DALTON
FULL PAPER

Synthesis and structural characterisation of titanium(IV) thiolate compounds

Claire J. Carmalt,[a] **Christopher W. Dinnage,**[a] **Ivan P. Parkin,**[a] **Andrew J. P. White**[b] **and David J. Williams**[b]

[a] *Department of Chemistry, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London, UK WC1H 0AJ. E-mail: c.j.carmalt@ucl.ac.uk*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY*

Received 28th July 2000, Accepted 6th September 2000
First published as an Advance Article on the web 3rd October 2000

Synthetic and structural studies have been performed for two thiolate complexes of titanium(IV). The reaction between $Ti(NEt_2)_4$ and 10 equivalents of C_6F_5SH at room temperature resulted in the formation of the ionic complex $[Et_2NH_2]_3[Ti(SC_6F_5)_5][SC_6F_5]_2$. The related reaction between $Ti(NEt_2)_4$ and 4 equivalents of C_6F_5SH at room temperature, in the presence of a two electron donor ligand L (2,6-dimethylpyridine or tetrahydrothiophene), resulted in the isolation of the ionic complex $[Et_2NH_2][Ti(SC_6F_5)_4(NEt_2)]$. However, if the reaction between $Ti(NEt_2)_4$ and 4 equivalents of C_6F_5SH is carried out without the addition of L, the first compound is formed rather than the second. The two new complexes have been characterised by X-ray crystallography. $[Et_2NH_2]_3[Ti(SC_6F_5)_5][SC_6F_5]_2$ is the first structurally characterised example of a five-co-ordinate homoleptic sulfur-bonded titanium complex. Both adopt similar sheet structures held together by π–π and C–F · · · π interactions.

Titanium disulfide (TiS_2) has attracted much technological attention in the past decade because it is one of the most effective cathode materials in high-energy rechargeable batteries.[1,2] In addition, TiS_2 films are used as a solid lubricant due to the weak van der Waals interactions between adjacent layers of the TiS_2 lattice.[1,3] The conventional chemical vapour deposition (CVD) approach to the synthesis of TiS_2 films involves the reaction of $TiCl_4$ with H_2S at 430–540 °C.[4] More recently, the CVD reactions between $TiCl_4$ and organothiols (*e.g.* Bu^tSH) at temperatures in excess of 200 °C were reported to result in the formation of highly pure TiS_2.[5] However, the aforementioned CVD routes to TiS_2 films depend on the mixing of two chemical species in the gas phase which can give rise to a range of stoichiometries in the final product.[1] Accordingly, attention has turned recently to the development of single-source precursors to overcome this problem.[1] The use of a single-source precursor in a CVD process could also reduce toxic or malodorous waste. However, only three TiS_2 single-source precursors have been synthesized and employed in deposition studies, namely $[TiCl_4(HSR)_2]$ [R = cyclohexyl (**1**) or cyclopentyl (**2**)][6] and $[Ti(SBu^t)_4]$ **3**.[7,8] Compounds **1** and **2** resulted in the formation of high quality TiS_2 films *via* single-source CVD within the temperature range 200–600 °C,[6] although precursors with Ti–Cl bonds are potentially corrosive to the metal substrate at CVD temperatures.[9] A preliminary study describing the CVD of compound **3** observed the formation of amorphous TiS films at temperatures between 130 and 200 °C.[7] More recently, the deposition of thin films of TiS_2 from **3** was reported at temperatures in the range 110–350 °C.[8] It has been suggested that the formation of TiS may have resulted from hydrolysis of the films, accounting for the loss of sulfur.

We are interested in developing homoleptic titanium(IV) thiolate complexes as CVD precursors to TiS_2. Homoleptic titanium thiolate complexes should reduce the possibility of contamination from species such as C or Cl in the resulting films and address some of the foregoing problems. Furthermore, titanium thiolate complexes represent a class of compound that has only been studied to a limited extent.[10] Early preparative routes to titanium thiolates involved the reaction of $[Ti(NR'_2)_4]$ (R′ = Me or Et) and HSR (R = Me, Et or Pr^i) resulting in the formation of complexes of the type $[Ti(SR)_4(HSR)_x(NHR'_2)_y]$ **4** (where $(x + y)$ varied from 0.8 to 1.33).[11] The first homoleptic titanium thiolate complex, namely $[Ti(SC_6F_5)_4]$ **5** was reportedly prepared *via* the reaction of $TiCl_4$ with 4 equivalents of HSC_6F_5. However, the product was only characterised by IR spectroscopy.[12] More recently, a number of titanium(IV) complexes with unidentate thiolate ligands have been structurally characterised, examples of which include $[Ti(SC_6HMe_4\text{-}2,3,5,6)_4]$ **6**,[13] $[TiCl_2(SBu^t)(Diars)]$ **7** [where Diars is *o*-phenylenebis(dimethylarsine)],[14] $[Me_2NH_2][Ti_2(\mu\text{-}SMe)_3(SMe)_6]$ **8**,[15] $[Ti_3(\mu\text{-}SMe)_6(SMe)_6]$ **9**,[15] $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC_6F_5)_2]$ **10**[16] and $[Et_4N]_2[Ti(SPh)_6]$.[17]

