

Synthesis and structure of titanium tetrathiolate and tantalum pentathiolate complexes. Metal–sulfur bonding in early transition metal compounds ☆

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Abstract

The reaction of TiCl_4 with potassium 2,3,5,6-tetramethylbenzenethiolate ($\text{KS-2,3,5,6-Me}_4\text{C}_6\text{H}$) in THF gives $[\text{Ti}(\text{S-2,3,5,6-Me}_4\text{C}_6\text{H})_4]$ (**1**) in 50% yield. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.666(4)$, $b = 19.417(5)$, $c = 8.916(7)$ Å, $\alpha = 97.09(2)$, $\beta = 110.30(2)$, $\gamma = 87.95(3)^\circ$, $V = 1880(3)$ Å³, $Z = 2$. The monomeric $[\text{Ti}(\text{S-2,3,5,6-Me}_4\text{C}_6\text{H})_4]$ has a distorted tetrahedral structure with Ti–S bonds of 2.292(6) Å. One of the thiolate groups has a very acute M–S–C angle of 86.5(5)°. The reaction of TaCl_5 with excess ($\text{LiS-2,3,5,6-Me}_4\text{C}_6\text{H}$) in hexane gives $[\text{Ta}(\text{S-2,3,5,6-Me}_4\text{C}_6\text{H})_5]$ (**2**). Compound **2** crystallizes in the triclinic space group, $P\bar{1}$ with $a = 11.165(9)$, $b = 11.890(5)$, $c = 18.675(11)$ Å, $\alpha = 90.87(4)$, $\beta = 101.83(6)$, $\gamma = 96.77(5)^\circ$, $V = 2407(5)$ Å³ with $Z = 2$. $[\text{Ta}(\text{S-2,3,5,6-Me}_4\text{C}_6\text{H})_5]$ is a monomeric compound with a distorted five-coordinate geometry. The average Ta–S bond distance is 2.37(3) Å and Ta–S–C_{av} angle is 116(7)°. Structural comparisons of **1** and **2** with analogous phenolate complexes reveal large values for $\Delta[(\text{M}-\text{S}) - (\text{M}-\text{O})]$. The extent of the S to M π -bonding in these electron deficient early transition metal thiolates is considerably reduced compared to the O to M π -bonding in phenolate analogs. The observation of the acute Ti–S–C angles suggests that the limited thiolate metal π -bonding in **1** can not compensate for the strong electron deficiency of the Ti(IV) center.

Keywords: Crystal structures; Titanium complexes; Tantalum complexes; Thiolate complexes

1. Introduction

In the last few years, there has been a major effort to investigate the chemistry of Groups 4 and 5 transition metals with chalcogenide ligands. Prior to this time, molecular compounds of these metals with sulfur ligands were chiefly limited to complexes with 1,2-dithiolene, dithiocarbamate and similar ligands [1,2]. The chemistry of solid-state materials of early transition metal chalcogenides has been the subject of continuous development [3]. Recent work in the area of molecular compounds has included the synthesis of cluster compounds [4–8], complexes with the 1,2-ethanedithiolate [9,10] and benzenethiolate ligands [11], and chalcogenide ligands [12].

Abbreviations: (S-2,3,5,6-Me₄C₆H)¹⁻ = 2,3,5,6-tetramethylbenzenethiolate; (O-2,6-i-Pr₂C₆H₃)¹⁻ = 2,6-diisopropylphenolate; (O-2,3,5,6-Me₄C₆H)¹⁻ = 2,3,5,6-tetramethylphenolate.

*This paper is dedicated to F. Albert Cotton on the occasion of his 65th birthday. His vast contributions to the field and spirit of Inorganic Chemistry are fondly acknowledged.

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genide ligands [12]. Herein we describe the synthesis and crystal structures of the $\text{Ti}(\text{SR})_4$ and $\text{Ta}(\text{SR})_5$ complexes. These compounds are the first structurally characterized examples of neutral monomeric compounds of Groups 4 and 5 transition metals with exclusively monodentate thiolate ligands. Neutral homoleptic complexes of metals from Groups 4 and 5 with benzenethiolate and pentafluorobenzenethiolate have been reported but were not definitively characterized [13,14].

2. Experimental

All reactions were done with freshly dried solvent and under a dinitrogen atmosphere.

