



The synthesis and structural characterization of $[\text{Et}_4\text{N}]_2[\text{Ti}(\text{SPh})_6]$ and trimeric $[\text{Ti}_3\text{O}(\text{SPh})_3\text{Cl}_4(\text{CH}_3\text{CN})_5] \cdot \text{CH}_3\text{CN} \cdot (\text{C}_2\text{H}_5)_2\text{O}$ complexes

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Abstract

The reaction of TiCl_4 with 6 equiv. of NaSPh in the presence of organic cations such as Et_4N^+ or PPh_4^+ proceeds to yield a novel homoleptic arylthiolate Ti(IV) complex, $[\text{Ti}(\text{SPh})_6]^{2-}$. The Et_4N salt of $[\text{Ti}(\text{SPh})_6]^{2-}$ has been structurally determined. The coordination geometry around the metal ion is a regular octahedron in which the central titanium ion is located on the crystallographic inversion center. The infrared (IR) spectrum of compound **I** exhibits the characteristic Ti–S bond stretching vibrations of thiophenolate ligands at 480 and 430 cm^{-1} , and the ^1H NMR spectrum in CD_3CN displays characteristic Et_4N^+ resonance peaks and six thiophenolate resonance peaks which are consistent with the solid state structure. The reaction of TiCl_4 with 3 or 4 equiv. of NaSPh in CH_3CN yields the unexpected mixture of dark purple $[\text{TiCl}_3(\text{CH}_3\text{CN})_3]$ and dark red $[\text{Ti}_3\text{O}(\text{SPh})_3\text{Cl}_4(\text{CH}_3\text{CN})_5] \cdot \text{CH}_3\text{CN} \cdot (\text{C}_2\text{H}_5)_2\text{O}$ (**II**) complexes. Complex **II** has been structurally determined by single X-ray crystallography. The IR spectrum of complex **II** exhibits a $\mu_3\text{-O}$ stretching vibration at 600 cm^{-1} and Ti–S vibrations of the thiophenolate ligand at 481 and 429 cm^{-1} . ©2000 Elsevier Science Ltd All rights reserved.

Keywords: Oxo ligands; Thiolates; Titanium; Trimers

1. Introduction

There has been an enormous study of the transition metal complexes with aliphatic or aromatic thiolate ligands, because they exhibit a variety of structural types with various nuclearities [1–9], and certain complexes can be used as precursors for corresponding transition metal sulfide complexes [10–15]. Among the transition metal thiolate complexes, mononuclear species with homoleptic thiolate ligands are fundamental types that can be used to derive cluster and cage types of molecules or corresponding thiometalates. Such early transition metal complexes with homoleptic thiolate ligands have been reported extensively in the last few years. For example, $\text{M}(\text{SPh})_6^{n-}$ ($n = 1, 2$; $\text{M} = \text{Nb}, \text{Ta}$) [16], $\text{M}(\text{SPh})_4^{2-}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) [17,18] and $\text{M}(\text{S}_2\text{C}_2\text{H}_4)_3^-$ ($\text{M} = \text{Nb}, \text{Ta}$) [19], $\text{M}(\text{S}_2\text{C}_2\text{H}_4)_3^{n-}$ ($n = 1, 2$; $\text{M} = \text{Ti}, \text{Co}, \text{Cr}$) [20,21] have been synthesized and fully characterized. In contrast to the other groups, the types and structural pattern of group IV metal thiolate complexes have not been fully studied. Recently, Tatsumi et al. reported $\text{Zr}(\text{tBuS})_5^-$ and $\text{Zr}(\text{tBuS})_6^{2-}$ complexes [22].

