Inorg. Chem. **2000,** *39,* 2693−2695 **2693**

Synthesis and Characterization of a Homoleptic Thiolate Complex of Titanium(IV)

Claire J. Carmalt,*,† Christopher W. Dinnage,† Ivan P. Parkin,† and Jonathan W. Steed‡

Department of Chemistry, Christopher Ingold Laboratories,
University College London, 20 Gordon Street,
London WC1H 0AJ, United Kingdom,
and Department of Chemistry, King's College London,
Strand, London WC2R 2LS, United Kingdom

Received November 29, 1999

Introduction

Early transition-metal thiolate complexes have received some attention in recent years because of their importance in a wide range of areas including biological systems, hydrodesulfurization, and some organic transformations.[1] Much of the work has focused on the synthesis and characterization of this class of compounds, and the known chemistry of these species is very limited. In the particular case of titanium thiolate complexes, interest has grown due to the fact that such compounds might serve as single-source precursors for the CVD (chemical vapor deposition) of titanium disulfide (TiS_2).[2,3] In turn, TiS_2 is useful for applications such as the active cathode material in high-energy rechargeable batteries[2] and as a solid lubricant.[4,5] A stable titanium thiolate complex, namely, $[Ti(S\text{-}t\text{-}Bu)_4]$ (**1**),[6,7] has been isolated, characterized, and tested as a single-source precursor to TiS_2. Preliminary studies describing the CVD of **1** observed the formation of amorphous TiS films at 130−200 °C.[6] However, more recent studies have shown that TiS_2 films can be grown from **1** under similar conditions (substrate temperatures 150−270 °C).[7] It has been suggested that the formation of TiS from **1** may be the result of hydrolysis of the films, which accounts for the loss of sulfur. Other single-source precursors to TiS_2 include $[TiCl_4(HSR)_2]$ (**2**, R = cyclohexyl; **3**, R = cyclopentyl),[8] although precursors with Ti−Cl bonds are potentially corrosive to metal substrates at CVD temperatures.[8]

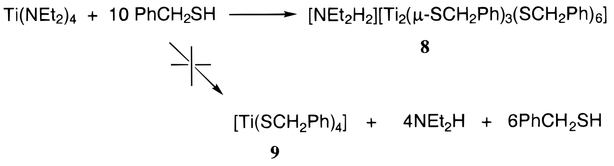
Titanium thiolate complexes represent a class of compounds which have only been studied to a limited extent.[1] Early preparative routes to titanium thiolates involved the reaction of $[Ti(NR'_2)_4]$ (R′ = Me or Et) and R″SH (R″ = Me, Et, or *i*-Pr), resulting in the formation of complexes of general formula $[Ti(SR'')_4(HSR'')_x(NHR'_2)_y]$ (where $x + y$ varied from 0.8 to 1.33).[9] Titanium(IV) complexes containing unidentate thiolate ligands which have been structurally characterized include $[Ti(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$ (**4**),[10] $[Ti_3(SMe)_{12}]$ (**5**),[11] $[NMe_2H_2][Ti_2(SMe)_9]$ (**6**),[11] and $[TiCl_2(S\text{-}t\text{-}Bu)(Diars)]$ (**7**) [Diars is *o*-phenylene bis(dimethylarsine)].[12]

In this paper, we present the synthesis and characterization of a homoleptic thiolate complex of titanium. Our motivation was to explore further the utility of titanium thiolates as precursors to titanium sulfide.

Results and Discussion

Initial attempts to prepare homoleptic thiolate complexes of titanium involved the addition of 10 equiv of benzyl mercaptan ($PhCH_2SH$) to a toluene solution of $[Ti(NEt_2)_4]$ at room temperature. An immediate color change from orange to blood red was observed, and after workup a dark red solid resulted. Crystallization from CH_2Cl_2−hexane mixtures afforded a 60% yield of dark red crystalline **8** (Scheme 1). Analytical and spectroscopic data for **8** indicated that the ionic species $[NEt_2H_2][Ti_2(\mu\text{-}SCH_2Ph)_3(SCH_2Ph)_6]$ had formed rather than the expected product $[Ti(SCH_2Ph)_4]$ (**9**). The structure of **8** was confirmed by X-ray crystallography, the results of which are shown in Figure 1; selected bond lengths and angles are presented in Table 1. Compound **8** crystallizes in the monoclinic space group $P2_1/c$. The structure of **8** is ionic, comprising $[NEt_2H_2]^+$ cations and $[Ti_2(\mu\text{-}SCH_2Ph)_3(SCH_2Ph)_6]^-$ anions, with no close interionic contacts. In the anion in **8** the two titanium atoms are each coordinated by three terminal (Ti−S 2.3183(9)−2.4090(10) Å) and three bridging (Ti−S 2.5132(10)−2.5609(9) Å) $PhCH_2S$ ligands. Thus, the coordination number at each titanium center is six, and the geometry is approximately octahedral (*trans*-S−Ti−S 158.75(3)−172.34(3)°; *cis*-S−Ti−S 75.53(3)−102.35(3)°). As such, the structure is similar to that of the anion $[Ti_2(SMe)_9]^-$ in **6**[11] in which the Ti_2S_9 framework also has a face-sharing bioctahedral arrangement.

