A Class of Single-Source Precursors to Titanium Disulfide Films. Synthesis, Structure, and Chemical Vapor Deposition Studies of [$TiCl_4(HSR)_2$]

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Titanium disulfide is one of the desirable cathode materials for lithium batteries.[2] Recent emphasis on the development of thin-film batteries has underscored the need for high-purity, crystallographically oriented, stoichiometric coatings.[3] The majority of chemical vapor deposition (CVD) routes to TiS_2 films are based on the reaction between titanium tetrachloride and hydrogen sulfide, organic sulfides, or disulfides.[3-5] Recently we reported a new atmospheric pressure CVD process for TiS_2 films, which relies upon the reaction of titanium tetrachloride with organothiols at temperatures ≥200 °C and affords highly pure, crystallographically oriented, stoichiometric, adhesive coatings.[5] It was envisaged that use of a single-source precursor in the deposition of TiS_2 films could provide precise control of titanium and sulfur stoichiometry, could reduce toxic/odiferous waste, and would eliminate the problem of mixing two or more gaseous reactants in a low-pressure CVD reactor. However, no such precursor had been described in the literature. Herein we report the synthesis of the first class of single-source precursors to high quality TiS_2 films. These complexes are of the formula [$TiCl_4(HSR)_2$] and are obtained upon treatment of titanium tetrachloride with alkanethiols. Significantly, the crystallographic orientation of the films produced from these precursors is ideal for use as cathodes in lithium batteries.

Treatment of titanium tetrachloride with 2 equiv of cyclohexanethiol or cyclopentanethiol in hexane at ambient temperature and subsequent evaporation of the solvent afforded spectroscopically pure yellow solids of [$TiCl_4(C_6H_{11}SH)_2$] (**1**, 77%) and [$TiCl_4(C_5H_9SH)_2$] (**2**, 89%), respectively (eq 1).[6,7] Sublimation of these crude products (60 °C, 0.1 mmHg) yielded analytically pure, moisture-sensitive yellow crystals of **1** and **2**. Complexes **1** and **2** were fully characterized by spectroscopic and analytical techniques.[8] In addition, an X-ray crystal structure of **1** was determined (vide infra). The infrared spectra showed sharp S--H stretches (**1**, ν_{SH} = 2492 cm^{-1}; **2**, ν_{SH} = 2520, 2505 cm^{-1}), which is consistent with strong S–H···X (X = S or Cl) hydrogen bonding.[9] For comparison, neat cyclohexanethiol showed an S–H absorption at 2557 cm^{-1}.

$$TiCl_4 + 2RSH \xrightarrow{\text{hexane, 0 °C}} [TiCl_4(HSR)_2] \qquad (1)$$

1, R = C_6H_{11}, 77%
2, R = C_5H_9, 89%

Figure 1 shows a perspective view of the *cis*-adduct **1** along with selected bond distances and angles.[10] The titanium–sulfur bond lengths are 2.663(2) Å (Ti–S(1)) and 2.646(2) Å (Ti–S(2)) and are in the range expected for titanium–sulfur bonds.[11] The titanium–chlorine bonds that are *trans* to each other (Ti–Cl(3) = 2.300(2) Å; Ti–Cl(4) = 2.263(2) Å) are slightly longer than the ones that are *trans* to the sulfur atoms (Ti–Cl(1) = 2.221(2) Å; Ti–Cl(2) = 2.226(2) Å). Examination of the bond angles about titanium reveals small but significant distortions from idealized octahedral geometry. The *cis*-chlorines are bent toward the sulfurs (range = 78.4–92.6°, average = 85.2°) and the S(1)–Ti–S(2) angle is 79.8(1)°. The trans angles (S(1)–Ti–Cl(1) = 165.4(1)°; S(2)–Ti–Cl(2) = 171.4(1)°; Cl(3)–Ti–Cl(4) = 161.7(1)°) also deviate from the idealized value of 180°. While it is tempting to propose that S–H···X hydrogen bonding is responsible for the structural distortions in **1**, simple adducts of titanium tetrachloride with no hydrogen bond donors (e.g., [$TiCl_4((MeCO)_2O)$],[12a] [$TiCl_4(MeCOCMe_2COMe)$],[12b] [$TiCl_3(THF)_3$][12c]) also show small deviations from octahedral geometry.