2.1. Syntheses

2.1.1. $[\text{Ti}(\text{S-2,3,5,6-Me}_4\text{C}_6\text{H})_4]$ (**1**)

The potassium salt of 2,3,5,6-tetramethylbenzenethiolate was generated by combining 2,3,5,6-tetrame-

thylbenzenethiol [15] (1.11 g, 6.67 mmol) and potassium metal (0.266 g, 6.80 mmol) in 30 ml of THF and 1 ml of ethanol. The white thiolate salt precipitated. After all the potassium had been consumed, the solvent was removed and the salt was dried under vacuum at 60 °C. TiCl_4 (0.27 g, 1.4 mmol) was added directly to the salt. Upon addition of THF (100 ml) to the mixture, a deep red–orange solution immediately developed. After stirring for 3 h the solvent was removed under vacuum, leaving a black solid residue. The residue was partially dissolved in hot hexane (100 ml) to give a red–orange solution. This suspension was filtered and washed with two 15 ml portions of hot hexane. The red–orange filtrate was concentrated under vacuum and within a few minutes, the dark product crystallized. The solution was reduced in volume to about 20 ml. The product which was obtained by filtration, was washed with 10 ml of hexane and dried under vacuum. Yield 0.47 g, 48%. The compound is soluble in acetonitrile, THF, methylene chloride, toluene, hot hexanes and chloroform, giving red solutions. $^1\text{H NMR}$ (CD_2Cl_2): δ 6.94 (s, 4H), 2.20 (s, 24H), 2.15 (s, 24H). The $^1\text{H NMR}$ spectra also showed the presence of small amounts of free thiol.

2.1.2. $[\text{Ta}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_5]$ (2)

The lithium salt of 2,3,5,6-tetramethylbenzenethiolate ($\text{LiS}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}$) was generated from the reaction of the thiol (1.00 g, 6.03 mmol) and lithium (0.045 g, 6.5 mmol) in THF. The solution was filtered and the filtrate was evaporated to dryness. Hexane (70 ml) was

added to a mixture of the thiolate and TaCl_5 (0.354 g, 0.988 mmol). The reaction mixture was stirred at room temperature for 1 h and then heated at 60 °C for 5 h. The intense red–orange reaction mixture was filtered to remove LiCl . The filtrate was concentrated to 50 ml and cooled to -20 °C. The red–orange crystalline product was removed by filtration. $^1\text{H NMR}$ (C_6D_6): δ 6.66 (1H, s), 2.56 (6H, s), 2.06 (6H, s).

2.2. X-ray crystallography

2.2.1. $[\text{Ti}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4]$

Crystals suitable for X-ray structure determination were grown from a saturated hexane solution. A dark red crystal was coated with mineral oil and wedged in a capillary tube and used for the subsequent unit cell determination and data collection. Standard procedures were followed [16]. The triclinic unit cell was determined and is listed in Table 1, along with data collection and refinement parameters. The structure was solved by Patterson and difference Fourier methods. The methyl carbon atoms were refined with isotropic temperature factors. All other non-hydrogen atoms were refined with anisotropic temperature factors. Fractional atomic coordinates for the non-hydrogen atoms are given in Table 2. Selected bond distances and bond angles are listed in Table 3.

2.2.2. $[\text{Ta}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_5]$

The air and moisture sensitive crystals were suspended in a layer of mineral oil and examined under a microscope. A suitable crystal was sealed in a capillary

Table 1
Summary of crystal data and intensity collection for 1

Empirical formula	$\text{TiS}_4\text{C}_{40}\text{H}_{52}$	$\text{TaS}_5\text{C}_{50}\text{H}_{65}$
Formula weight	709.02	1010.3
Crystal system	triclinic	triclinic
a (Å)	11.666(4)	11.165(9)
b (Å)	19.417(5)	11.890(5)
c (Å)	8.916(7)	18.675(11)
α (°)	97.09(2)	90.87(4)
β (°)	110.30(2)	101.83(6)
γ (°)	87.95(3)	96.77(5)
V (Å ³)	1880(3)	2407(5)
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z value	2	2
D_{calc} (g cm^{-3})	1.253	1.394
μ (Mo $K\alpha$) (cm^{-1})	4.77	26.51
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation, λ (Å)	Mo $K\alpha$, 0.71069	Mo $K\alpha$
Temperature	r.t.	r.t.
2θ (max) (°)	50.0	50.0
No. observations ($I > 3.00\sigma I$)	1548	4683
No. variables	326	505
Residuals: R , R_w	0.077, 0.102	0.060, 0.076
Goodness-of-fit indicator	2.69	1.87
Maximum shift in final cycle	0.06	0.04

Table 2
Fractional atomic coordinates for [Ti(S-2,3,5,6-Me₄C₆H)₄]

