

Adducts of titanium tetrachloride with organosulfur compounds. Crystal and molecular structures of TiCl₄(C₄H₈S)₂ and (TiCl₄)₂(CH₃SSCH₃)

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Abstract—Treatment of titanium tetrachloride with a range of organothiols affords adducts of the formula $TiCl_4(HSR)_2$ in 77–89% yields. Reaction of titanium tetrachloride with organic sulfides gives sulfide adducts of the formula $TiCl_4(SR_2)_2$ in 87–98% yields. These complexes are volatile and monomeric with cis-organosulfur ligands. Treatment of titanium tetrachloride with methyl disulfide affords the adduct $(TiCl_4)_2(CH_3SSCH_3)$ in 98% yield, which adopts a dinuclear structure with a Ti_2Cl_8 core and a bridging disulfide ligand. The crystal structures of $TiCl_4(C_4H_8S)_2$ and $(TiCl_4)_2(CH_3SSCH_3)$ were determined. The relevance of these observations to the chemical vapor deposition of titanium disulfide and trisulfide films is discussed. © 1997 Elsevier Science Ltd

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Titanium disulfide is one of the desirable cathode materials for lithium batteries [1]. Titanium disulfide films have also been used as a solid lubricant due to weak Van der Waals interactions between adjacent layers in the lattice [2]. The majority of Chemical Vapor Deposition (CVD) routes to titanium disulfide films are based on the reaction between titanium tetrachloride and hydrogen sulfide, organic sulfides, or disulfides [3–5]. Schleich [4] has recently disclosed that the CVD reaction between titanium tetrachloride and di-tert-butyl disulfide affords titanium trisulfide films at temperatures between 200-260°C, mixtures of titanium trisulfide and titanium disulfide films between 260-400°C, and titanium disulfide films above 400°C. In contrast, di-tert-butyl sulfide reacted with titanium tetrachloride at $\geq 260^{\circ}$ C to give titanium disulfide films. Recently we reported a new atmospheric pressure CVD process for titanium disulfide films, which relies upon the reaction of titanium

tetrachloride with organothiols at temperatures $\geq 200^{\circ}$ C, and affords highly pure, crystallographically oriented, stoichiometric, adhesive coatings [6]. We subsequently disclosed that complexes of the formula TiCl₄(HSR)₂ (R = alkyl) constitute the first single-source precursors for the CVD of titanium disulfide films [7]. Significant aspects of the processes based upon organothiols include a large drop in the minimum deposition temperature for titanium disulfide film deposition ($\geq 200^{\circ}$ C versus $\geq 400^{\circ}$ C for hydrogen sulfide) and the fact that no carbon or chlorine impurities were detected in the films.

The differences observed between the use of organothiols, organosulfides, and organodisulfides in the deposition of titanium disulfide films raise the possibility that there are corresponding variations in the reactions between titanium tetrachloride and the respective sulfur sources. Since there is very little known about the reactivity of titanium tetrachloride toward organosulfur compounds [8–11], we have initiated an investigation of the solution coordination chemistry of titanium tetrachloride with sulfur

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donors. Herein we describe the reaction of titanium tetrachloride with several sulfides and disulfides and also report the crystal structures of two complexes.

EXPERIMENTAL

General considerations

All manipulations were performed under an inert atmosphere using either glovebox or Schlenk line techniques. Hexane was distilled from sodium. Chloroform-d and dichloromethane- d_2 was dried over activated 4 Å molecular sieves. Titanium tetrachloride and the organosulfur compounds were used as received from Aldrich Chemical Co.

¹H NMR and ¹³C{¹H} NMR spectra were obtained at 300 or 75 MHz in chloroform-*d* or dichloromethane- d_2 . Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of $TiCl_4(HSC_6H_{11})_2$ (1)

A 200-cm³ Schlenk flask was charged with titanium tetrachloride (2.00 cm³, 18.2 mmol), dichloromethane (30 cm^3) , and a stir bar and was fitted with a septum. The solution was cooled to 0° C, and cyclohexylthiol (4.46 cm³, 36.48 mmol) was added by syringe to afford a clear, deep yellow solution. The solution was allowed to reach ambient temperature and was stirred for 2 h. The volatiles were pumped off and the resultant yellow solid was extracted with hexane (100 cm³) and filter through a 2 cm pad of Celite to afford a clear, yellow solution. This solution was kept at -20° C, to afford needle shaped yellow crystals of 1. The supernatant was removed by cannulation and the crystals were vacuum dried (5.96 g, 84% based upon titanium tetrachloride): m.p. 78°C (dec with sublimation); IR (Nujol, cm⁻¹) 2492 (m, S—H stretch), 1340 (w), 1263 (w), 1210 (w), 1022 (w), 995 (m), 886 (w), 875 (w), 809 (w), 755 (s, broad), 727 (s), 667 (w); ¹H NMR (CDCl₃, 23°C, δ) 3.11 (m, CHSH), 2.33 (s, S-H, 2.06 (m, CH_2), 1.74 (m, CH_2), 1.60 (m, CH_2), 1.35 (m, CH_2); ¹³C{¹H} NMR (CDCl₃, 23°C, ppm) 42.60 (s, CHSH), 36.68 (s, 2 CH₂), 26.09 (s, 2 CH₂), 25.16 (s, CH₂). Found: C, 33.82; H, 5.68. Calc. for $C_{12}H_{24}Cl_4S_2Ti: C, 34.14; H, 5.73\%.$