We have previously reported the synthesis and structural characterisation of the homoleptic titanium thiolate $[Et_2NH_2][Ti_2(\mu\text{-}SCH_2Ph)_3(SCH_2Ph)_6]$ **11** and pyrolysis studies.[18] In this paper, we report the synthesis and structures of two ionic titanium(IV) thiolate complexes, $[Et_2NH_2]_3[Ti(SC_6F_5)_5][SC_6F_5]_2$ **12** and $[Et_2NH_2][Ti(SC_6F_5)_4(NEt_2)]$ **13**.

Results and discussion

Initial attempts to prepare neutral monomeric thiolates of titanium involved the addition of 10 equivalents of pentafluorobenzenethiol (HSC_6F_5) to a toluene solution of $Ti(NEt_2)_4$ at room temperature. An immediate change from orange to dark red was observed and work-up of the reaction mixture yielded a dark red solid. Crystallisation from CH_2Cl_2–hexanes mixtures afforded a 75% yield of dark red crystalline **12**. Analytical and spectroscopic data for **12** are consistent with the formation of $[Et_2NH_2]_3[Ti(SC_6F_5)_5][SC_6F_5]_2$ rather than the neutral complex $[Ti(SC_6F_5)_4]$ **5** (Scheme 1).

An X-ray analysis of crystals of complex **12** revealed the structure to comprise the homoleptic penta(pentafluorobenzenethiolato)titanate(IV) complex anion shown in Fig. 1,

DOI: 10.1039/b006115h

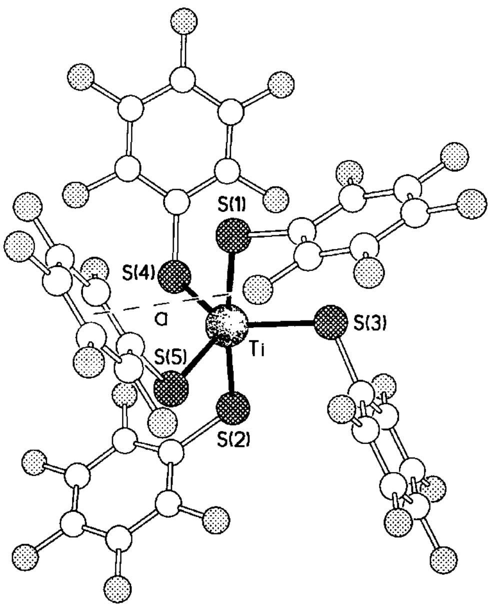
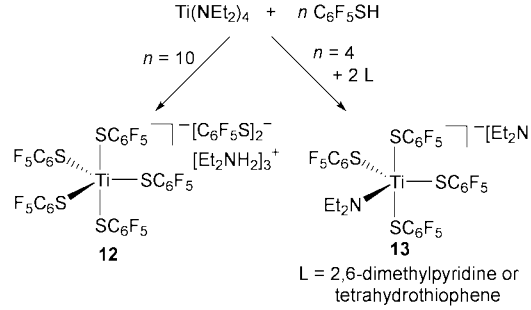


Fig. 1 The molecular structure of the anion in the structure of complex **12**, showing the weak intramolecular C–F···π interaction (*a*); the F···π distance is 3.43 Å and the C–F···π angle 144°. Only the titanium and sulfur atoms have been labelled for clarity.



Scheme 1

Table 1 Selected bond distances (Å) and angles (°) for compounds **12** and **13**

Compound **12**		Compound **13**	
Ti–S(1)	2.386(1)	Ti–S(1)	2.417(1)
Ti–S(2)	2.406(1)	Ti–S(2)	2.427(1)
Ti–S(3)	2.350(2)	Ti–N	1.849(4)
Ti–S(4)	2.356(2)		
Ti–S(5)	2.357(2)		
S(3)–Ti–S(4)	115.52(7)	N–Ti–S(1)	119.86(3)
S(3)–Ti–S(5)	126.47(7)	N–Ti–S(2)	105.90(3)
S(4)–Ti–S(5)	117.14(6)	S(1)–Ti–S(1A)	120.27(6)
S(3)–Ti–S(1)	88.22(5)	S(1)–Ti–S(2)	83.39(3)
S(4)–Ti–S(1)	92.24(5)	S(1)–Ti–S(2A)	80.92(3)
S(5)–Ti–S(1)	98.65(5)	S(2A)–Ti–S(2)	148.20(5)
S(3)–Ti–S(2)	84.76(5)		
S(4)–Ti–S(2)	89.10(5)		
S(5)–Ti–S(2)	87.07(5)		
S(1)–Ti–S(2)	172.73(6)		