Atom	x	y	z
Ti	0.5350(3)	0.7451(2)	0.3192(4)
S1	0.4628(4)	0.7008(2)	0.4965(5)
S2	0.3975(4)	0.7641(2)	0.0741(6)
S3	0.6015(4)	0.8540(2)	0.4448(6)
S4	0.6838(4)	0.6729(3)	0.2763(6)
C11	0.349(1)	0.6356(8)	0.438(2)
C12	0.250(1)	0.6524(8)	0.481(2)
C13	0.163(1)	0.6033(8)	0.452(2)
C14	0.174(1)	0.5343(9)	0.376(2)
C15	0.275(1)	0.5187(7)	0.332(2)
C16	0.369(1)	0.5691(7)	0.361(2)
C21	0.299(1)	0.6926(7)	0.035(2)
C22	0.318(1)	0.6299(8)	-0.045(2)
C23	0.231(1)	0.5783(7)	-0.082(2)
C24	0.131(1)	0.5879(8)	-0.035(2)
C25	0.108(1)	0.6492(8)	0.036(2)
C26	0.194(1)	0.7025(7)	0.071(2)
C31	0.468(1)	0.8933(6)	0.458(2)
C32	0.401(1)	0.9294(7)	0.334(2)
C33	0.293(2)	0.9610(7)	0.330(2)
C34	0.258(1)	0.9599(8)	0.462(2)
C35	0.324(1)	0.9281(7)	0.591(2)
C36	0.432(1)	0.8936(7)	0.585(2)
C41	0.782(1)	0.7472(8)	0.342(2)
C42	0.796(1)	0.7889(8)	0.244(2)
C43	0.874(1)	0.8444(8)	0.298(2)
C44	0.938(1)	0.8571(8)	0.466(2)
C45	0.925(1)	0.8166(8)	0.567(2)
C46	0.851(1)	0.7629(8)	0.519(2)
C12A	0.227(1)	0.7186(8)	0.565(2)
C13A	0.049(2)	0.6082(9)	0.494(2)
C15A	0.292(1)	0.4471(8)	0.247(2)
C16A	0.481(1)	0.5536(7)	0.318(2)
C22A	0.424(1)	0.6234(9)	-0.104(2)
C23A	0.251(1)	0.5073(9)	-0.170(2)
C25A	-0.003(1)	0.6547(9)	0.075(2)
C26A	0.167(1)	0.7717(9)	0.156(2)
C32A	0.439(2)	0.9390(10)	0.190(2)
C33A	0.209(2)	1.0026(10)	0.200(2)
C35A	0.290(2)	0.9229(10)	0.741(2)
C36A	0.509(1)	0.8602(9)	0.728(2)
C42A	0.727(2)	0.7717(9)	0.068(2)
C43A	0.892(2)	0.8951(10)	0.193(2)
C45A	0.999(2)	0.8317(11)	0.754(2)
C46A	0.831(2)	0.7161(10)	0.631(2)

under a nitrogen atmosphere. Unit cell determination and data collection were performed at room temperature using standard procedures previously described [16]. Relevant parameters are given in Table 1. The structure was solved by Patterson and Fourier methods. Least-squares refinement with all the non-hydrogen atoms anisotropic gave R (R_w) = 0.060 (0.076). The methyl hydrogens of the thiolate ligands could not be located from a difference Fourier map nor could they be calculated because of the lack of geometric constraint. Since 48 hydrogen atoms are thus not incorporated in the structure factor calculations, a higher than normal

Table 3
Selected bond distances (Å) and bond angles (°) for [Ti(S-2,3,5,6-Me₄C₆H)₄] (1)

Ti-S1	2.294(4)	Ti-C11	3.573(13)
Ti-S2	2.283(4)	Ti-C21	3.123(11)
Ti-S3	2.293(3)	Ti-C31	3.170(10)
Ti-S4	2.297(4)	Ti-C41	2.821(12)
S1-S2	3.919(4)	S1-S4	3.734(5)
S1-S3	3.590(4)	S2-S3	3.613(4)
S2-S4	3.705(5)	S3-S3	3.872(4)
S1-Ti-S2	117.81(14)	S2-Ti-S3	104.28(13)
S1-Ti-S3	103.02(13)	S2-Ti-S4	108.00(14)
S1-Ti-S4	108.86(14)	S3-Ti-S4	115.06(14)
Ti-S1-C11	123.3(4)	Ti-S3-C31	102.8(3)
Ti-S2-C21	100.5(4)	Ti-S4-C41	86.5(4)

R value is obtained. Fractional atomic coordinates for the non-hydrogen atoms are given in Table 4. Selected bond distances and angles are listed in Table 5.