Preparation of $TiCl_4(HSC_5H_9)_2$ (2)

A 100-cm³ Schlenk flask was charged with cyclopentylthiol (0.20 cm³, 1.83 mmol), hexane (15 cm³), a stir bar and was fitted with a rubber septum. This solution was cooled to 0°C, and titanium tetrachloride (0.1 cm³, 0.91 mmol) was added *via* a syringe to give a clear, deep yellow solution. This solution was allowed to reach ambient temperature and stirred for 2 h. The solution was placed at -20° C for 6 h to afford yellow crystals of **2**. The solvent was transferred and the crystals were vacuum dried to afford **2** (0.28 g, 78% based upon titanium tetrachloride) : m.p. 60°C (dec. with sublimation); IR (Nujol, cm⁻¹) 2520 (m, S—H), 2505 (m, S—H), 1310 (s), 1261 (s), 1236 (m), 1158 (w), 1089 (w), 1020 (m), 794 (s), 715 (s); ¹H NMR (CDCl₃, 23°C, δ) 3.53 (m, CHSH), 2.95 (s, SH), 2.09 (s, CH₂), 1.72 (s, CH₂), 1.57 (s, CH₂); ¹³C{¹H} NMR (CDCl₃, 23°C, ppm) 44.52 (s, CHSH), 36.25 (s, 2CH₂), 24.57 (s, 2CH₂). Found : C, 30.26; H, 4.99. Calc. for C₁₀H₂₀Cl₄S₂Ti : C, 30.48; H, 5.12%.

Preparation of $TiCl_4(C_4H_8(SH)_2)$ (3)

A 100-cm³ Schlenk flask was charged with 2,3-butanedithiol (0.86 cm³, 6.9 mmol), dichloromethane (10 cm³), and a stir bar and was fitted with a rubber septum. This solution was cooled to 0°C, and titanium tetrachloride (0.75 cm³, 6.90 mmol) was added via a syringe to give a yellow solution. The solution was allowed to reach ambient temperature and was stirred for 3 h. This solution was filtered through a 2 cm pad of Celite to give a clear, yellow solution. Hexane (75 cm³) was carefully layered on the dichloromethane layer. The system was allowed to equilibrate for 24 h. The solvent was decanted by cannula and the crystals were vacuum dried to afford 3 as yellow rods (1.87 g, 87% based on titanium tetrachloride): m.p. 98°C (dec); IR (Nujol, cm⁻¹) 2724 (w), 2678 (w), 2518 (s, S-H), 1443 (s), 1381 (s), 1325 (m), 1294 (w), 1257 (w), 1236 (w), 1221 (w), 1144 (m), 1092 (m), 1061 (w), 1051 (w), 1040 (w), 994 (w), 983 (w), 968 (w), 958 (w), 865 (s), 828 (w), 766 (w), 715 (w), 679 (w), 642 (w); ¹H NMR (CDCl₃, 23°C, δ) 3.95 (m, CH), 3.72 (broad s, S-H), 3.59 (m, CH), 3.55 (broad s, S-H), 1.67 (d, J = 5.7 Hz, CH₃), 1.58 (d, J = 6.9 Hz, CH₃); ¹³C{¹H} (CDCl₃, 23°C, ppm) 52.10 (broad s, CH), 49.38 (broad s, CH), 22.68 (s, CH₃), 18.43 (s, CH₃). Found: C, 15.46; H, 3.24. Calc. for C₄H₁₀Cl₄S₂Ti: C, 15.40; H, 3.23%.

Preparation of TiCl₄(HSCH₂CH₂CH₃)₂

A 5-mm NMR tube was charged with titanium tetrachloride (0.010 cm³, 0.090 mmol) and chloroform-d (0.70 cm³) and was fitted with a rubber septum. *n*-Propylthiol (0.020 cm³, 0.20 mmol) was added into the NMR tube by syringe to afford a bright yellow solution of TiCl₄(HSCH₂CH₂CH₃)₂: ¹H NMR (CDCl₃, 23°C, δ) 3.15 (broad s, S—H), 2.97 (t, CH₂CH₂CH₃, J = 6.9 Hz), 1.78 (sextet, CH₂CH₂CH₃, J = 7.2 Hz), 1.04 (t, CH₂CH₂CH₃, J = 7.5 Hz); ¹³C{¹H} NMR (CDCl₃, 23°C, ppm) 34.23 (s, CH₂CH₂CH₃), 25.09 (s, CH₂CH₂CH₃), 12.98 (s, CH₂CH₂CH₃).