Scheme 1



The behavior of **6** in solution (at room temperature) was described as being complicated, and it was suggested that **6** dissolves to afford $[Ti_3(SMe)_{12}]$ (**5**) and at least one other compound. At lower temperatures the ^1H NMR spectrum of **6** undergoes a series of changes which were tentatively assigned to the presence of **5** and possibly a complex of the type $[Ti(SMe)_4(HSMe)_x(NHMe_2)_y]$.[11] In contrast, the room temperature ^1H NMR spectrum of **8** contains only peaks which can be assigned directly to compound **8**, therefore suggesting that in solution **8** is more stable than **6**. However, at lower temperatures (0 to −90 °C; 10° intervals) the ^1H NMR spectrum of **8** also undergoes a series of changes, and it is clear that the behavior of **8** in solution (at low temperatures) is also complicated.

Unfortunately, the low volatility of complex **8** precluded studies by conventional LPCVD or APCVD. However, we

---

† University College London.

‡ King's College London.

(1) Stephan, D. W.; Nadasdi, T. T. *Coord. Chem. Rev.* **1996**, *147*, 147 and references therein.

(2) *CVD of Nonmetals*; Rees, W. S., Jr., Ed.; VCH Publishers: Weinheim, 1996.

(3) Lewkebandara, T. S.; Winter, C. H. *Adv. Mater.* **1994**, *6*, 237. Bochmann, M. *Chem. Vap. Deposition* **1996**, *2*, 85.

(4) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41.

(5) Bill, R. C. *Wear* **1985**, *106*, 283.

(6) Bochmann, M.; Hawkins, I.; Wilson, L. M. *Chem. Commun.* **1988**, 344.

(7) Cheon, J.; Gozum, J. E.; Girolami, G. S. *Chem. Mater.* **1997**, *9*, 1847.

(8) Winter, C. H.; Lewkebandara, T. S.; Proscia, J. W.; Rheingold, A. L. *Inorg. Chem.* **1994**, *33*, 1227.

(9) Bradley, D. C.; Hammersley, P. A. *J. Chem. Soc. A* **1967**, 1894.

(10) Corwin, D. T.; Corning, J. F.; Koch, S. A.; Millar, M. *Inorg. Chim. Acta* **1995**, *229*, 335.

(11) Stüer, W.; Kirschbaum, K.; Giolando, D. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1981.

(12) Jones, R. A.; Schwab, S. T.; Whittlesey, B. R. *Polyhedron* **1984**, *3*, 505.

10.1021/ic991382g CCC: $19.00

Table 1. Selected Bond Distances (Å) and Angles (deg) for **8**

Ti(1)−S(1)	2.5609(9)	Ti(1)−S(2)	2.5395(10)	Ti(1)−S(3)	2.5364(9)
Ti(1)−S(4)	2.3308(9)	Ti(1)−S(5)	2.3183(9)	Ti(1)−S(6)	2.3582(10)
Ti(2)−S(1)	2.5132(10)	Ti(2)−S(2)	2.5249(9)	Ti(2)−S(3)	2.5295(10)
Ti(2)−S(7)	2.3366(11)	Ti(2)−S(8)	2.4090(10)	Ti(2)−S(9)	2.3484(11)