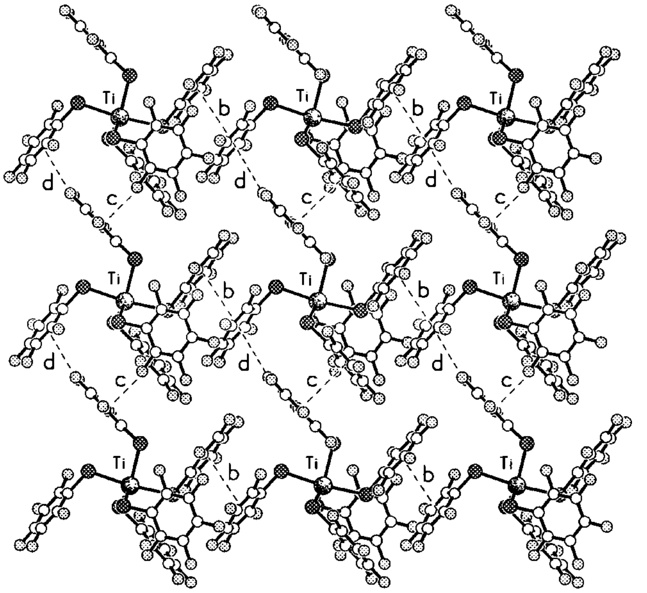


Fig. 2 View, in parallel projection down the crystallographic *b* axis, of the packing of the anions in complex **12**, showing their paddle-like conformation and their interleaving and linking *via* π–π and C–F···π interactions to form two-dimensional sheets. The centroid–centroid and mean interplanar separations (Å) are (*b*) 3.68, 3.51 and (*c*) 3.76, 3.45; for the C–F···π interaction (*d*) the F···π distance is 3.24 Å and the C–F···π angle is 143°; the angle subtended at the S(2) ring centroid by the vectors *b* and *d* is 159°.

together with two pentafluorobenzenethiolate monoanions and three diethylammonium monocations. The geometry at titanium is distorted trigonal bipyramidal, with S(3), S(4) and S(5) forming the equatorial plane, the titanium lying 0.13 Å out of this plane in the direction of one of the axial sulfur atoms [S(1)]. The angles subtended at the metal centre by the equatorial atoms are in the range 115.5(1) to 126.5(1)°, and the two axial sulfur atoms subtend an angle of 172.7(1)° at the metal centre (Table 1). The Ti–S bond lengths fall into two distinct groups with those to the equatorial sulfur atoms [2.350(2)–2.357(2) Å] being *ca.* 0.04 Å shorter than those to the axial ones [2.386(1) and 2.406(1) Å], the shorter of these two axial bonds being to S(1) (the sulfur that the titanium is displaced towards, see above). The Ti–S bonds observed in the present structure are similar to those in **6** [average Ti–S 2.361(2) Å][13] and **7** [average Ti–S 2.332(3) Å],[14] and to the terminal Ti–S bond lengths in **8** [2.321(1)–2.362(1) Å],[15] **9** [Ti–S 2.3134(7)–2.3177(7) Å],[15] and **11** [Ti–S 2.3308(9)–2.4090(10) Å].[18] However, as expected, the foregoing Ti–S bond distances are shorter than those reported for bridging thiolate ligands, for example in **11** the bridging Ti–S bond distances span the range 2.513(1)–2.561(1) Å.[18] It is also worth noting that the Ti–S bond distances in **12** are also shorter than those observed in [Ti(η^5-$C_5H_4SiMe_3$)$_2$(SC_6F_5)$_2$] **10** [Ti–S 2.431(2) and 2.438(2) Å] as a result of the trimethylsilylcyclopentadienyl groups in **10**.[16] The rotations about the Ti–S bonds are such that the C_6F_5 rings attached to two of the sulfur atoms in the equatorial plane [S(4) and S(5)] are oriented "above" this plane, with that attached to S(3) "below". This overall conformation is, in part, stabilised by a weak C–F···π interaction[19] from one of the *ortho* fluorine atoms of the S(1) based C_6F_5 ring to the S(5) ring (interaction *a* in Fig. 1).