3

Preparation of TiCl₄(HSCH(CH₃)₂)₂

In a fashion similar to TiCl₄(HSCH₂CH₂CH₃)₂, titanium tetrachloride (0.010 cm³, 0.090 mmol) and isopropylthiol (0.020 cm³, 0.20 mmol) were reacted to afford a bright yellow solution of TiCl₄(HS-CH(CH₃)₂)₂ in chloroform-*d* (0.70 cm³): ¹H NMR (CDCl₃, 23°C, δ) 3.29 (m, *H*SCH(CH₃)₂), 2.12 (broad s, HSCH(CH₃)₂), 1.35 (d, *J* = 6.6 Hz, HSCH(CH₃)₂); ¹³C{¹H} NMR (CDCl₃, 23°C, ppm) 33.16 (s, HSCH(CH₃)₂), 26.92 (s, HSCH(CH₃)₂).

Preparation of $TiCl_4(SC_4H_8)_2$ (4)

A 100-cm³ Schlenk flask was charged with titanium tetrachloride (0.10 cm³, 0.91 mmol), hexane (30 cm³), a stir bar and was fitted with a rubber septum. The contents were cooled to 0°C and tetrahydrothiophene (0.16 cm³, 1.8 mmol) was added by syringe to afford an orange solution. This solution was stirred for 1.5 h and the volatiles were pumped off to afford 4 as an orange solid (0.29 g, 87% based on titanium tetrachloride) : m.p. 132°C (with sublimation) ; IR (Nujol, cm⁻¹) 1438 (s), 1424 (m), 1405 (w), 1304 (m), 1252 (s), 1204 (w), 1128 (m), 1090 (broad, w), 1066 (m), 1013 (s), 955 (m), 879 (w), 869 (w), 798 (s), 659 (m); ¹H NMR (CDCl₃, 23°C, δ) 3.35 (t, J = 6.0 Hz, SCH₂), 2.13 (m, SCH_2CH_2); ¹³C{¹H} NMR (CDCl₃, 23°C, ppm) 39.90 (s, SCH₂), 29.81 (s, SCH₂CH₂). Found: C, 24.95; H, 4.28. Calc. for C₈H₁₆Cl₄S₂Ti: C, 26.25; H, 4.41%.

Preparation of $TiCl_4(SC_5H_{10})_2$ (5)

In a fashion similar to the preparation of 1, titanium tetrachloride (0.10 cm³, 0.91 mmol) and pentamethylene sulfide (0.19 cm³, 1.8 mmol) were reacted to afford 5 as an orange solid (0.35 g, 97% based on titanium tetrachloride): m.p. 127°C (with sublimation); IR (Nujol, cm⁻¹) 1453 (s), 1435 (s), 1420 (s), 1367 (w), 1352 (m), 1346 (m), 1336 (m), 1300 (m), 1266 (m), 1258 (m), 1231 (m), 1210 (m), 1202 (m), 1143 (w), 1095 (m), 1064 (m), 1013 (m), 966 (s), 961 (s), 894 (s), 838 (w), 828 (w), 813 (m), 739 (w), 719 (w), 678 (w), 645 (w), 636 (m); ¹H NMR (CDCl₃, 23°C, δ) 3.11 (t, J = 6.0 Hz, SCH₂), 1.92 (m, CH₂), 1.62 (m, CH_2); ¹³C{¹H} NMR (CDCl₃, 23°C, ppm) 37.97 (s, SCH₂), 27.02 (s, CH₂), 25.42 (s, CH₂). Found: C, 30.41; H, 5.13. Calc. for C₁₀H₂₀Cl₄S₂Ti: C, 30.48; H, 5.12%.

Preparation of $TiCl_4((CH_3)_2S)_2$ (6)

In a fashion similar to the preparation of 1, titanium tetrachloride (3.0 cm³, 27.4 mmol) and dimethyl sulfide (4.02 cm³, 54.7 mmol) were reacted to afford 6 as an orange solid (8.41 g, 98% based on titanium tetrachloride) : m.p. 79–82°C; IR (Nujol, cm⁻¹) 1597

(w), 1426 (s), 1422 (s), 1411 (m), 1366 (w), 1325 (w), 1303 (w), 1258 (m), 1104 (w), 1095 (w), 1089 (w), 1066 (w), 1062 (w), 1028 (m), 1019 (m), 978 (w), 970 (w), 922 (w), 916 (w), 796 (m); ¹H NMR (CDCl₃, 23°C, δ) 2.54 (s, CH₃); ¹³C{¹H} NMR (CDCl₃, 23°C, ppm) 25.00 (s, CH₃). Found : C, 15.17; H, 3.75. Calc. for C₄H₁₂Cl₄S₂Ti : C, 15.30; H, 3.85%.