S(5)−Ti(1)−S(4)	98.64(3)	S(8)−Ti(2)−S(1)	102.35(3)
S(5)−Ti(1)−S(6)	92.27(4)	S(9)−Ti(2)−S(8)	88.96(3)
S(4)−Ti(1)−S(6)	99.54(4)	S(7)−Ti(2)−S(8)	98.20(3)
S(5)−Ti(1)−S(3)	95.66(3)	S(9)−Ti(2)−S(3)	98.68(3)
S(4)−Ti(1)−S(3)	165.02(3)	S(7)−Ti(2)−S(3)	171.75(3)
S(6)−Ti(1)−S(3)	84.26(3)	S(8)−Ti(2)−S(3)	88.53(3)
S(5)−Ti(1)−S(2)	96.14(4)	S(9)−Ti(2)−S(2)	92.05(3)
S(4)−Ti(1)−S(2)	98.44(3)	S(7)−Ti(2)−S(2)	97.41(3)
S(6)−Ti(1)−S(2)	158.75(3)	S(8)−Ti(2)−S(2)	164.39(3)
S(3)−Ti(1)−S(2)	75.53(3)	S(2)−Ti(2)−S(3)	75.91(3)
S(5)−Ti(1)−S(1)	172.34(3)	S(9)−Ti(2)−S(1)	168.63(3)
S(4)−Ti(1)−S(1)	83.45(3)	S(7)−Ti(2)−S(9)	86.26(3)
S(6)−Ti(1)−S(1)	94.65(3)	S(7)−Ti(2)−S(1)	91.00(3)
S(3)−Ti(1)−S(1)	81.79(3)	S(1)−Ti(2)−S(3)	82.87(3)
S(2)−Ti(1)−S(1)	76.23(3)	S(1)−Ti(2)−S(2)	77.35(3)
Ti(2)−S(1)−Ti(1)	86.14(3)	Ti(2)−S(2)−Ti(1)	86.35(3)
Ti(2)−S(3)−Ti(1)	86.32(3)		

Table 2. Crystallographic Data for **8**

empirical formula	$C_{68}H_{75}N_1S_9Ti_2$	fw	1276.62
space group	$P2_1/c$	V (Å^3)	6479(2)
cryst syst	monoclinic	Z	4
a (Å)	21.573(4)	T (K)	100(2)
b (Å)	17.224(3)	λ (Å)	0.71070
c (Å)	17.577(4)	ρ_{calcd} (g cm^{-1})	1.309
β (deg)	97.287(16)	μ (mm^{-1})	0.576
F(000)	2684	no. of reflns collected	55 504
no. unique reflns	14 854	cryst size (mm)	0.3 × 0.1 × 0.1
θ range (deg)	2.55−27.50	R^a(all data)	0.0834
R^a($I > 2\sigma(I)$)	0.0521	wR'^b(all data)	0.1303
wR$'^b$ ($I > 2\sigma(I)$)	0.1162		

[a] $R = \sum(\Delta F)/\sum(F_o)$. [b] $wR' = [\sum\{w(\Delta F^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $P = [\max(F_o^2) + 2(F_c^2)]/3$ and $a = 0.0003$.

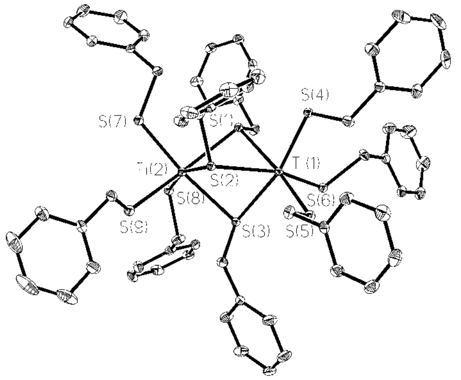


Figure 1. Molecular structure of the anion in **8** showing the atom numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted.

investigated the pyrolysis of **8** to gain some insight into the decomposition pathway. A sample of **8** was heated in a quartz tube at 500, 600, 800, and 1000 °C under dynamic vacuum for 3 h. The byproducts formed during decomposition were collected in a liquid N_2 cooled trap and analyzed by ^{1}H NMR. The resulting gray/black solids were analyzed by powder X-ray diffraction (XRD) and EDAX. Powder XRD[13] of the material obtained at the thermolysis temperatures 500, 600, and 800 °C revealed it was X-ray amorphous. In addition, the EDAX data showed a degree of inhomogeniety in these solids, particularly for the material isolated after the sample was heated to 600 °C, with the ratio Ti:S varying over a number of spots. However, powder XRD of the gray/black material obtained after the sample was heated to 1000 °C showed that nanocrystalline Ti_2S_3 had formed. The formation of the sesquisulfide Ti_2S_3 (at 1000 °C) was confirmed by the EDAX data, which showed good agreement to a 2:3 ratio of Ti:S over a number of spots. The NMR spectrum of the byproducts obtained when **8** was thermolyzed showed resonances assigned to Et_2NH and $(PhCH_2)_2S_2$.