3. Results and discussion

[Ti(S-2,3,5,6-Me₄C₆H)₄] (1) and [Ta(S-2,3,5,6-Me₄-C₆H)₅] (2) are readily prepared by the reaction of TiCl₄ and TaCl₅ with excess alkali metal thiolate (MS-2,3,5,6-Me₄C₆H) in THF or hexane. The resultant red (1) and red-orange (2) crystalline compounds are immediately decomposed upon exposure to air or moisture. The ¹H NMR spectra of 1 and 2 show single sets of thiolate resonances at room temperature.

3.1. Structure of [Ti(S-2,3,5,6-Me₄C₆H)₄]

The X-ray crystal structure revealed [Ti(S-2,3,5,6-Me₄C₆H)₄] to be monomeric with a distorted tetrahedral TiS₄ core. The Ti-S bonds (2.292(6) Å) in 1 are considerably shorter than the Ti-S bonds in Ti(SCH₂CH₂S)₃²⁻ (2.428(10) Å) [9]; this is consistent with the difference in tetrahedral versus octahedral coordination. Other structurally characterized titanium thiolate complexes include Ti(diars)Cl₂(SC(CH₃)₃)₂ and Cp₂Ti(SPh)₂ and Cp₂Ti(SMe)₂ [17–19]. As seen in Fig. 1, the complex has an approximate mirror plane which bisects atoms S3 and S4 and the S1-Ti-S2 angle. The distortion in the TiS₄ core is consistent with this mirror S1-Ti-S3 (103.0(1°)|S2-Ti-S3 (104.0(1°) and S1-Ti-S4 (108.3(1°)|S2-Ti-S4 (108.0(1°). For each thiolate ligand, the plane of M-S-C group is approximately perpendicular to the plane of the aryl group. This metal-thiolate conformation is typical for aromatic thiolates with two *ortho*-substituents [20].

The most distinctive feature of the structure is the geometric arrangement of the thiolate ligands. To our knowledge, the Ti-S4-C41 angle of 86.5(5)° is the smallest reported value for a M-S-C angle of a terminal thiolate ligand. The aromatic rings of thiolate ligands

Table 4
Fractional atomic coordinates for [Ta(S-2,3,5,6-Me₄C₆H)₅]

Atom	x	y	z
Ta	0.02548(6)	0.19688(5)	0.22909(3)
S1	0.2422(3)	0.1964(3)	0.2463(2)
S2	-0.1723(3)	0.2505(3)	0.1762(2)
S3	0.0163(3)	0.2062(3)	0.3525(2)
S4	-0.0453(3)	0.0075(3)	0.1901(2)
S5	0.0800(3)	0.3555(3)	0.1591(2)
C11	0.347(1)	0.289(1)	0.2080(7)
C12	0.404(1)	0.389(1)	0.2485(7)
C13	0.495(1)	0.455(1)	0.2222(8)
C14	0.526(1)	0.422(1)	0.1568(8)
C15	0.468(1)	0.327(1)	0.1167(8)
C16	0.373(1)	0.259(1)	0.1408(7)
C17	0.368(1)	0.421(1)	0.3198(8)
C18	0.564(2)	0.565(1)	0.2626(10)
C19	0.508(1)	0.294(1)	0.0452(8)
C10	0.303(1)	0.153(1)	0.0960(8)
C21	-0.285(1)	0.155(1)	0.2046(7)
C22	-0.343(1)	0.061(1)	0.1595(8)
C23	-0.431(1)	-0.014(1)	0.1850(9)
C24	-0.463(1)	0.006(1)	0.2510(9)
C25	-0.414(1)	0.103(1)	0.2930(8)
C26	-0.322(1)	0.178(1)	0.2686(8)
C27	-0.313(1)	0.039(1)	0.0845(8)
C28	-0.491(2)	-0.124(1)	0.1373(11)
C29	-0.457(2)	0.125(1)	0.3651(8)
C20	-0.274(1)	0.288(1)	0.3161(8)
C31	0.161(1)	0.264(1)	0.4149(7)
C32	0.167(1)	0.381(1)	0.4354(7)
C33	0.276(1)	0.425(1)	0.4875(7)
C34	0.362(2)	0.355(1)	0.5189(8)
C35	0.343(2)	0.238(1)	0.4989(9)
C36	0.236(1)	0.191(1)	0.4469(7)
C37	0.071(2)	0.458(1)	0.4010(10)
C38	0.297(2)	0.551(1)	0.5113(10)
C39	0.442(2)	0.163(2)	0.5392(10)
C30	0.218(1)	0.064(1)	0.4279(8)
C41	0.027(1)	-0.083(1)	0.2594(8)
C42	-0.033(1)	-0.114(1)	0.3155(8)
C43	0.021(1)	-0.185(1)	0.3662(8)
C44	0.130(1)	-0.224(1)	0.3603(8)
C45	0.186(1)	-0.200(1)	0.3022(8)
C46	0.131(1)	-0.128(1)	0.2505(8)
C47	-0.155(2)	-0.074(2)	0.3221(10)
C48	-0.032(2)	-0.217(1)	0.4361(9)
C49	0.297(1)	-0.257(1)	0.2940(9)
C40	0.190(1)	-0.103(1)	0.1825(7)
C51	-0.035(1)	0.423(1)	0.1057(7)
C52	-0.072(1)	0.521(1)	0.1342(7)
C53	-0.158(1)	0.580(1)	0.0903(8)
C54	-0.213(1)	0.539(1)	0.0212(8)
C55	-0.183(1)	0.439(1)	-0.0075(8)
C56	-0.092(1)	0.380(1)	0.0341(8)
C57	-0.017(2)	0.563(1)	0.2149(8)
C58	-0.196(2)	0.691(1)	0.1180(9)
C59	-0.250(1)	0.396(1)	-0.0865(8)
C50	-0.062(2)	0.273(1)	0.0030(9)