It is interesting that four of the five SC_6F_5 units [those associated with S(1), S(2), S(3) and S(5)] are oriented such that their planes are aligned essentially orthogonally to the crystallographic 010 plane [maximum inclination 14° for the S(2) ring] creating a paddle-wheel-like motif, *i.e.* all of the Ti–S–Ar bends are in the same sense. The remaining ring, based on S(4), is nearly parallel to the 010 plane (inclined by *ca.* 27°). This paddle-wheel motif facilitates the interleaving of adjacent complexes which are cemented together by π–π stacking interactions between the S(1) ring in one complex and the S(2) ring in the next (interaction *b* in Fig. 2) and also between the S(3) and S(5) rings in neighbouring complexes (interaction *c* in Fig. 2); the S(1)/S(2) and S(3)/S(5) pairs of rings are inclined by 4 and 9° respectively. These interactions combine to form an extended two-dimensional sheet of complex anions whose upper and lower surfaces are bounded by the S(4) rings that are not involved in the aforementioned π–π stacking. This arrangement is further stabilised by a C–F···π interaction (*d* in Fig. 2)

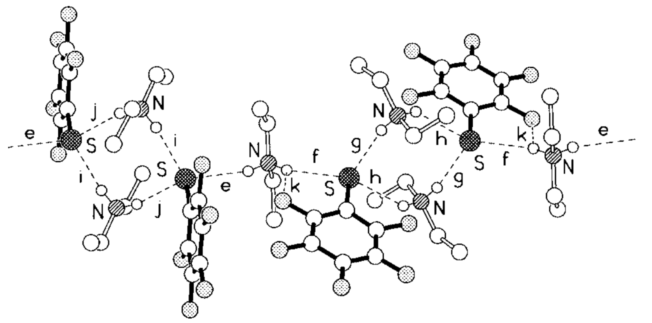


Fig. 3 Part of one of the N–H···S linked cation/anion hydrogen bonded chains present in the crystals of complex **12**. N···S, H···S distances (Å) and N–H···S angles (°); (*e*) 3.23, 2.38, 158; (*f*) 3.27, 2.42, 156; (*g*) 3.30, 2.41, 167; (*h*) 3.38, 2.60, 145; (*i*) 3.32, 2.45, 163 and (*j*) 3.27, 2.39, 166. The N–H···F interaction (*k*) has N···F, H···F 3.10, 2.47 Å and N–H···F 127°.

between one of the fluorine atoms of an S(3) ring to the "opposite" face of the π-stacked S(2) ring.

The space between parallel anionic two-dimensional sheets is occupied by the three unique $[Et_2NH_2]^+$ cations and two $[C_6F_5S]^-$ anions. These are linked *via* N–H···S hydrogen bonds to form a chain that extends along the crystallographic *c* direction, utilising all six of the available donor N–H hydrogen atoms (interactions *e* to *j* in Fig. 3). These cation/anion chains are linked to the anionic sheets by weak C–F···π interactions from a fluorine on one of the $[C_6F_5S]^-$ rings of the chain to one of the bounding S(4) rings of the sheet; the F···π distance is 3.32 Å, the C–F···π angle is 128° and the F···π vector is inclined by *ca.* 71° to the S(4) ring plane.

It is interesting to compare the structure of complex **12** with those of **7** and **11**. A similar synthetic methodology was used for the preparation of **7** and **11** in which $Ti(NEt_2)_4$ was treated with 10 equivalents of HSR (**7**, R = Me;[15] **11**, R = CH_2Ph[18]). However, in contrast to **12**, this results in the formation of binuclear face-sharing octahedral complexes.

The ^1H NMR spectrum of complex **12** recorded at room temperature (CD_2Cl_2) consists of a triplet in the methyl region and a quartet in the methylene region, corresponding to the $[Et_2NH_2]^+$ cations. The chemical shifts in the ^{19}F NMR spectrum were similar to those reported for the SC_6F_5 group in other perfluorophenyl thiolate derivatives and consisted of three multiplets at δ −132.9, −160.9 and −165.3.[16] This suggests that **12** exhibits fluxional behaviour between the $[Ti(SC_6F_5)_5]^-$ anion and the $[SC_6F_5]^-$ anions in solution since no peaks are observed for the $[SC_6F_5]^-$ anions in **12**.

With a view to developing a neutral monomeric titanium(IV) thiolate, it was decided to introduce a two electron donor ligand, L [2,6-dimethylpyridine or tetrahydrothiophene (C_4H_8S)], into the reaction and to limit the amount of thiol present. Accordingly, $Ti(NEt_2)_4$ was treated with 4 equivalents of HSC_6F_5, in the presence of 2,6-dimethylpyridine at room temperature (Scheme 1). A dark red crystalline product (**13**) was obtained in a 65% yield by diffusion of an overlayer of hexanes into a saturated CH_2Cl_2 solution of **13**. Analytical and spectroscopic data are consistent with the ionic species $[Et_2NH_2]$-$[Ti(SC_6F_5)_4(NEt_2)]$ as shown by the crystal structure analysis, but not with the expected complex $[Ti(SC_6F_5)_4(L)_x]$ **14**.