Reports on titanium complexes with thiolate ligands are limited to a few complexes, including $\text{Ti}(\text{S-2,4,6-}^i\text{Pr}_3\text{C}_6\text{H}_2)_4^-$, $\text{Ti}(\text{S-2,4,6-}^i\text{Bu}_3\text{C}_6\text{H}_2)_4^-$ [23] and dithiolate complexes of titanium [20,21]. Recently, Giolando et al. reported on the synthesis and structural characterization of dimeric $\text{Ti}_2(\text{SMe})_9^-$, trimeric $\text{Ti}_3(\text{SMe})_{12}$ complexes which were obtained from the reaction of $\text{Ti}(\text{NR}_2)_4$ with RSH ($\text{R} = \text{Me}, \text{Et}$) [24].

We are interested in obtaining Ti(IV) homoleptic monodentate thiolate complexes, potential starting materials for corresponding thiotitanates. Here, we report the synthesis and structural characterization of the homoleptic arylthiolate titanium complex $[\text{Ti}(\text{SPh})_6]^{2-}$ (**I**) and the trimeric $[\text{Ti}_3\text{O}(\text{SPh})_3\text{Cl}_4(\text{CH}_3\text{CN})_5] \cdot \text{CH}_3\text{CN} \cdot (\text{C}_2\text{H}_5)_2\text{O}$ (**II**).

2. Experimental

All manipulations were performed using standard Schlenk line techniques under dinitrogen atmosphere. Diethyl ether was distilled after being refluxed with sodium–benzophenone. Acetonitrile was distilled after being refluxed over CaH_2 before use. TiCl_4 , Et_4NBr and PPh_4Cl were purchased from Aldrich and used as received. Sodium thiophenolate

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(NaSPh) was prepared from the reaction of sodium and thio-phenol in diethyl ether.

2.1. $[Et_4N]_2[Ti(SPh)_6]$ (I)

A 250-ml Schlenk flask was charged with 2.26 g (17.23 mmol) of NaSPh, 1.10 g (5.30 mmol) of Et_4NBr and a stirring bar. To this mixture was added 50 ml of CH_3CN via a cannula with stirring at ambient temperature and 0.29 ml (2.65 mmol) of $TiCl_4$ was injected using a syringe. The color of the solution turned to dark red immediately. After 2 h, the solution was filtered through a fine porosity fritted funnel; to the dark red filtrate, 50 ml of diethyl ether was added and the resulting solution was left to stand at ambient temperature. Finally, dark red crystalline materials were obtained in 80% yield. Calc. for $TiS_6N_2C_{52}H_{70}$: C, 64.83; H, 7.27; N, 2.92; S, 19.97. Found: C, 64.91; H, 7.34; N, 3.01; S, 21.52%. FT-IR (cm^{-1}): $\nu(Ti-SPh)$; 480, 430. 1H NMR in acetonitrile- d_3 : $\delta(CH_3$ in Et_4N^+); 1.18 (t, 24H), $\delta(CH_2$ in Et_4N^+); 3.21 (q, 16H), $\delta(C_6H_5$ in Sph ligand); 6.97–7.42 (m, 30H). The Ph_4P^+ salt was also obtained by a similar synthetic procedure in 80% yield. Calc. for $TiS_6P_2C_{84}H_{70}$: C, 73.05; H, 5.07. Found: C, 73.23; H, 5.12%. IR (KBr disc) (cm^{-1}): $\nu(Ti-SPh)$, 480 and 420.

2.2. $[Ti_3O(SPh)_3Cl_4(CH_3CN)_5] \cdot CH_3CN \cdot (C_2H_5)_2O$ (II)