Table 5
Selected bond distances (Å) and bond angles (°) for [Ta(S-2,3,5,6-Me₄C₆H)₅] (2)

Ta-S1	2.375(3)	S1-C11	1.776(11)
Ta-S2	2.391(3)	S2-C21	1.757(10)
Ta-S3	2.330(3)	S3-C31	1.838(10)
Ta-S4	2.349(3)	S4-C41	1.821(11)
Ta-S5	2.402(3)	S5-C51	1.736(12)
S1-Ta-S2	156.68(9)	S2-Ta-S4	90.15(9)
S1-Ta-S3	97.04(10)	S2-Ta-S5	78.25(9)
S1-Ta-S4	101.04(10)	S3-Ta-S4	105.1(1)
S1-Ta-S5	78.85(9)	S3-Ta-S5	125.3(1)
S2-Ta-S3	99.7(1)	S4-Ta-S5	129.4(1)
Ta-S1-C11	127.2(3)	Ta-S4-C41	108.1(3)
Ta-S2-C21	107.9(3)	Ta-S5-C51	119.9(4)
Ta-S3-C31	115.1(3)		

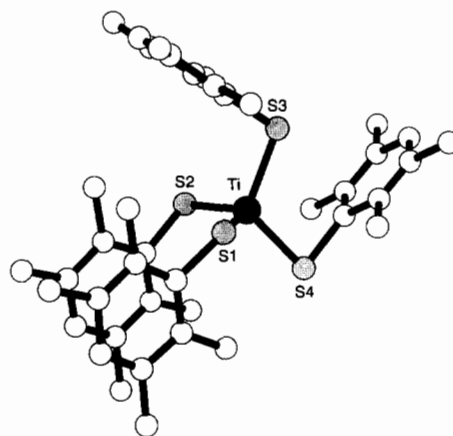


Fig. 1. Structural diagram of [Ti(S-2,3,5,6-Me₄C₆H)₄].

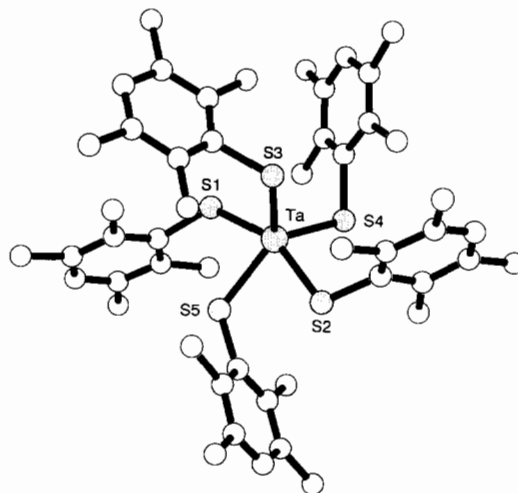


Fig. 2. Structural diagram of [Ta(S-2,3,5,6-Me₄C₆H)₅].

1 and **2** are nearly parallel. The distorted structure of **1** can be contrasted with the symmetric structure of [Fe(S-2,3,5,6-Me₄C₆H)₄]¹⁻ which has crystallographic

S₄ symmetry with all the Fe-S bonds equal to 2.283(2) Å and the Fe-S-C angles equal to 102.7(2)° [20]. The acute Ti-S4-C41 angle results in a short Ti-C41 distance of 2.82(1) Å. It is likely that electron deficient Ti atoms are interacting with the aromatic ring of this thiolate ligand. The folding of the dithiolene ligand in the X-

ray structure of $[(C_5H_5)_2Ti(S_2C_2H_2)]$ has been interpreted to indicate an interaction between the Ti and the C=C π orbital of the SCH=CHS ligand [21].