Preparation of (TiCl₄)₂(CH₃SSCH₃) (7)

A 250-cm³ Schlenk flask was charged with titanium tetrachloride (3.0 cm³, 27.4 mmol), hexane (60 cm³), and a stir bar and was fitted with a rubber septum. The contents were cooled to 0°C and dimethyl disulfide (4.93 cm³, 54.7 mmol) was added *via* a syringe to afford an orange solution. This solution was stirred for 1.5 h and the volatiles were pumped off to afford 7 as a yellow-brown solid (6.34 g, 98% based on titanium tetrachloride) : m.p. 63–64°C (dec. with sublimation) ; IR (Nujol, cm⁻¹) 1605 (w), 1446 (s), 1408 (w), 1365 (w), 1257 (w), 1084 (w), 1075 (w), 1058 (w), 1022 (w), 799 (m) ; ¹H NMR (CDCl₃, 23°C, δ) 2.56 (s, CH₃), ¹³C{¹H} NMR (CDCl₃, 23°C, ppm) 23.20 (s, CH₃). Found: C, 5.12; H, 1.27. Calc. for C₂H₆Cl₈S₂Ti₂: C, 5.07; H, 1.28%.

Crystal structure determinations of 4 and 7

Crystals of 4 and 7 were grown by sublimation. Suitable crystals were selected and mounted in nitrogen-flushed, thin-walled capillary tubes. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 25 reflections $(20^{\circ} \le 2\theta \le 25^{\circ})$. The systematic absences in the diffraction data for 4 are consistent with the space groups *Pnma* and *Pn2*₁*a*; for 7, *P*I and *P1*. *E*-statistics suggested the centrosymmetric alternative for 4 and the non-centrosymmetric space group for 7. The space group assignments were verified subsequently through further refinement. The η parameter refined to 0.87(7), indicating that the absolute structure has been determined for 7.

Structure 4 was solved by direct methods while 7 was solved with a sharpened Patterson map. Both structures were completed by subsequent difference Fourier syntheses and were refined by full-matrix least-squares procedures. The tetrahydrothiophene carbon atoms of 4 were initially refined anisotropically, however, this led to unacceptable bond distances caused by the averaging of the positions of unique atoms with reflections on the mirror plane. Thus, the tetrahydrothiophene carbon atoms were refined isotropically with a restrained refinable bond distance. All other non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

RESULTS

Organothiol adducts

Stable, easily isolated adducts were obtained upon treatment of titanium tetrachloride with two equivalents of cyclohexylthiol, cyclopentylthiol, or 2,3butanedithiol in hexane at ambient temperature. Workup afforded spectroscopically pure yellow solids of $TiCl_4(C_6H_{11}SH)_2$ (1, 77%), $TiCl_4(C_5H_9SH)_2$ (2, 89%), and TiCl₄(C₄H₈(SH)₂) (3, 87%), respectively (eq. (1)). Sublimation of these crude products (60° C, 0.1 mmHg) yielded analytically pure, moisture-sensitive yellow crystals of 1-3. Complexes 1-3 were fully characterized by spectroscopic and analytical techniques. The X-ray crystal structure of 1 has been previously published [7]. Compound 3 exists as a 1:1 mixture containing syn- and anti-2,3-butanedithiol ligands. The mixture is evident in the NMR spectra, which reveal resonances for two similar 2,3-butanedithiol ligands. The infrared spectra showed sharp S—H stretches (1, $v_{SH} = 2492 \text{ cm}^{-1}$; 2 $v_{SH} = 2520$, 2505 cm⁻¹; 3, $v_{SH} = 2518$ cm⁻¹), at values slightly lower than the neat thiols, (e.g., cyclohexylthiol, 2557 cm⁻¹). We propose that the lower S---H stretches in 1-3 are due to S—H···X (X = S or Cl) hydrogen bonding [12].



Reaction of titanium tetrachloride with low-boiling organothiols, such as 1-propanethiol (b.p. 67°C) and 2-propanethiol (b.p. 57°C), afforded adducts of the formula TiCl₄(RSH)₂. However, these adducts were exceptionally difficult to handle, due to their high volatility (estimated vapor pressures ≥ 10 mmHg at 22°C). Use of hexane as solvent gave isolation difficulties, since evaporation of the solvent also led to loss of the desired complexes. It was found that the isopropylthiol and propanethiol adducts could be prepared by mixing titanium tetrachloride with 2 equivalents of the thiol at ambient temperature. Using this procedure, relatively pure samples were obtained, which were characterized by ¹H and ¹³C{¹H} NMR spectroscopy. Despite the absence of a solvent, we were unable to purify $TiCl_4(nPrSH)_2$ or $TiCl_4(iPrSH)_2$ on the small scales (ca. 2 mmol) that were used. It is likely that the adducts readily dissociate to titanium tetrachloride and the respective thiols. The adducts were not explored further, since they posed no advantage over the more easily manipulated complexes 1-3.