2.2.1. Method A

A 250-ml Schlenk flask was charged with 1.39 g (10.60 mmol) of NaSPh and a stirring bar. To this flask 30 ml of CH_3CN was added via a cannula with stirring at ambient temperature, and 0.29 ml (2.65 mmol) of $TiCl_4$ was injected using a syringe. The color of the solution turned to dark red. After 2 h, the solution was filtered through a fine porosity fritted funnel. To the red filtrate 100 ml of diethyl ether was added and the resulting solution was stood at ambient temperature. Dark purple crystals and dark red crystals were isolated and dried under vacuum. Finally, a 1:1 mixture of dark purple crystals of $TiCl_3(CH_3CN)_3$ and dark red crystals of $[Ti_3O(SPh)_3Cl_4(CH_3CN)_5] \cdot CH_3CN \cdot (C_2H_5)_2O$ were obtained (see below). The total yield was approximately 70% (based on Ti). 1H NMR in DMF- d_7 : $\delta(CH_2$ in CH_3CN in ligand and free CH_3CN); 1.95 (br, 27H), $\delta(CH_3$ in Et_2O); 3.382 (q, 4H), $\delta(CH_3$ in Et_2O); 1.068 (t, 6H), $\delta(C_6H_5$ in Sph ligand); 7.126–7.277 (m, 15H).

2.2.2. Method B

$TiCl_4$, 0.18 ml (1.68 mmol), was injected using a syringe into a 250-ml Schlenk flask containing 20 ml of CH_3CN . To this solution 0.01 ml (0.56 mmol) of H_2O diluted in 10 ml of CH_3CN was added and the solution was stirred at ambient temperature for 10 min. The solution was transferred via a cannula to a 250-ml schlenk flask charged with 0.88 g (6.72 mmol) of NaSPh and 20 ml of CH_3CN . After 2 h, the solution was filtered through a fine porosity fritted funnel; then to the red filtrate 100 ml of diethyl ether was added and the resulting

solution was stood at ambient temperature. Finally, a dark red powder of $[Ti_3O(SPh)_3Cl_4(CH_3CN)_5] \cdot CH_3CN \cdot (C_2H_5)_2O$ was obtained in 74% yield.

Calc. for $Ti_3S_3O_2N_6Cl_4C_{34}H_{43}$: C, 43.03; H, 4.53; N, 8.85; S, 10.14. Found: C, 43.24; H, 4.24; N, 8.76; S, 12.01%. FT-IR (cm^{-1}): $\nu(Ti-O)$, 600.5; $\nu(CH_3CN)$, 2310.3, 2280; $\nu(Ti-SPh)$, 481, 429. 1H NMR in DMF- d_7 : $\delta(CH_3$ in CH_3CN ligand and free CH_3CN); 1.92–1.97 (m, 18H), $\delta(CH_2$ in Et_2O); 3.28 (q, 4H), $\delta(CH_3$ in Et_2O); 1.06 (t, 6H), $\delta(C_6H_5$ in Sph ligand); 7.252–7.285 (m, 15H).

2.3. X-ray crystallography

Single X-ray diffraction data for both crystals are presented in Table 1. Diffraction data were collected at ambient temperature on a Bruker P4 four circle diffractometer using Mo $K\alpha$ radiation. Intensity data were collected by using a $\theta-2\theta$ step scan technique and for all data sets the condition of the crystal was monitored by measuring 2 standard reflections. The solutions of both structures were carried out by a combination of heavy atom Patterson techniques, direct methods and Fourier techniques. The refinement of the structures by full-matrix least-squares methods was based on 2640 unique reflections ($2\theta=45^\circ$, $I>2\sigma$) for compound **I**, and 4361 unique reflections ($2\theta=22.5^\circ$, $I>2\sigma$) for compound **II**. Anisotropic temperature factors were used for all non-hydrogen atoms in compounds **I** and **II**, except solvent molecules packed in the lattice for compound **II**. At the current stage of refinement on 312 parameters for compound **I** and 459 parameters for compound **II** with all atoms present in the asymmetric units, $R=0.0383$, $R_w=0.0989$ for compound **I** and $R=0.0715$, $R_w=0.1982$ for compound **II**.