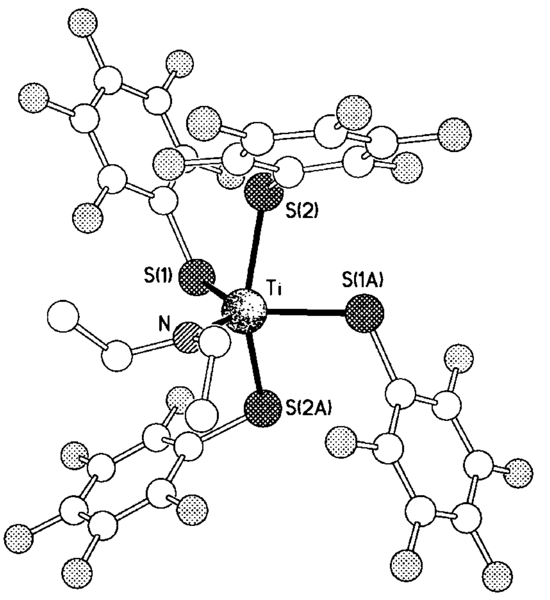


Fig. 4 The molecular structure of the anion in the structure of complex **13**, showing the highly distorted trigonal bipyramidal/square pyramidal co-ordination at titanium. Only the titanium and sulfur atoms have been labelled for clarity.

The single crystal structure determination of complex **13** reveals a structure that is very similar to that of the complex anion in **12** but with one of the pentafluorobenzenethiolate ligands replaced by a diethylamino unit to give the C_2 symmetric diethylammonium salt of (diethylamido)tetra(pentafluorobenzenethiolato)titanate(IV) (Fig. 4). The geometry at titanium is again distorted trigonal bipyramidal with S(1), S(1A) and N occupying the equatorial sites. The equatorial plane, including the titanium atom, is perfectly flat, a geometric consequence of the twofold axis that passes along the Ti–N bond and bisects the S(1)–Ti–S(1A) angle; the unique angles at titanium within this plane are 119.9(1) and 120.3(1)° (Table 1). The "axial" sulfur atoms subtend an angle of 148.2(1)° at the metal centre, producing a substantially greater distortion in the co-ordination geometry than is observed in **12** [172.7(1)°]. Indeed, the geometry in **13** could be considered as being intermediate between trigonal bipyramidal and square pyramidal, with in the latter case the diethylamino nitrogen atom occupying the apical position. The Ti–S bond lengths exhibit an expected difference between those in axial [2.427(1) Å, S(2)] and equatorial positions [2.417(1) Å, S(1)]. These distances are both significantly longer than those in **12** but the difference is noticeably less and may reflect the trend towards square pyramidal co-ordination. The Ti–N bond length of 1.849(4) Å is short, indicating a degree of partial double bond character, an assignment reinforced by the trigonal planar geometry of the nitrogen centre [the angles at nitrogen are 117.3(4), 121.3(2) and 121.3(2)°]. The Ti–N bond distance is similar to those found in related amido complexes such as $[Ti(NEt_2)_2(PhNNNPh)_2]$ (Ti–NEt_2 1.883 Å).[20] The trigonal plane of the nitrogen atom is rotated by *ca.* 18° out of the equatorial co-ordination plane, and there is a weak intramolecular C–H···F interaction between one of the terminal methyl hydrogen atoms of the diethylamino substituent and the proximal *ortho* fluorine atom on the S(1) ring [C···F, H···F distances 3.09, 2.43 Å; C–H···F angle 126°].

The rotations about the Ti–S bonds are again of interest, with all of the SC_6F_5 ligands being bent towards the diethylamino ligand (or alternatively, in the context of a square pyramidal geometry, away from the four basal sulfur atoms). This geometry results in the creation of a cleft within which the diethylammonium cation is located. The cation is positioned such that the two ammonium hydrogen atoms are directed towards S(1) and S(1A), indicating possible weak N–H···S hydrogen bonding interactions [N···S, H···S distances (Å) and N–H···S angles (°); 3.38, 2.60, 146 and 3.59, 2.79, 147 respectively].† As was the case for four of the five SC_6F_5 rings in **12**, here all four are oriented essentially orthogonally to the crystallographic *ac* plane [the maximum deviation from orthogonal being *ca.* 13 ° for the S(2) ring] and again adopt a paddle-wheel-like conformation, the Ti–S–Ar bends all being

---

† The two different geometries are a consequence of the cation being disordered about the crystallographic twofold axis.