Bronze-colored titanium disulfide films were prepared from **1** under low-pressure CVD conditions (static vacuum, total reactor

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(7) Use of more volatile alkanethiols (e.g., methanethiol, ethanethiol, 2-propanethiol, etc.) also afforded complexes of the presumed formula [$TiCl_4(HSR)_2$]. However, the extremely high volatilities of these complexes (much higher than that of **1** and **2**) made their manipulation and characterization extremely difficult. Hence, cyclopentanethiol and cyclohexanethiol were used to obtain more tractable complexes.

(8) Spectral and analytical data for **1**: mp 78 °C dec with sublimation; IR (Nujol, cm^{-1}) 2492 (m, sharp), 1340 (w), 1263 (w), 1210 (w), 1022 (w), 995 (m), 886 (w), 875 (w), 809 (w), 755 (s, br), 727 (s), 667 (w); ^{1}H NMR ($CDCl_3$, δ, 23 °C) 3.11 (m, C*H*SH), 2.33 (s, S–*H*), 2.06 (m, C*H*$_2$), 1.74 (m, C*H*$_2$), 1.60 (m, C*H*$_2$), 1.35 (m, C*H*$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm, 23 °C) 42.6 (s, *C*HSH), 36.68 (s, 2 *C*H$_2$), 26.09 (s, 2 *C*H$_2$), 25.16 (s, *C*H$_2$). Anal. Calcd for $C_{12}H_{22}Cl_4S_2Ti$: C, 34.14; H, 5.73. Found, C, 33.82; H, 5.68. Spectral and analytical data for **2**: mp 60 °C dec with sublimation; IR (Nujol, cm^{-1}) 2520 (m), 2505 (m), 1310 (s), 1261 (s), 1236 (m), 1158 (w), 1089 (w), 1020 (m), 794 (s), 715 (s); ^{1}H NMR ($CDCl_3$, δ, 23 °C) 3.53 (m, C*H*SH), 2.95 (s, S*H*), 2.09 (s, C*H*$_2$), 1.72 (s, C*H*$_2$), 1.57 (s, 2 C*H*$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm, 23 °C) 44.52 (*C*HSH), 36.25 (s, 2 *C*H$_2$), 24.57 (s, 2 *C*H$_2$). Anal. Calcd for $C_{10}H_{20}Cl_4S_2Ti$: C, 30.48; H, 5.12. Found: C, 30.26; H, 4.99.

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(10) Crystal data for **1**: $C_{12}H_{24}Cl_4S_2Ti$, triclinic, $P\bar{1}$, a = 6.1340(10) Å, b = 11.615(6) Å, c = 13.892(6) Å, α = 100.78(4)°, β = 99.52(3)°, γ = 100.97(4)°, V = 933.6(7) Å^3, Z = 2, D_x = 1.500 g cm^{-3}, μ(Mo Kα) = 12.34 cm^{-1}, T = 233 K. Of 3450 data collected ($2\theta_{max}$ = 50°, Siemens P4), 3302 were independent and 2521 were observed ($5\sigma F_o$). All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were treated as idealized contributions. $R(F)$ = 5.33%, $R_w(F)$ = 9.26%. All computations used the SHELXTL-PLUS (Version 4.2) library of programs (G. Sheldrick, Siemens, Madison, WI). Further data are contained in the supplementary material.

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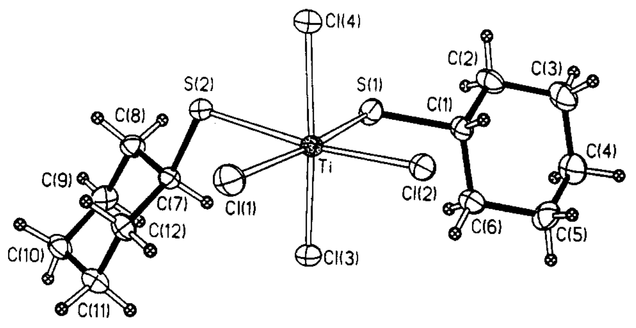