Table 1
Crystallographic data for $[Et_4N]_2[Ti(SPh)_6]$ (I) and $[Ti_3O(SPh)_3Cl_4(CH_3CN)_5] \cdot CH_3CN \cdot (C_2H_5)_2O$ (II)

	I	II
Formula	$TiS_6N_2C_{52}H_{70}$	$Ti_3S_3O_2N_6Cl_4C_{34}H_{43}$
FW	963.36	948.96
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a (Å)	11.113(2)	13.139(1)
b (Å)	11.414(2)	8.653(1)
c (Å)	13.075(2)	38.544(3)
α (°)	112.89(1)	
β (°)	92.29(1)	90.94(1)
γ (°)	118.77(1)	
Z	2	4
V (Å ³)	1285.2(4)	4381.5(7)
T (°C)	20	20
λ (Å ³)	0.71073	0.71073
ρ_{calc} (g cm ⁻³)	1.245	1.439
μ (cm ⁻¹)	4.46	9.58
R^a	0.0383	0.0715
R_w^b	0.0989	0.1982

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|^2)]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

2.4. Other physical measurements

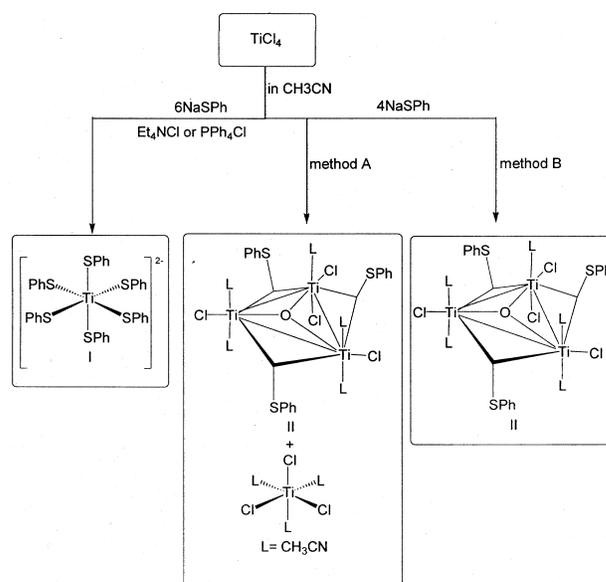
^1H NMR spectra (300 MHz) were obtained with a Varian Gemini 300 spectrometer. IR spectra were measured with a Nicolet Magna IR-760 spectrophotometer. C, H and N analyses were obtained with a Thermoquest EA-1110 CHNS analyzer.

3. Results and discussion

3.1. Synthesis and spectroscopic results

The reactions between titanium tetrachloride and sodium thiophenolate were investigated in CH_3CN at room temperature with different stoichiometries. The Et_4N^+ salts of compound **I** could be obtained from the reaction of TiCl_4 with 6 equiv. of NaSPh in CH_3CN solution in the presence of Et_4NBr . Upon the addition of solvent, the solution of the reaction mixture immediately turned to a deep red color, and was stirred for 2 h at ambient temperature under N_2 atmosphere. The solution was then filtered and dark red crystals of Et_4N^+ ‘salts’ were isolated with 80% yield by the slow diffusion of diethyl ether into the filtrate solution. The Ph_4P^+ ‘salts’ were also obtained in 70% yield using a similar method. The red crystals of compound **I** were very sensitive to air and moisture and even decomposed in a dry N_2 glove box within several days. The reaction of TiCl_4 with 4 equiv. of NaSPh in CH_3CN at ambient temperature produced a 1:1 mixture (as evidenced by ^1H NMR spectroscopy) of dark purple $[\text{TiCl}_3(\text{CH}_3\text{CN})_3]$ and dark red $[\text{Ti}_3\text{O}(\text{SPh})_3\text{Cl}_4(\text{CH}_3\text{CN})_5] \cdot \text{CH}_3\text{CN} \cdot (\text{C}_2\text{H}_5)_2\text{O}$ complexes. Both complexes were identified by single crystal X-ray analysis.