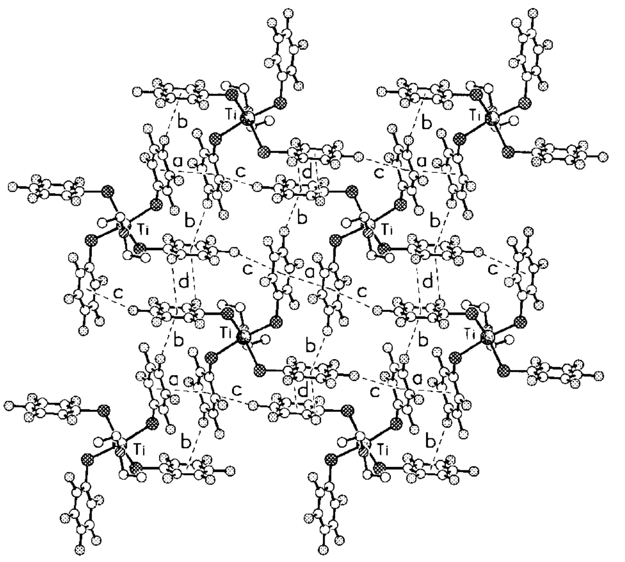


Fig. 5 View of part of one of the anionic two-dimensional sheets of π–π, C–F···π and F···π linked complexes present in the structure of complex **13**. The π–π interaction (*a*) has centroid–centroid and mean interplanar separations of 3.49 and 3.32 Å respectively. F···π distances (Å), C–F···π angles (°): (*b*) 3.09, 135; (*c*) 3.26, 152; (*d*) centroid–centroid, mean interplanar separation, and F··· π distance 4.57, 3.23 and 3.35 Å respectively.

in the same sense. As can be seen in Fig. 5, this conformation again facilitates the interleaving of the rings of adjacent complexes to form a two-dimensional sheet in the crystallographic *ac* plane. This arrangement is stabilised by a combination of π–π (*a*), C–F···π (*b* and *c*) and F···π (*d*) interactions, with the "upper" and "lower" surfaces being dominated by the coordinated and cationic NEt_2 units. There are in addition, however, short non-bonded F···F contacts (2.76 Å) between a *meta* fluorine atom of the S(1) rings in one sheet and their counterparts on the S(2) rings in the next.

Treatment of $Ti(NEt_2)_4$ with an excess of tetrahydrothiophene (C_4H_8S) in toluene solution, followed by the addition of four equivalents of HSC_6F_5, resulted, after work-up, in the formation of a dark red crystalline solid. Analytical and spectroscopic data were again consistent with the formation of complex **13** rather than the anticipated product **14**. The two-electron donor ligands (L) may be involved in the reaction leading to the formation of **13**, however, no product containing L was isolated in either reaction. It is interesting that **5** was reported to show no reactivity towards common donor ligands such as pyridine or PPh_3.[12]

In an attempt to isolate the neutral homoleptic species $[Ti(SC_6F_5)_4]_n$, compound **13** was heated *in vacuo* (100 °C, 10^{-3} mmHg). It was expected that **13** would lose amine and thiol to produce $[Ti(SC_6F_5)_4]_n$ as has been observed in some related metal thiolate salts.[21] However, prolonged heating of **13** resulted in an insoluble brown solid (**15**). Analytical data for **15** show the presence of nitrogen in the complex suggesting that **13** has not lost all the amine. It is likely that some form of polymer was produced as a result of heating **13**.

Finally, $Ti(NEt_2)_4$ was treated with four equivalents of HSC_6F_5 but without the addition of co-ordinating ligands. A dark red crystalline solid was isolated, the ^1H NMR of which indicated that complex **12** had formed rather than **13** as was initially expected. This suggests that the presence of L in the reaction mixture to produce **13** does affect the final product obtained.

In summary, two novel ionic thiolate complexes of titanium(IV), namely $[Et_2NH_2]_3[Ti(SC_6F_5)_5][SC_6F_5]_2$ **12** and $[Et_2NH_2][Ti(SC_6F_5)_4(NEt_2)]$ **13**, have been synthesized and structurally characterised. Both adopt similar sheet structures held together by π–π and C–F···π interactions. Unfortunately, their low volatility precluded thin film growth by CVD. However, compounds **12** and **13** can serve as precursors to TiS_2 *via* a novel thio 'sol–gel' methodology, the details of which will be described in a future publication.[22]

Experimental

General procedures

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box. All solvents were distilled from appropriate drying agents prior to use (sodium–toluene, THF and hexanes; CaH_2 for CH_2Cl_2) and $Ti(NEt_2)_4$[23] was prepared by literature methods. All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London (UCL).