In conclusion, a new homoleptic thiolate complex of titanium(IV) has been synthesized and structurally characterized. Pyrolysis of **8** resulted in the formation of the sesquisulfide Ti_2S_3 at 1000 °C. We are currently investigating the formation of neutral monomeric titanium(IV) thiolates to study the CVD of these complexes.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a MBraun Unilab glovebox. All solvents were distilled from appropriate drying agents prior to use (sodium for toluene and hexanes; potassium for THF; CaH_2 for CH_2Cl_2). All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London (UCL).

Physical Measurements. NMR spectra were recorded on Brüker AMX300 or DRX500 spectrometers at UCL. The NMR spectra are referenced to CD_2Cl_2, which was degassed and dried over molecular sieves prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ (0.00 ppm). Mass spectra (CI) were run on a micromass ZABSE instrument, and IR spectra on a Nicolet 205 instrument. Melting points

---

(13) PDF-2 database, International Center for Diffraction Data, Swarthmore, PA 19081, 1990.

were obtained in sealed glass capillaries under argon and are uncorrected. Thermolysis studies were performed in a Carbolite tube furnace. Powder XRD measurements were recorded on a Siemens D5000 transmission diffractometer using germanium-monochromated Cu Kα_1 radiation (λ = 1.5406 Å) as thin films. EDAX was performed on a Hitachi S570.

Synthesis of 8. Benzyl mercaptan (2.1 mL, 17.8 mmol) was added dropwise to an orange solution of $Ti(NEt_2)_4$ (0.6 mL, 1.66 mmol) in toluene (20 mL) at room temperature with stirring. The solution turned dark red immediately on addition of the thiol. The mixture was stirred for 2 h at room temperature, and then the solvent was removed in vacuo. The resulting dark red oil was dissolved in toluene (20 mL) and filtered through Celite. The solution was reduced in volume to approximately 10 mL under vacuum and cooled to −20 °C, which over a period of days resulted in the formation of a dark red solid. This solid was redissolved in CH_2Cl_2 (4 mL), and an overlayer of hexanes (20 mL) was added carefully. Solvent diffusion over a period of days at −20 °C afforded dark red crystals of **8** (0.518 g, 60% yield), mp 103−105 °C. Anal. Calcd for $C_{68}H_{75}N_1S_9Ti_2$: C, 59.57; H, 5.60; N, 1.04. Found: C, 60.07; H, 5.63; N, 1.59. ^1H NMR (CD_2Cl_2): δ 0.85 (t, 6H, NCH_2CH_3), 2.40 (q, 4H, NCH_2CH_3), 4.90 (s, 6H, μ-$SCH_2C_6H_5$), 5.32 (s, 12H, t-$SCH_2C_6H_5$), 7.26−7.65 (m, 45H, $SCH_2C_6H_5$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 13.1 (NCH_2CH_3), 43.7 (NCH_2CH_3), 51.6 ($SCH_2C_6H_5$), 128.8−145.8 ($SCH_2C_6H_5$).

X-ray Structure Determination of 8. Crystals of **8** were mounted on a glass fiber using silicone grease and cooled on the diffractometer. Crystallographic measurements were carried out with a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo Kα radiation using ϕ rotations with 2° frames and a detector-to-crystal distance of 25 mm. Integration was carried out by the program DENZO-SMN.[14] Data sets were corrected for Lorentz and polarization effects and for the effects of absorption using the program Scalepack.[14] The structure was solved using the direct methods option of SHELXS-97[15] and developed using conventional alternating cycles of least-squares refinement and difference Fourier synthesis (SHELXL-97)[15] with the aid of XSeed.[16] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were fixed in idealized positions and allowed to ride. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. All calculations were carried out on a Silicon Graphics Indy workstation or an IBM-PC compatible personal computer. Crystal data and details of the data collections and refinements are given in Table 2.

Acknowledgment. We thank EPSRC for financial support and a studentship (C.W.D.) and King's College London and EPSRC for provision of the diffractometer system. C.J.C. is also grateful to the Royal Society for a Dorothy Hodgkin fellowship and London University Central Research Fund for financial support.

Supporting Information Available: X-ray crystallographic file in CIF format for the structure of compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991382G

---

(14) Otwinowski, Z.; Minor, W. In *Methods in Enzymology;* Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1996.

(15) Sheldrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, Germany, 1997.

(16) Barbour, L. J. *XSeed—A Graphical Interface for the Solution and Refinement of X-ray Crystal Structures*; Univeristy of Missouri: Columbia, MO, 1999.