Figure 1. Perspective view of **1**. Selected bond lengths (Å) and angles (deg): Ti–Cl(1) = 2.221(2), Ti–Cl(2) = 2.226(2), Ti–Cl(3) = 2.300(2), Ti–Cl(4) = 2.263(2), Ti–S(1) = 2.663(2), Ti–S(2) = 2.646(2); Cl(1)–Ti–Cl(2) = 101.6(1), Cl(1)–Ti–Cl(3) = 94.4(1), Cl(2)–Ti–Cl(3) = 95.0(1), Cl(1)–Ti–Cl(4) = 96.6(1), Cl(2)–Ti–Cl(4) = 97.0(1), Cl(3)–Ti–Cl(4) = 161.7(1), Cl(1)–Ti–S(1) = 165.4(1), Cl(2)–Ti–S(1) = 92.6(1), Cl(3)–Ti–S(1) = 80.7(1), Cl(4)–Ti–S(1) = 85.0(1), Cl(1)–Ti–S(2) = 86.3(1), Cl(2)–Ti–S(2) = 171.4(1), Cl(3)–Ti–S(2) = 87.9(1), Cl(4)–Ti–S(2) = 78.4(1), S(1)–Ti–S(2) = 79.8(1).

pressure 0.1–0.2 mmHg) using a hot-walled reactor within the temperature range 200–600 °C. Complex **1** was slowly sublimed (50 °C, 0.1 mmHg)[13] into the heated reaction zone containing a glass or silicon substrate supported on a ceramic stage. Passage of the vaporous precursor over the heated substrate resulted in titanium disulfide coatings. Films produced on glass substrates from **1** (ca. 2.3 mmol) using a 3-min deposition time afforded film thicknesses of 13 000 Å at 400 °C and 5000 Å at 500 °C. This gives growth rates of approximately 70 Å s^{-1} at 400 °C and 30 Å s^{-1} at 500 °C. Films deposited on silicon and glass substrates at $\geq$400 °C revealed a nearly exclusive (001) crystallographic orientation. This is a desirable orientation for use as the cathode in lithium batteries.[3b] Films fabricated at $\leq$300 °C showed several crystallographic orientations, but the (001) orientation was the predominant form. X-ray photoelectron spectroscopy of films made at 300 and 400 °C disclosed undetectable ($\leq$2%) carbon or chlorine contamination.

We next sought to analyze the organic byproducts that were formed during film depositions from **1**. Volatile compounds were trapped in a liquid nitrogen condenser. The identity and ratio of products was analyzed by ^{1}H and ^{13}C{^{1}H} NMR. At 400 °C, the products consisted of an 85:15 ratio of cyclohexene and cyclohexyl chloride. No other species were observed. At 500 °C, cyclohexene and chlorocyclohexane were observed in a 68:32 ratio, while at 600 °C the ratio was 60:40. The exact mechanistic sequence by which cyclohexene and cyclohexyl chloride are produced is not clear at present, since a number of pathways (e.g., concerted cleavage of C–S bond, radical cleavage of C–S bond, dissociation of cyclohexanethiol followed by elimination of hydrogen sulfide to form cyclohexene, etc.) could provide the observed products. Experiments are in progress to probe this issue.

In summary, complexes of the type $[TiCl_4(HSR)_2]$ comprise the first single-source precursors to high-quality titanium disulfide films having low carbon and chlorine contamination. The vapor pressures of these precursors (1–2 mmHg at 22 °C for **1** and **2**) are high enough for practical use in CVD reactors.[7,13] Importantly, the crystallographic orientation of the films is ideal for use as cathodes in lithium batteries. We are continuing to study precursors to layered metal sulfides and to carry out detailed analyses of the films. These studies will be reported in due course.

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Supplementary Material Available: Tables S1–S6, listing full experimental details for data collection and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen postional parameters for **1** and Figures S7 and S8 giving X-ray diffraction and X-ray photoelectron spectroscopy data for the titanium disulfide films (16 pages). Ordering information is given on any current masthead page.

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(13) Complexes **1** and **2** have vapor pressures of 1–2 Torr at 22 °C, as determined by differential pressure measurements.