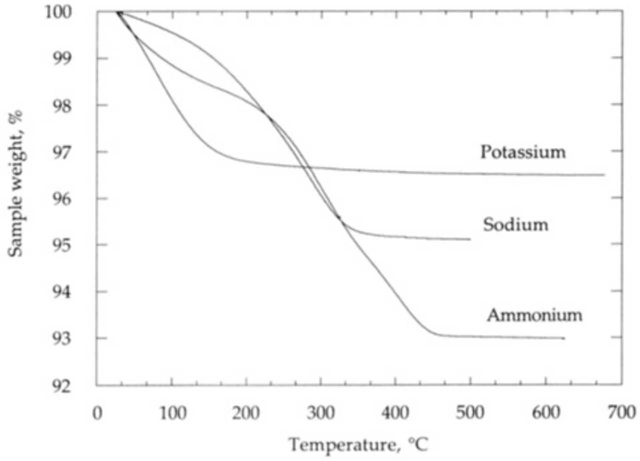

Figure 4. TGA scans of the sodium, potassium, and ammonium pyrochlores.

The thermal stability of the sodium pyrochlore and hexagonal phases has been investigated by TGA, which showed a continuous water loss from ambient to 350 °C (Figure 4). The pyrochlore took up most of the water upon exposure to air over a period of 1 week. The hexagonal phase also absorbed 2–3% by weight of water after a few days. X-ray studies showed that the cubic sample remained stable up to 400 °C and then decomposed into a mixture of $Na_2W_4O_{13}$[9] and a few lines characteristic of $Na_2W_6O_{19}$.[10] On the other hand, the hexagonal samples were stable until 500 °C and above that decomposed into $Na_2W_4O_{13}$ and WO_3. The potassium pyrochlore phase in contrast to the sodium analogue lost its water by 150 °C; this is consistent with the earlier report for $MNbWO_6\cdot H_2O$ compounds.[11] The ammonium compound appears to lose all its water and ammonium by 450 °C, but the structure also falls apart; up to 400 °C and 6.5 wt % loss the pyrochlore structure remains intact.

The pyrochlore $Na_{1.10}W_2O_{6.55}\cdot1.4H_2O$, with space group $Fd3m$, is defective at both 16(d) and 8(b) sites; the water molecules are probably located in the 32(e) sites as in $BaCdCl_6\cdot5H_2O$.[12] Hexagonal $Na_{0.3}WO_{3.15}\cdot0.55H_2O$ seems to contain more water than expected from structural considerations. A similar discrepancy in water content was noted[3] in $WO_3\cdot{}^1/_3H_2O$, and it was attributed to adsorbed water. A detailed structural study of both the pyrochlore and hexagonal phases by powder neutron diffraction techniques is under way.

---

(8) Freedman, M. L. *J. Am. Chem. Soc.* **1959**, *81*, 3834.

(9) Viswanathan, K. *J. Chem. Soc., Dalton Trans.* **1974**, 2170.

(10) Reau, J.-M.; Fouassier, C. *Bull. Soc. Chim. Fr.* **1971**, 398.

(11) Murphy, D. W.; Cava, R. J.; Rhyne, K.; Roth, R. S.; Santoro, A.; Zahurak, S. M.; Dye, J. L. *Solid State* Ionics **1986**, *18–19*, 799.

(12) Ledesert, M.; Raveau, B. *J. Solid State Chem.* **1987**, *67*, 340.

While investigating tungstic acids, Freedman[8] had isolated two sodium-containing phases labeled as phase C and phase X. Although they[13] did not analyze their diffractograms, our indexing/least-squares analysis of their data indicates that these are hexagonal (with a = 7.317 Å and c = 7.773 Å) and cubic (a = 10.26 Å) phases similar to what we have obtained in this study. Their patterns however contained additional lines presumably due to impurity phases; we believe that the use of the hydrothermal technique reported here has assisted in the formation of impurity free phases. They report one composition for the X phase corresponding to $(Na_2O)_{0.29}WO_3 \cdot 1.1H_2O$, not dissimilar to the composition found here; their titration data suggest that a significant proportion of the sodium can be exchanged for hydrogen.

Acknowledgment. We thank Henry Eichelberger for the SEM studies and Allan Jacobson for suggesting the use of the Parr bombs, and the partial support of the National Science Foundation under grant DMR-8913849 is gratefully acknowledged.

---

[13] Freedman, M. L.; Leber, S. *J. Less Common Met.* **1964**, *7*, 427.

Preparation of Indium Antimonide Using a Single-Source Precursor

Alan H. Cowley,* Richard A. Jones,*
Christine M. Nunn, and Donald L. Westmoreland

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

Received January 22, 1990

The narrow bandgap and high electron mobility of InSb render this material very attractive for high-speed circuits, infrared detectors, and novel quantum well devices. Several techniques have been employed for the preparation of InSb;[1] however, the production of this material by organometallic chemical vapor deposition (OMCVD) has been relatively little explored.[2] We report the first example of the use of a single-source precursor for the deposition of InSb. Preliminary experiments indicate that this method is also valid for GaSb preparation.