The synthesis of compound **I** was accomplished by the simple ligand exchange reaction of chloride by thiophenolate group (Scheme 1). The precipitation of NaCl facilitated the completion of the reaction. This method afforded a simple and convenient route to obtain the monomeric titanium thiolate complex in high yield. When the reaction stoichiometry of 1:4 ($\text{Ti}:\text{PhS}^-$) was used to obtain the cluster type Ti-thiolate complex, the hydrolyzed complex **II** was inadvertently produced. In this reaction, titanium was reduced to +3 oxidation state with the concomitant oxidation of PhS^- to $1/2\text{PhSSPh}$. This kind of reduction mechanism was reported earlier in the synthesis of $[\text{Ph}_4\text{P}]_2[\text{Nb}(\text{SPh})_6]$ [16]. The oxygen in complex **II** presumably came from a trace of water in the CH_3CN solution. In fact, complex **II** could be obtained in excellent yield (74%) when the stoichiometric amount of water (3:1 molar ratio with TiCl_4 and H_2O) was added to the reaction medium. A similar reaction was reported by Müller’s group [26] in which the reaction system $3\text{TiCl}_4:6\text{S}(\text{SiMe}_3)_2:3/2\text{O}_2$ led to a $[\text{Ti}_3\text{O}(\text{S}_2)_6\text{Cl}_6]^{2-}$ complex in which the oxygen atom came from the inert gas containing small amounts of O_2 . Further study will verify a more detailed reaction mechanism.



Scheme 1.

The IR spectrum of $[\text{Et}_4\text{N}]_2[\text{Ti}(\text{SPh})_6]$ exhibited the characteristic thiophenolate ligand Ti–S bond stretching vibrations at 480 and 430 cm^{-1} , which is typical of most metal thiolate complexes. The ^1H NMR spectrum in CD_3CN displayed the characteristic Et_4N^+ resonance peaks and six thiophenolate resonance peaks, which is consistent with the solid state structure. In the IR spectra the $\mu_3\text{-O}$ stretching vibration in the $[\text{Ti}_3\text{O}(\text{SPh})_3\text{Cl}_4(\text{CH}_3\text{CN})_5] \cdot \text{CH}_3\text{CN} \cdot (\text{C}_2\text{H}_5)_2\text{O}$ (**II**) complex was observed at 600 cm^{-1} , and doublet peaks at 2310 and 2280 cm^{-1} were assigned to the $\text{C}\equiv\text{N}$ vibrations in the CH_3CN ligand. Also the Ti–S vibrations in the thiophenolate ligand were observed at 481 and 429 cm^{-1} . The ^1H NMR spectrum in $\text{DMF-}d_7$ displayed the characteristic CH_2 (δ 3.382) and CH_3 (δ 1.608) resonance peaks from one diethyl ether molecule and three thiophenolate resonance peaks (δ 7.126–7.277). In the ^1H NMR spectra of the product, which was prepared by method A, a broad single resonance peak at δ 1.95 due to five coordinated CH_3CN , free CH_3CN molecule in complex **II** and coordinated CH_3CN in $\text{TiCl}_3(\text{CH}_3\text{CN})_3$ were observed. The integral ratio of those peaks compared to the thiophenolate ligands suggested that $\text{TiCl}_3(\text{CH}_3\text{CN})_3$ and complex **II** existed as a 1:1 mixture. However, the ^1H NMR spectra for the product prepared by method B suggested that only complex **II** was produced by this method.

3.2. X-ray structures

The structures of compounds **I** and **II** were determined; the ORTEP diagrams of the anion in complex **I** and complex **II** are shown in Figs. 1 and 2.