A survey of the structures of Ti(IV) L_4 complexes reveals a variety of structural and electronic methods used to counteract the severe electron deficiency of the metal center [22–24]. The conformation of the thiolate ligand in **1** is reminiscent of the structures of $M(CH_2Ph)_4$ ($M=Ti, Zr, Hf$) in which some of the $M-C_a-C_b$ angles were unexpectedly small (i.e. 92°) with a resultant short Ti– C_b distance of 2.61 Å and a postulated interaction between the metal center and the aromatic ring [22].

3.2. Structure of $[Ta(S-2,3,5,6-Me_4C_6H)_5]$

The X-ray structure revealed the compound to be a five-coordinate monomer (Fig. 2). The structure of the TaS_5 core is intermediate between the structures of a trigonal bipyramid and a square pyramid. Viewed as a trigonal bipyramid, S1 and S2 would be the axial ligands ($S1-Ta-S2=157^\circ$). Alternatively, S3 would be the axial ligand of a distorted square pyramidal structure. Although the steric effects of the thiolate ligands likely have major influence on the distortions, it is difficult to define the effects.

A number of other five-coordinate tantalum compounds have been described [25]. Relevant to this work is the electron diffraction study of $TaCl_5$ which has a trigonal bipyramidal structure in the gas phase [26]. The crystal structure of a tantalum(V) pentaphenolate revealed it to be a dimer with two bridging phenolates and four terminal phenolates on each metal $[Ta_2(O-p-tolyl)_{10}]$ [27]. In studies with many different metals, we and others have found that 2,6-disubstituted benzenethiolate and phenolate ligands tend to form monomeric compounds in cases where less sterically encumbered ligands form dimers and clusters [20,28,29].

The average Ta–S bond distance of 2.37(3) Å in **2** can be compared with the distance in the dithiolene complex, $[Ta(S_2C_6H_4)_3]^{1-}$ (2.43(1) Å), in the 1,2-ethanedithiolate complex, $[Nb(edt)_3]^{1-}$ (2.434(7) Å) and in $[Ta(SPh)_6]^{1-}$ (2.445(9) Å) [10,11,30]. The difference results from the lower coordination of **2**. The Ta–S–C angles in **2** range from 107.9(3) to 127.2(3)° with an average angle of 116(7)°. There is no apparent correlation between the size of the Ta–S–C angles and the length of the Ta–S bonds. The Ta–S–C angles in **2** are much smaller than the terminal Ta–O–C angles (153.5°) in $[Ta_2(O-p-tolyl)_{10}]$ [19]. In this and other Ta(V) phenolate compounds, the short Ta–O bonds and the increased Ta–O–C angles have been ascribed to substantial Ta–O multiple bonding character [31]. There is no indication of any interaction between the Ta and the π system of the aromatic thiolate ligands as was observed in **1** or between the metal and the

C–H bonds of the *ortho* methyl groups as was observed in $[Ru(S-2,4,6-i-Pr_3C_6H_2)_4]$ [32]. The low symmetry of **2** again makes it difficult to rationalize the range of Ta–S–C angles in terms of the conformation of the thiolate ligands.

3.3. Metal–sulfur bonding in high valent early transition metal thiolates

$[Ti(S-2,3,5,6-Me_4C_6H)_4]$ (**1**) and $[Ta(S-2,3,5,6-Me_4C_6H)_5]$ (**2**) are formally severely electron deficient compounds with electron counts of 8 and 10, respectively. π Donation by the thiolate sulfur to the metal is an obvious means of alleviating this situation. Such π donation is a characteristic feature of alkoxide and phenolate complexes of high valent early transition metals. In this large class of compounds, shortened M–O bonds and increased M–O–C angles are observed [33–35].