In designing an appropriate precursor, we sought systems with strong In-Sb bonds and with hydrocarbon groups capable of undergoing clean, facile decomposition. By analogy with our GaAs precursor,[3] we decided on a target molecule of the type $[Me_2In(\mu\text{-Sb-}t\text{-Bu}_2)]_n$. Initial experiments indicated that the chemistry of Sb to be significantly different from that of As and P. For example, the reaction of t-$Bu_2SbSiMe_3$ with $InCl_3$ afforded the 1:2 stoichiometry product $[(t\text{-Bu}_2Sb)(Cl)In(\mu\text{-Sb-}t\text{-Bu}_2)]_2$ regardless of the reactant mole ratio employed.[4] Moreover, attempts to prepare $[Me_2In(\mu\text{-Sb-}t\text{-Bu}_2)]_n$ by methylation of $[Cl_2In(\mu\text{-Sb-}t\text{-Bu}_2)]_3$ met with failure. We have now succeeded in the preparation of $[Me_2In(\mu\text{-Sb-}t\text{-Bu}_2)]_3$ (1) via the following sequence of steps:

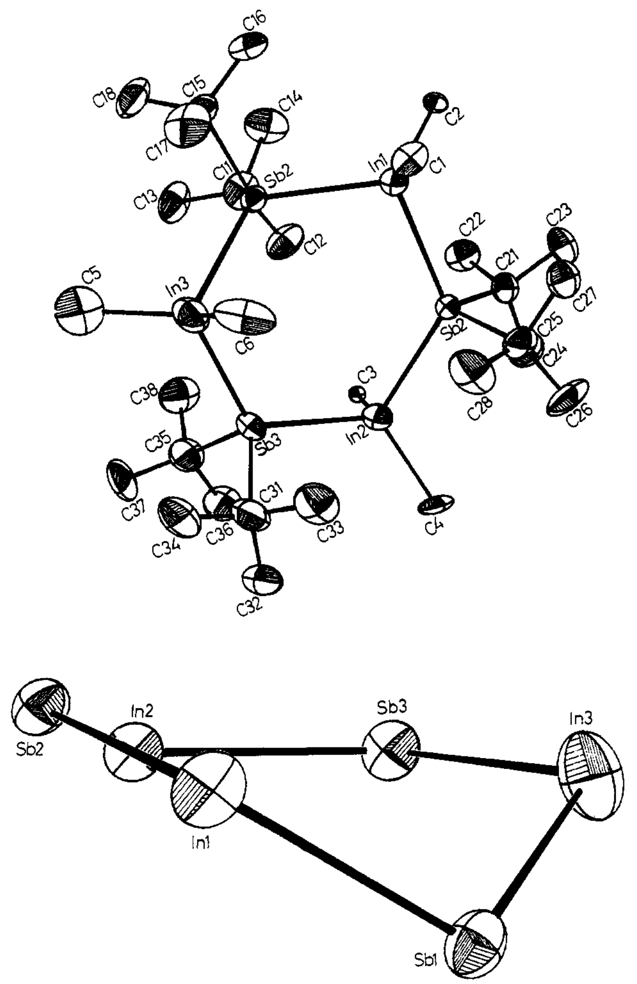

Figure 1. Top: view of 1 showing the atom numbering scheme. Bottom: In_3Sb_3 skeleton of 1. Important bond distances (Å) and angles (deg): In(1)-Sb(1), 2.822 (1); In1)-Sb(2), 2.889 (1); In(2)-Sb(2), 2.864 (1); In(2)-Sb(3), 2.838 (2); In(3)-Sb(3), 2.858 (2); In(3)-Sb(1), 2.860 (2); Sb(1)-In(1)-Sb(2), 103.65 (5); Sb(2)-In(2)-Sb(3), 109.43 (5); Sb(1)-In(3)-Sb(3), 107.73 (5); In(1)-Sb(1)-In(3), 115.84 (5); In(1)-Sb(2)-In(2), 127.79 (4); In(2)-Sb(3)-In(3), 121.28 (6).

$$t\text{-Bu}_2\text{SbSiMe}_3 \xrightarrow{\text{EtOH}} t\text{-Bu}_2\text{SbH} \xrightarrow{\text{MeLi}} t\text{-Bu}_2\text{SbLi} \xrightarrow{\text{Me}_2\text{InCl}} 1$$

Di-*tert*-butylstibine and t-Bu_2SbLi are new compounds; however, they are unstable at ambient temperature and can be generated only in situ. In a typical experiment, ethanol (0.38 g, 8.35 mmol) was added to a solution of 2.58 g (8.35 mmol) of t-$Bu_2SbSiMe_3$ in 50 mL of THF at −78 °C. After brief warming to room temperature (15 min) the stirred solution of t-Bu_2SbH was recooled to −78 °C and treated with MeLi (5.5 mL of 1.55 M solution in hexane). The resulting solution of t-Bu_2SbLi was stirred at −78 °C for 20 min, following which it was warmed to room temperature and stirred for 1 h. The t-Bu_2SbLi solution was then recooled to −78 °C and added via cannula to a suspension of 1.5 g (8.35 mmol) of Me_2InCl in 25 mL of THF. After the resulting bright yellow mixture was stirred at room temperature for 90 min, all solvents and volatiles were removed by evacuation. The residue was extracted with hexane and filtered Celite to give an orange solution. Concentration and cooling of this solution (−20 °C) resulted in the formation of pale orange crystalline 1 (mp 139–141

---

[1] Webb, J. B.; Halpin, C.; Noad, J. P. *J. Appl. Phys.* **1986**, *60*, 2949, and references therein.

[2] Chiang, P. K.; Bedair, S. M. *J. Electrochem. Soc.* **1984**, *131*, 2422.

[3] Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B. Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248.

[4] Barron, A. R.; Cowley, A. H.; Jones, R. A.; Nunn, C. M.; Westmoreland, D. L. *Polyhedron* **1988**, *7*, 77.

0897-4756/90/2802-0221$02.50/0