Organosulfides

Treatment of titanium tetrachloride with two equivalents of tetrahydrothiophene, pentamethylene sulfide, or dimethyl sulfide in hexane at ambient temperature, followed by evaporation of the solvent afforded spectroscopically pure orange solids of $TiCl_4(C_4H_8S)_2$ (4, 87%), $TiCl_4(C_5H_{10}S)_2$ (5, 97%), and TiCl₄(C₂H₆S)₂ (6, 98%), respectively (eq. (2)). Sublimation of these crude products (25-50°C, 0.1 mmHg) yielded analytically pure, moisture-sensitive orange crystals of 4-6. Complexes 4-6 were fully characterized by spectroscopic and analytical techniques. The ¹H and ¹³C{¹H} NMR spectra of 4-6 were particularly diagnostic of the adduct structures and showed downfield shifts relative to the free ligands. For example, 6 revealed resonances at δ 2.54 in the ¹H NMR spectrum and 25.00 ppm in the ¹³C{¹H} NMR spectrum. The analogous values for free dimethyl sulfide were δ 2.04 and 17.81 ppm. The vapor pressures of 4-6 were estimated to be ca. 1-2 mmHg at 22°C, as determined by differential pressure measurements. Again, these vapor pressures may reflect equilibrium dissociation of the complex to thiol and titanium tetrachloride. These values are similar to that of 1, which we have previously reported to be a single-source precursor to titanium disulfide films [7]. Complexes 4-6 have been previously reported, and our physical data generally agree with those of previous workers [9-11].

TiCL	+	2 B ₂ S	hexane, 23 °C	
11014	•	21.20	TiCl ₄ (R ₂ S) ₂ 4, R ₂ = (CH ₂) ₄	(2)
			5, R ₂ = (CH ₂) ₅	
			6, R ₂ = 2 CH ₃	

Organodisulfides

Treatment of titanium tetrachloride with dimethyl disulfide (≥ 0.5 equiv.) under conditions used to prepare 1–6 afforded (TiCl₄)₂(CH₃SSCH₃) (7, 98%) as a yellow-brown powder upon workup (eq. (3)). NMR analysis of 7 revealed intact methyl groups with downfield shifts (¹H NMR δ 2.56, ¹³C{¹H} NMR 23.20 ppm), relative to free methyl disulfide (¹H NMR δ 2.38, ¹³C{¹H} NMR 21.94 ppm), which suggested an adduct structure. The microanalysis results for 7 were incompatible with a structure analogous to 1–6, but rather implied a formulation with a 2:1 ratio between titanium tetrachloride and methyl disulfide. The molecular geometry of 7 was established by an X-ray structure determination (*vide infra*). Complex 7 was easily sublimed and possessed a vapor pressure similar

to **1–6**. Treatment of titanium tetrachloride with isopropyl disulfide or tert-butyl disulfide under conditions used to prepare **7** afforded complicated



Crystal structures of 4 and 7

mixtures that we are still studying.

The crystal structures of 4 and 7 were determined in order to establish their nuclearities and molecular geometries. X-ray data were collected under the conditions summarized in Table 1. Bond lengths and bond angles are provided in Tables 2 and 3. Perspective views of 4 and 7 are shown in Figs 1 and 2.

Complex 4 crystallized as a distorted octahedral monomer with cis-tetrahydrothiophene ligands. The tetrahydrothiophene ligands were disordered; the disorder was treated as described in the experimental section. The titanium-chlorine bonds that were trans to sulfur atoms (Ti—Cl(1) 2.232(8) Å, Ti—Cl(3) 2.233(8) Å) were *ca.* 0.05 Å shorter than the chlorines that were mutually trans (Ti—Cl(2,2A) 2.280(4) Å). The shorter bond lengths of the titanium-chlorine bonds that are trans to sulfur can be understood by the weaker trans influence of sulfur, relative to chloride. The titanium-sulfur bond lengths were 2.626(7) Å (Ti—S(1)) and 2.625(7) Å (Ti—S(2)). The cischlorine-titanium-chlorine angles ranged from 97.0– 98.9° (av. = 97.5°), while the chlorine-titanium-

Table 1. Experimental crystallographic data for 4 and 7

	4	7
Chemical formula	C ₈ H ₁₆ Cl ₄ S ₂ Ti	$C_2H_6Cl_8S_2Ti_2$
Formula weight	366.0	473.6
Space group	Pnma (No. 62)	P1 (No. 1)
a (Å)	14.285(5)	6.403(2)
b (Å)	8.574(3)	7.224(4)
c (Å)	12.580(3)	9.410(3)
α (°)		110.66(3)
β (°)		101.48(2)
γ (°)		99.15(4)
$V(Å^3)$	1540.7(8)	386.5(7)
Z	4	1
T (K)	296	296
$\lambda(\mathbf{\hat{A}})$	0.71073	0.71073
$\rho_{\rm cale}$ (g cm ⁻³)	1.578	2.035
μ (cm ⁻¹)	14.90	26.48
Trans. coeff.		0.538-0.492
$R(F)^{a}$ (%)	5.29	4.11
$R(wF)^{a}$ (%)	6.24	4.34