The structures of **1** and **2** reported here, provide an opportunity to evaluate the occurrence of similar π donation in early transition metal thiolate compounds. A comparison of the structure of **1** with $[Ti(O-2,3,5,6-Me_4C_6H)_4]$ (**3**) and related $[Ti^{IV}(OAr)_4]$ complexes shows some interesting differences in the coordination of a thiolate versus a phenolate ligand to the Ti(IV) center [24]. The structure of **3** is characterized by very short Ti–O bond distances (1.77(2) Å) and large Ti–O–C angles (156°); both structural features are consistent with substantial π -donation from the oxygens to the metal [24]. The difference in the Ti–S and Ti–O distances in **1** and **3** is 0.52 Å (Table 6). This value is substantially greater than the 0.44 Å difference in the crystal radii of O^{2-} and S^{2-} [45]. It is also greater than the 0.44 Å difference in the Fe–S and Fe–O distances in $[Fe^{III}(S-2,3,5,6-Me_4C_6H)_4]^{1-}$ and $[Fe^{III}(O-2,3,5,6-Me_4C_6H)_4]^{1-}$ [20,37]; the 0.42 Å difference in the Mo–S and W–O distances in $[Mo^{IV}(S-2,4,6-Me_3C_6H_2)_4]$ and $[W^{IV}(O-2,6-Me_2C_6H_3)_4]$ [40,41]; and, the 0.44 Å difference in the Ga–S and Ga–O distances in the $[Ga^{III}(E-2,3,5,6-Me_4C_6H)_4]^{1-}$ pair [38,39].

Although there is no structurally characterized example of a monomeric $Ta(OR)_5$ compound, the numerous $Ta(OAr)_xL_{(5-x)}$ complexes and the monomeric $Nb(O-2,6-Me_2C_6H_3)_5$ compound provide a value of 1.90 Å for the Ta–O bond distance [31,46]. The difference between the Ta–S distance in **2** and this Ta–O distance is 0.47 Å.

Large differences between the M–S and M–O bond distances appear to be characteristic of Group 4b compounds in the M(IV) oxidation state. Howard and Parkin have recently analyzed the trends in metal–chalcogenide bond distances in two structurally characterized series of compounds: $(\eta^5-C_5Me_4Et)_2-Zr(E)(py)$ and $(\eta^5-C_5Me_5)_2Zr(EH)(\eta^1-OC(Ph)=CH_2)$; in both of the Zr(IV) series of compounds, the

Table 6
Metrical parameter in $[M^{III,IV}(SR)_4]$ and $[M^{III,IV}(OAr)_4]$ compounds

Compound	Ref	M–E (Å)	M–E–C (°)	$\Delta[(M-S)-(M-O)]$
$[Ti^{IV}(S-2,3,5,6-Me_4C_6H)_4]$		2.292(6)	103(15)	} 0.52
$[Ti^{IV}(O-2,3,5,6-Me_4C_6H)_4]$	[24]	1.77(2)	158(10)	
$[Ti^{III}(S-2,4,6-i-Pr_2C_6H_2)_4]^{1-}$	[36]	2.360(3)	112(2)	} 0.45
$[Ti^{III}(O-2,6-i-Pr_2C_6H_2)_4]^{1-}$	[24]	1.91(5)	145(7)	
$[Fe^{III}(S-2,3,5,6-Me_4C_6H)_4]^{1-}$	[20]	2.283(2)	102.7(2)	} 0.44
$[Fe^{III}(O-2,3,5,6-Me_4C_6H)_4]^{1-}$	[37]	1.847(13)	137(4)	
$[Ga^{III}(SPh)_4]^{1-}$	[38]	2.257(1)	104(5)	} 0.44
$[Ga^{III}(O-2,6-Me_2C_6H_3)_4]^{1-}$	[39]	1.820(3)	128.1(3)	
$[Mo^{IV}(S-2,4,6-i-Pr_3C_6H_2)_4]$	[40]	2.262(1)	107.6(2)	} 0.42
$[W^{IV}(O-2,6-Me_2C_6H_3)_4]$	[41]	1.843(4)	160.7(4)	
$[Mo^{IV}(S-t-Bu)_4]$	[42]	2.235(3)	118.8(6)	
$[W^{IV}(S-t-Bu)_4]$	[43]	2.236(4)	119.5(6)	
$[V^{IV}(S-t-Bu)_4]$	[44]	2.218(2)	116.3(2)	
$[V^{III}(S-t-Bu)_4]^{1-}$	[44]	2.297(14)	116.6(31)	
$[Ru^{IV}(S-2,4,6-i-Pr_3C_6H_2)_4]$	[32]	2.23(6)	114(2)	

$\Delta[(Zr-S)-(Zr-O)]$ is 0.51 Å [12]. Additional examples of a large $\Delta[(M-S)-(M-O)]$ (0.50 Å) are provided by $(\eta^5-C_5H_5)_2Ti(SPh)_2$ (Ti–S 2.41 Å) and $(\eta^5-C_5H_5)_2Ti(OPh)_2$ (Ti–O 1.91 Å) [18,47].