Physical measurement

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

Preparations

$[Et_2NH_2]_3[Ti(SC_6F_5)_5][SC_6F_5]_2$ 12. *Method 1.* Pentafluorobenzenethiol (2.25 cm^3, 16.90 mmol) was added dropwise to an orange solution of $Ti(NEt_2)_4$ (0.6 cm^3, 1.66 mmol) in toluene (20 cm^3) at room temperature with stirring. The solution turned dark red immediately on addition of the thiol. The mixture was stirred for 2 hours at room temperature and then the solvent was removed *in vacuo*. The resulting dark red oil was dissolved in toluene (20 cm^3) and filtered through Celite to give a dark red solution. Cooling to −20 °C overnight afforded a 75% yield of red crystalline complex **12**. Single crystals suitable for crystallography were obtained by dissolving the solid in CH_2Cl_2 (4 cm^3) and overlaying this solution with hexanes (20 cm^3). Solvent diffusion at room temperature over a period of days afforded dark red needles of **12** (mp 108–112 °C).

Method 2. HSC_6F_5 (0.44 cm^3, 3.30 mmol) was added dropwise to an orange solution of $Ti(NEt_2)_4$ (0.3 cm^3, 0.83 mmol) in toluene (20 cm^3) at room temperature with stirring. The solution turned dark red immediately on addition of the thiol. The mixture was treated as above. Calc. for $C_{54}H_{36}F_{35}N_3S_7Ti$: C, 38.9; H, 2.16; N, 2.52. Found C, 40.06; H, 2.28; N, 2.84%. ^1H NMR (CD_2Cl_2): δ 1.49 (t, 18H, NCH_2CH_3), 3.29 (q, 12H, NCH_2CH_3) and 8.33 (s, 6H, NH_2). ^{13}C-{^1H} NMR (CD_2Cl_2): δ 11.2 (NCH_2CH_3), 42.0 (NCH_2CH_3), 121, 137, 145 (SC_6F_5). ^{19}F-{^1H} NMR (CD_2Cl_2, reference $CFCl_3$): δ −132.9 (m, 10F, $F^{2,6}$ of C_6F_5), −160.9 (m, 5F, F^4 of C_6F_5) and −165.3 (m, 10F, $F^{3,5}$ of C_6F_5).

$[Et_2NH_2][Ti(SC_6F_5)_4(NEt_2)]$ 13. *Method 1.* 2,6-Dimethylpyridine (0.39 cm^3, 3.34 mmol) was added to an orange solution of $Ti(NEt_2)_4$ (0.6 cm^3, 1.66 mmol) in toluene (20 cm^3) at room temperature. Pentafluorobenzenethiol (0.88 cm^3, 6.60 mmol) was added dropwise and the solution turned dark red immediately. After stirring for 2 hours at room temperature the solvent was removed *in vacuo*. The resulting dark red oil was dissolved in toluene (20 cm^3) and filtered through Celite to give a dark red solution. Cooling to −20 °C overnight resulted in the formation of a 65% yield of crystalline red complex **13**. Single crystals suitable for crystallography were obtained by dissolving the solid in CH_2Cl_2 (4 cm^3) and overlaying this solution with hexanes (20 cm^3). Solvent diffusion over a period of days at room temperature afforded dark red crystals (mp 148–150 °C).

Method 2. Tetrahydrothiophene (0.38 cm^3, 3.34 mmol) was added to an orange solution of Ti(NEt$_2$)$_4$ (0.6 cm^3, 1.66 mmol) in toluene (20 cm^3) at room temperature. Subsequent treatment as above resulted in the formation of a 65% yield of a crystalline red solid. Calc. for $C_{32}H_{22}F_{20}N_2S_4Ti$: C, 38.79; H, 2.22; N, 2.83. Found C, 38.83; H, 2.10; N, 3.17%. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.05 (t, 6H, $\mathrm{NCH_2C}\mathit{H}_3$), 1.50 (t, 6H, $\mathrm{H_2NCH_2C}\mathit{H}_3$), 3.45 (q, 4H, $\mathrm{H_2NC}\mathit{H}_2\mathrm{CH_3}$), 4.34 (q, 4H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$) and 7.30 (s, 2H, $\mathit{H}_2\mathrm{NCH_2CH_3}$). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 11.6 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 12.7 ($\mathrm{H_2NCH_2}\mathit{C}\mathrm{H_3}$), 43.4 ($\mathrm{H_2N}\mathit{C}\mathrm{H_2CH_3}$), 49.7 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 121, 147, 146 (SC$_6F_5$). ^{19}F-{^{1}H} NMR (CD$_2$Cl$_2$, reference CFCl$_3$): δ −132.5 (m, 8F, F^{2,6} of C$_6$F$_5$), −160.5 (m, 4F, F^4 of C$_6$F$_5$) and −164.9 (m, 8F, F^{3,5} of C$_6$F$_5$).

X-Ray crystallography

Crystals of complexes **12** and **13** were grown from CH$_2$Cl$_2$–hexanes mixtures at room temperature.