^{*a*} $R = (\Sigma |\Delta F|) / \Sigma |F_{o}|$; $wR = [(\Sigma w |\Delta F|^2) / \Sigma w F_{o}^2]^{1/2}$.

sulfur angles ranged from $81.1-90.1^{\circ}$ (av. = 83.9°). chlorine-titanium-chlorine The trans angle (Cl(2)-Ti-Cl(2A)) was 158.0(2)°, which is a considerable deviation from the idealized 180° angle. The chlorine-titanium-sulfur angles were 171.3(3) (Cl(1)-Ti-S(2)) and $171.0(3)^{\circ}$ (Cl(3)-Ti-S(1)). The slightly extended angles associated with cis chlorine-titanium-chlorine can be attributed to steric crowding about the titanium center caused by the shorter titanium-chlorine bonds, relative to the titanium-sulfur bonds. Such distortions were compensated by chlorine-titanium-sulfur angles that were slightly less than 90°. The disorder in the tetrahydrothiophene ligands, while successfully modeled, led to large uncertainties in the bond lengths associated with the ligands.

Complex 7 crystallized as a Ti₂Cl₈ unit with each sulfur of the dimethyl disulfide ligand bonded to a titanium atom. There were three distinct types of titanium-chlorine bonds present in 7. The bridging chlorides (Cl(1), Cl(2)) were symmetrically bonded and showed titanium-chlorine bond lengths ranging from 2.450–2.482 Å (av. = 2.464 Å). The equatorial chlorides (Cl(3), Cl(4), Cl(6), Cl(7)) (all trans to bridging chlorides) exhibited titanium-chlorine bond lengths of 2.187–2.200 Å (av. = 2.194 Å). These bonds are ca. 0.09 Å shorter than the titanium-chlorine bond in 4 that is trans to a terminal chloride. The shorter equatorial titanium-chlorine bonds in 7 are the result of a diminished trans influence of a bridging chloride, relative to a terminal chloride. The third type of titanium-chlorine bond was represented by the chlorines trans to the sulfurs. These bond lengths were 2.190(3) Å (Ti(1)-Cl(5)) and 2.184(3) Å (Ti(2)-Cl(8)), and were not significantly different than the equatorial titanium-chlorine bond lengths. The geometry about each titanium exhibited substantial deviations from idealized octahedral geometry. The cis chlorine-titanium-chlorine angles ranged from 87.4-102.6°, with an average value of 95.1°. The angles associated with the bridging chlorides (Cl(1)-Ti(1)-Cl(2) 79.0(1), Cl(1)-Ti(2)—Cl(2) 78.8(1) $^{\circ}$) were constrained to be considerably less than an idealized 90° by the Ti_2Cl_2 ring. The trans chlorine-titanium-chlorine angles ranged from $159.7-164.6^{\circ}$ (av. = 161.8°). The data for the dimethyl disulfide ligand in 7 merit discussion. The sulfur-sulfur bond length was 2.052(3) Å, while the sulfur-carbon bond lengths were 1.784(5) Å (S(1)-C(1)) and 1.801(6) Å (S(2)-C(2)). The angles associated with the dimethyl disulfide ligand illustrate the geometrical distortions that are required to bind this ligand to the Ti₂Cl₈ moiety. The sulfurs were bent in toward the center of the Ti₂Cl₂ core. In addition, each sulfur was bent out of the plane containing Ti(1), Cl(5), Ti(2), and Cl(8) (i.e., S(1)—Ti(1)—Cl(1)72.6(1)°, S(1) - Ti(1) - Cl(2) $86.2(1)^{\circ}$, S(1) - Ti(1) - Cl(3)79.5(1)°, S(1) - Ti(1) - Cl(4)S(2) - Ti(2) - Cl(1)**91.8(1)**°; $84.6(1)^{\circ}$, S(2)—Ti(2)—Cl(2) 73.1(1)°, S(2)—Ti(2)—Cl(6)

Ti—Cl(1)	2.232(8)	Ti—Cl(2)	2.280(4)
TiCl(3)	2.233(8)	Ti-S(1)	2.626(7)
Ti - S(2)	2.625(7)	Ti-Cl(2A)	2.280(4)
S(1) - C(1)	1.823(18)	S(1)— $C(1A)$	1.823(18)
S(2) - C(3)	1.811(17)	S(2)—C(3A)	1.811(17)
C(1) - C(2)	1.549(31)	C(1) - C(2'A)	1.433(37)
C(2)—C(2')	1.549(42)	C(2)-C(2A)	1.077(47)
C(2)-C(2'A)	0.739(42)	C(2')-C(1A)	1.433(37)
C(2')C(2A)	0.739(42)	C(2')—C(2'A)	1.723(69)
C(3)—C(4)	1.549(30)	C(3)—C(4'A)	1.449(38)
C(4) - C(4')	1.549(44)	C(4)—C(4A)	1.107(51)
C(4)—C(4'A)	0.775(44)	C(4')—C(3A)	1.449(38)
C(4')—C(4A)	0.775(44)	C(4')C(4'A)	1.626(73)
Cl(1)—Ti—Cl(2)	97.0(2)	Cl(1)—Ti—Cl(3)	98.9(3)
Cl(2)—Ti—Cl(3)	97.3(2)	Cl(1)— Ti — $S(1)$	90.1(3)
Cl(2)— Ti — $S(1)$	81.5(1)	Cl(3)— Ti — $S(1)$	171.0(3)
Cl(1)— Ti — $S(2)$	171.3(3)	Cl(2)— Ti — $S(2)$	81.8(1)
Cl(3)—Ti—S(2)	89.8(3)	S(1)—Ti—S(2)	81.1(2)
Cl(1)— Ti — $Cl(2A)$	97.0(2)	Cl(2)— Ti — $Cl(2A)$	158.0(2)
Cl(3)—Ti—Cl(2A)	97.3(2)	S(1)— Ti — $Cl(2A)$	81.5(1)
S(2)— Ti — $Cl(2A)$	81.8(1)		