The selected bond distances and angles of anion in complex **I** are presented and compared with those of the $[\text{Ti}(\text{S}_2\text{C}_2\text{H}_4)_3]^{2-}$ anion [21] in Table 2. The coordination geometry around the metal ion is a regular octahedron in which the central titanium ion is located on the crystallo-

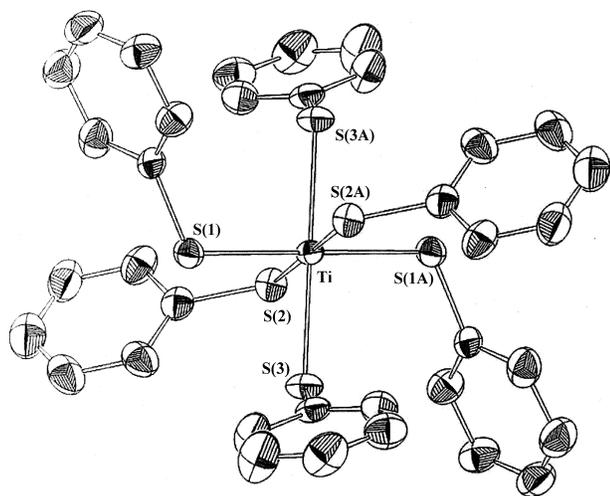


Fig. 1. Structure and labeling of the anion **I** in the $[\text{Et}_4\text{N}]_2[\text{Ti}(\text{SPh})_6]$ complex. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Symmetry-generated atoms have the suffix 'A'.

Table 2
Selected bond lengths (Å) and angles (°) for anion in complex **I** and $[\text{Ti}(\text{edt})_3]^{2-}$

	I	$[\text{Ti}(\text{edt})_3]^{2-}$ ^a
M–S(1)	2.4240(8) ^b	range 2.419(2)–2.438(2)
M–S(2)	2.4283(9)	mean 2.428
M–S(3)	2.4434(8)	
S–C	1.777(3)	range 1.789(7)–1.820(7)
	1.765(3)	mean 1.81
	1.767(3)	
S–M–S (neighbored)	84.05(3) ^b	range 82.8(1)–89.1(1)
	95.51(3)	
	84.44(3)	

^a From [21].

^b The numbers in parentheses represent the individual standard deviations.

Table 3
Selected bond lengths (Å) and angles (°) for complex **II**

Ti(1)–O	1.934(7) ^a	Ti(1)–Cl(1)	2.369(3)
Ti(2)–O	1.914(6)	Ti(1)–Cl(2)	2.396(3)
Ti(3)–O	1.917(7)	Ti(2)–Cl(3)	2.323(3)
Ti(1)–S(1)	2.574(3)	Ti(3)–Cl(4)	2.333(3)
Ti(1)–S(3)	2.576(3)	Ti(1)–Ti(3)	3.323(2)
Ti(2)–S(2)	2.560(3)	Ti(1)–Ti(2)	3.332(2)
Ti(2)–S(1)	2.585(3)	Ti(2)–Ti(3)	3.322(2)
Ti(3)–S(2)	2.553(3)	Ti–N (mean)	2.166
Ti(3)–S(3)	2.571(3)		
O–Ti–N (mean)	90.68	Ti–Ti–Ti (mean)	59.99
O–Ti(1)–Cl(1)	97.8(2) ^a	Ti–O _b –Ti (mean)	119.87
O–Ti(1)–Cl(2)	170.6(2)	N(1)–Ti(1)–S(1), S(3)	90.0(2), 92.1(2)
O–Ti(2)–Cl(3)	179.0(2)	N(2)–Ti(2)–S(1), S(2)	84.6(3), 96.6(3)
O–Ti(3)–Cl(4)	177.0(2)	N(3)–Ti(2)–S(1), S(2)	90.2(3), 90.2(3)
N(1)–Ti(1)–Cl(1)	176.0(3)	N(4)–Ti(3)–S(2), S(3)	97.2(3), 83.2(3)
N(1)–Ti(1)–Cl(2)	84.7(2)	N(5)–Ti(3)–S(2), S(3)	90.6(2), 90.1(3)
N(3)–Ti(2)–Cl(3)	87.8(3)	Cl(1)–Ti(1)–S(1), S(3)	89.24(10), 90.03(10)
N(2)–Ti(2)–Cl(3)	88.1(3)	Cl(2)–Ti(1)–S(1), S(3)	100.30(12), 100.37(11)
N(4)–Ti(3)–Cl(4)	90.0(3)	Cl(3)–Ti(2)–S(1), S(2)	101.17(13), 99.97(13)
N(5)–Ti(3)–Cl(4)	87.0(3)	Cl(4)–Ti(3)–S(2), S(3)	98.40(12), 102.03(12)
Ti–S _b –Ti (mean)	80.64	Cl(1)–Ti(1)–Cl(2)	91.57(11)