Crystal data for complex 12. $[C_4H_{12}N]_3[C_{30}F_{25}S_5Ti][C_6F_5S]_2$, $M = 1664.2$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.953(1)$, $b = 31.429(2)$, $c = 21.014(2)$ Å, $\beta = 91.58(1)°$, $V = 6571(1)$ Å^3, $Z = 4$, μ(Cu-Kα) = 4.48 mm^{-1}, $T = 183$ K; deep red platy needles, Siemens P4/RA diffractometer, ω scans, 9610 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full matrix least squares based on F^2 to give $R1 = 0.054$, $wR2 = 0.123$ for 6536 independent observed absorption corrected reflections $[|F_o| > 4\sigma(|F_o|)]$, $2\theta \leqslant 120°$.

Crystal data for complex 13. $[C_4H_{12}N][C_{28}H_{10}F_{20}NS_4Ti]$, $M = 990.7$, monoclinic, space group $C2/c$ (no. 15), $a = 15.200(1)$, $b = 17.615(1)$, $c = 14.117(2)$ Å, $\beta = 91.18(1)°$, $V = 3779.1(7)$ Å^3, $Z = 4$ (the complex has crystallographic C_2 symmetry), μ(Cu-Kα) = 5.18 mm^{-1}, $T = 193$ K; deep red blocks, Siemens P4/RA diffractometer, ω scans, 3093 independent reflections. The structure was solved and refined as above to give $R1 = 0.055$, $wR2 = 0.143$ for 2598 independent observed absorption corrected reflections $[2\theta \leqslant 128°]$.

CCDC reference number 186/2175.

See http://www.rsc.org/suppdata/dt/b0/b006115h/ for crystallographic files in .cif format.

Acknowledgements

We thank EPSRC (GR/M11981) for financial support and a studentship (C.W.D.). C.J.C. is also grateful to the Royal Society for a Dorothy Hodgkin fellowship and additional support and London University Central Research Fund for financial support.

References

1 T. S. Lewkebandara and C. H. Winter, *Adv. Mater.*, 1994, **6**, 237; M. Bochmann, *Chem. Vap. Deposition*, 1996, **2**, 85.
2 M. S. Whittingham, *Prog. Solid State Chem.*, 1978, **12**, 41.
3 R. C. Bill, *Wear*, 1985, **106**, 283.
4 W. S. Rees, Jr., *CVD of Nonmetals*, VCH Publishers, Weinheim, 1996.
5 C. H. Winter, T. S. Lewkebandara and J. W. Proscia, *Chem. Mater.*, 1992, **4**, 1144.
6 C. H. Winter, T. S. Lewkebandara, J. W. Proscia and A. L. Rheingold, *Inorg. Chem.*, 1993, **32**, 3807.
7 M. Bochmann, I. Hawkins and L. M. Wilson, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 344.
8 J. Cheon, J. E. Gozum and G. S. Girolami, *Chem. Mater.*, 1997, **9**, 1847.
9 C. H. Winter, T. S. Lewkebandara, J. W. Proscia and A. L. Rheingold, *Inorg. Chem.*, 1994, **33**, 1227.
10 D. W. Stephan and T. T. Nadasdi, *Coord. Chem. Rev.*, 1996, **147**, 147 and references therein.
11 D. C. Bradley and P. A. Hammersley, *J. Chem. Soc. A*, 1967, 1894.
12 R. J. H. Clark and D. Kaminaris, *Inorg. Chim. Acta*, 1974, **11**, L7.
13 D. T. Corwin, J. F. Corning, S. A. Koch and M. Millar, *Inorg. Chim. Acta*, 1995, **229**, 335.
14 R. A. Jones, S. T. Schwab and B. R. Whittlesey, *Polyhedron*, 1984, **3**, 505.
15 W. Stüer, K. Kirschbaum and D. M. Giolando, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1981.
16 E. Delgado, E. Hernández, A. Hedayat, J. Tornero and R. Torres, *J. Organomet. Chem.*, 1994, **466**, 119.
17 J. T. Kim, J. W. Park and S. M. Koo, *Polyhedron*, 2000, **19**, 1139.
18 C. J. Carmalt, C. W. Dinnage, I. P. Parkin and J. W. Steed, *Inorg. Chem.*, 2000, **39**, 2693.
19 For an overview of interactions involving an acceptor C$_6$F$_6$ group see I. Alkorta, I. Rozas and J. Elguero, *J. Org. Chem.*, 1997, **62**, 4687.
20 I. A. Guzei, L. M. Liable-Sands, A. L. Rheingold and C. H. Winter, *Polyhedron*, 1997, **16**, 4017.
21 S. Suh, J. H. Hardesty, T. A. Albright and D. M. Hoffman, *Inorg. Chem.*, 1999, **38**, 1627.
22 C. J. Carmalt, C. W. Dinnage and I. P. Parkin, *J. Mater. Chem.*, 2000, 10.1039/b002949l.
23 D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 1960, **82**, 3857.