Table 2. Bond lengths (Å) and selected angles (°) for 4

Table 3. Bond lengths (Å) and angles (°) for 7

$\frac{1}{\text{Ti}(1)-S(1)}$	2.712(3)	Ti(1)Cl(1)	2.459(3)
Ti(1)— $Cl(2)$	2.463(2)	Ti(1)— $Cl(3)$	2.200(2)
Ti(1)— $Cl(4)$	2.187(3)	Ti(1)— $Cl(5)$	2.190(3)
Ti(2) - S(2)	2.742(3)	Ti(2)— $Cl(1)$	2.482(3)
Ti(2)— $Cl(2)$	2.450(3)	Ti(2)—Cl(6)	2.193(3)
Ti(2)— $Cl(7)$	2.195(4)	Ti(2)—Cl(8)	2.184(3)
S(1)—S(2)	2.052(3)	S(1) - C(1)	1.784(5)
S(2)C(2)	1.801(6)		
S(1) - Ti(1) - Cl(1)	72.6(1)	S(1)—Ti(1)—Cl(2)	86.2(1)
Cl(1)— $Ti(1)$ — $Ti(2)$	79.0(1)	S(1) - Ti(1) - Cl(3)	79.5(1)
Cl(1) - Ti(1) - Cl(3)	91.1(1)	Cl(2) - Ti(1) - Cl(3)	164.6(1)
S(1) - Ti(1) - Cl(4)	91.8(1)	Cl(1) - Ti(1) - Cl(4)	160.1(1)
Cl(2)— $Ti(1)$ — $Cl(4)$	87.9(1)	Cl(3) - Ti(1) - Cl(4)	98.3(1)
S(1)-Ti(1)-Cl(5)	165.5(1)	Cl(1)— $Ti(1)$ — $Cl(5)$	93.0(1)
Cl(2)—Ti(1)—Cl(5)	92.7(1)	Cl(3) - Ti(1) - Cl(5)	99.6(1)
Cl(4)— $Ti(1)$ — $Cl(5)$	102.6(1)	S(2) - Ti(2) - Cl(1)	84.6(1)
S(2) - Ti(2) - Cl(2)	73.1(1)	Cl(1)— $Ti(2)$ — $Cl(2)$	78.8(1)
S(2)-Ti(2)-Cl(6)	91.0(1)	Cl(1)— $Ti(2)$ — $Cl(6)$	87.4(1)
Cl(2)Cl(6)	159.7(1)	S(2)—Ti(2)—Cl(7)	79.5(1)
Cl(1)Ti(2)Cl(7)	163.0(1)	Cl(2)—Ti(2)—Cl(7)	90.7(1)
Cl(6)—Ti(2)—Cl(7)	98.9(1)	S(2)-Ti(2)-Cl(8)	166.8(1)
Cl(1)— $Ti(2)$ — $Cl(8)$	93.5(1)	Cl(2)— $Ti(2)$ — $Cl(8)$	93.7(1)
Cl(6)—Ti(2)—Cl(8)	102.0(1)	Cl(7)—Ti(2)—Cl(8)	100.5(1)
Ti(1) - S(1) - S(2)	103.9(1)	Ti(2) - S(2) - S(1)	103.9(1)
Ti(1) - Cl(1) - Ti(2)	99.6(1)	Ti(1)— $Cl(2)$ — $Ti(2)$	100.4(1)
Ti(1) - S(1) - C(1)	109.2(2)	Ti(2) - S(2) - C(2)	110.4(2)
S(2) - S(1) - C(1)	102.3(2)	S(1)—S(2)—C(2)	103.4(2)

Titanium tetrachloride with organosulfur compounds



Fig. 1. Perspective view of 4 drawn with 35% probability ellipsoids.



Fig. 2. Perspective view of 7 drawn with 35% probability ellipsoids.