^a The numbers in parentheses represent the individual standard deviations.

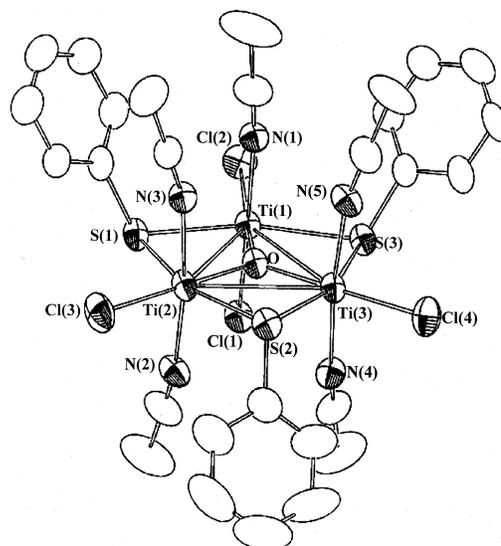


Fig. 2. Structure and labeling of complex **II**. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

graphic inversion center. The titanium–sulfur distances range from 2.424 to 2.443 Å, which are typical for metal–sulfur bonds in transition metal thiolate complexes. The slightly longer Ti–S distance (mean 2.432 Å) than that of $[\text{Ti}(\text{S}_2\text{C}_2\text{H}_4)_3]^{2-}$ (mean 2.428 Å) is mainly due to the chelating effect of dithiolate ligands in the $[\text{Ti}(\text{S}_2\text{C}_2\text{H}_4)_3]^{2-}$ complex. The S–M–S angles are 84.05, 84.44 and 95.51°, respectively.

The selected bond distances and angles of complex **II** are presented in Table 3. In complex **II**, the oxygen atom bridges three Ti atoms with μ_3 -mode and all four atoms exist nearly in the plane. The distance of Ti–O (1.922 Å) is comparable to that of $(\text{CpTi})_6(\mu_3\text{-S})_4(\mu_3\text{-O})_4$ (1.97 Å) [25]. The bond angles of Ti–O–Ti (119.87°) and the three nearly identical distances of three Ti–O bonds suggest that the oxygen atom

is located at the center of triangular geometry formed by three titanium atoms. Each titanium is contained within a pseudo-octahedral geometry in which two sulfur atoms, a chloride atom and an oxygen atom form the equatorial plane. All CH_3CN ligands are located in the axial position (O-Ti-N 90.68°) and all Cl ligands are located in the equatorial position (O-Ti-Cl 175.5°), except Cl(1) which is in the axial position (O-Ti(1)-Cl(1) 97.8°). The Ti–Ti distances in complex **II**, which range from 3.322 to 3.332 Å, are slightly longer than those in $[\text{Ti}_3\text{O}(\text{S}_2)_6\text{Cl}_6]^{2-}$ (3.14–3.18 Å) [26].

The reactivity characteristics of the anion in complex **I** and its conversion to titanium sulfide complexes as a precursor are currently under investigation in our laboratory.

Supplementary data

The full crystallographic data are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition numbers 136711 (**I**) and 136712 (**II**).

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