91.0(1)°, S(2)—Ti(2)—Cl(7) 79.5(1)°). In effect, the dimethyl disulfide ligand is bonded to the Ti₂Cl₈ fragment with an approximate C₂ axis that runs through the center of the S(1)—S(2) bond and the center of the Ti₂Cl₂ ring, although such symmetry is not crystallographically imposed. The sum of the angles about each sulfur (S(1) 315.4°, S(2) 317.7°) is slightly less than that expected for pyramidal, trisubstituted sulfur with one lone pair (*ca* 328.5°).

Solution structures

We sought to determine if the solid state structures established for 4 and 7 persisted in solution. It is possible that these structures happen to be the most crystalline phases, and that different structures could be present in solution. Accordingly, variable temperature ¹H NMR spectra were recorded for 6 and 7. With 6 in dichloromethane- d_2 the methyl singlet was invariant at δ 2.51 between +20 and -80°C. At -80°C, a trace of dimethyl sulfide (δ 2.06, *ca.* 10% of total integration) was present. With 7 in dichloromethane- d_2 , the methyl signal in the ¹H NMR spectrum moved steadily downfield from δ 2.52 at +20°C to δ 3.00 at -80°C. Between +20°C and -60°C, there was only one methyl singlet present. However, below -70°C a second minor methyl singlet appeared. At -80°C, the major species was at δ 3.00, the minor species appeared at δ 2.89, and the ratio between the two was 87:13. Free methyl disulfide (¹H NMR δ 2.38 at +20°C) was not observed at any temperature.

DISCUSSION

The motivation for the present study was to characterize complexes that might be involved in chemical vapor deposition processes. Furthermore, such compounds might serve as single-source precursors to titanium disulfide films. With thiols and sulfides, adducts are formed that are monomeric in the solid state by X-ray crystallography. The static chemical shift of the methyl groups in 6 suggests that there are not major changes in the coordination sphere of 6 in solution between +20 and -80° C. We propose that 6 is monomeric and 6-coordinate in solution, with a structure similar to that observed in the solid state. Based upon the easy formation of 1-6, it is very likely that adducts of the formula $TiCl_4(HSR)_2$ and $TiCl_4(R_2S)_2$ form in the gas phase, at least in equilibrium with titanium tetrachloride and the organosulfur compounds, and are present in a CVD reaction employing titanium tetrachloride and these sulfur compounds.

Complexes 4 and 5 did not serve as single-source precursors to films under CVD conditions, while 6 and 7 gave titanium disulfide films at reactor temperatures between 400-600°C [10]. We suggest that the failure of 4 and 5 to function as precursors to titanium disulfide films can be attributed to kinetically slow β hydrogen cleavage from the cyclic sulfur ligands due to the strained nature of such a transition state, relative to an acyclic sulfur ligand. We have previously noted that the atmospheric pressure CVD reaction of titanium tetrachloride with dimethyl sulfide or dimethyl disulfide fails to afford titanium disulfide films under conditions where tert-butythiol gives excellent coatings [6]. The presence of preformed titaniumsulfur bonds in 6 and 7 must provide a kinetically viable path for titanium disulfide film formation, while a similar path is inefficient in the two-component atmospheric pressure CVD process.

Adduct 7 adopts a very different structure than is found in 1–6. The dinuclear structure appears to form because the disulfide ligand cannot bind strongly to the small titanium center in a bidentate fashion. Instead, the methyl disulfide coordinates to two faces of a Ti_2Cl_8 unit, leading to a bridging methyl disulfide ligand. The large chemical shift change observed upon cooling 7 from +20 to -80° C raises the possibility that there is a major change that is occurring in the coordination sphere in this temperature range. While the data do not require a change in structure, a possible structure change would be a rapid equilibrium between dinuclear 7 and a monomeric titanium tetrachloride adduct with an η^2 -dimethyl disulfide ligand. Accordingly, 7 may simply be the most crystalline complex and may not be the major species in dichloromethane solution. Freezing point depression molecular weight measurements on 7 in cyclohexane and benzene designed to probe this point were inconclusive due to preciptation near the freezing points of these solvents.

Complex 7 functions as a single-source precursor to titanium disulfide films at reactor temperatures of 400-600°C [13]. Schleich has reported that the twocomponent CVD reaction of titanium tetrachloride with di-butyl disulfide affords titanium trisulfide films between 260-400°C, and titanium disulfide films above 400°C [4]. By contrast, di-tert-butyl sulfide gave titanium disulfide films above 260°C. It was proposed that di-butyl disulfide acts as a disulfido ion synthon, which leads to the sulfur-rich titanium phase as a kinetic product at low deposition temperatures. Our present data do not allow us to comment on Schleich's work in any detail. However, our results demonstrate that the interaction of organic sulfides and organic disulfides with titanium tetrachloride leads to different structure types. The formation of dinuclear adducts of organic disulfides may be a factor that leads to sulfur-rich phases at low temperatures. This could be a significant observation, given the current interest in the "design" of precursors to desired phases. We are continuing to explore the coordination chemistry of titanium tetrachloride with organosulfur compounds in the context of chemical vapor deposition and will report further studies in the near future.

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