In an attempt to qualify the decrease in the M–O and M–S distances due to π -bonding, M–O and M–S single bond distances can be estimated based on structural data for M–alkyl compounds [48]. Using the Ti–C distance in $Ti(CH_2Ph)_4$ (2.13 Å) [22] and the covalent radius of an sp^3 carbon (0.77 Å), an estimated covalent radius of Ti (1.36 Å) can be obtained. Using the single bond radii of O (0.66 Å) and S (1.04 Å), the Ti–S and Ti–O single bond distances of 2.40 and 2.02 Å are calculated. A comparison with the experimental values indicates a 0.11 Å decrease in the Ti–S bond distance in 1 and a 0.24 Å decrease in the observed Ti–O distance in 3. There is no structural characterized $Ta(CH_2R)_5$ compound, so the Ta–C distance of 2.23 Å in $[Li(N,N'-dimethylpiperazine)][Ta(CH_2C(CH_3)_3)_3(CC(CH_3)_3)]$ was chosen [49]. From this value and the C_{sp^3} covalent radius, a value of 1.46 Å is obtained for the covalent radius of Ta. Ta–O and Ta–S single bond distances are estimated to be 2.12 and 2.50 Å, respectively. The experimentally observed values indicate a 0.22 Å shortening of the Ta–O bonds and a 0.13 Å shortening of the Ta–S bonds in 2. These data suggest that there is significantly more π -bonding character in M–O bonds relative to M–S bonds for the high valent Groups 4 and 5 transition metals. It is the difference in this bonding that is responsible for the ~ 0.1 Å increase in $\Delta[(M-S)-(M-O)]$ found for these metals. Howard and Parkin have chosen to explain the abnormally short Zr–O distances as a function of the greater ionic character of the Zr–O versus Zr–S bonding in $(\eta^5-C_5Me_4Et)_2Zr(E)(py)$ and $(\eta^5-C_5Me_5)_2Zr(EH)-$

$(\eta^1-OC(Ph)=CH_2)$ rather than a difference in capacity of π -donation by O versus S [12]. Their analysis is based on the classic Shomaker–Stevenson equation which predicts a decrease in bond lengths when there is a large electronegativity difference between the component atoms. Several theoretical studies have recently addressed the equation of early transition metal–chalcogenide bonding [50,51]. It is obviously not straightforward to separate σ and π contributions or ionic and covalent contributions to metal–ligand bonding.

Based on the observation for high valent metal phenolate complexes, it might have been predicted that the M–S–C angles in 1 and 2 would be among the largest ever observed. Instead we have the situation where one of the Ti–S–C angle in 1 is the shortest angle ever observed for a monodentate thiolate. There is no major increase in the M–S–C angle for a thiolate bound to a high valent early transition metal. However, previous work has indicated that the value of the M–S–C angle in metal thiolate complexes is not a good indicator of the extent of M–S π -bonding [48,52–54]. Even in cases where thiolate to metal π -bonding has been indicated by shortened M–S distances and by conformational orientations, there was no large increase in the M–S–C angle. Although large M–O–Aryl angles are characteristic of high valent phenolate complexes, it has been noted that there is often not a direct correlation between the M–O–C angle and the M–O distance [31]. Any comparison of sulfur and oxygen angles must be prefaced by the observation that angles at sulfur are generally smaller than angles at oxygen (e.g. compare H_2S 92.2° versus H_2O 104.5°). The $3p-\pi$ non-bonding orbital of the thiolate sulfur can engage in $p\pi-d\pi$ bonding without increasing the M–S–C angle. In the limit of an M–S–C

angle of 180°, the sulfur could use two p orbitals for metal ligand π -bonding. The situation would necessitate a rehybridization of the sulfur orbitals with an increase in the s character of the σ bonding orbitals. The rehybridization of sulfur is more costly than for oxygen. An analogous situation exists for silicon compounds: the Si–S–Si angles in thiosilicates are in the narrow range (106–115°) while Si–O–Si angles in analogous silicates are observed in the range 120–180° [55]. The observation of the acute Ti–S–C angles suggests that the limited thiolate metal π bonding in **1** cannot compensate for the strong electron deficiency of the Ti(IV) center.

How does M–S bonding in **1** and **2** compare with that in $[M(SR)_x]$ compounds in neighboring groups in the Periodic Table and with different electron configuration (Table 6)? The structure of $[Ti^{III}(S-2,4,6-i-Pr_3C_6H_2)_4]^-$ (Ti–S 2.36 Å) indicates a 0.07 Å increase in the Ti–S bond distance upon reduction of Ti(IV) to Ti(III) [36]. The related difference in the Ti–O distances for $[Ti^{IV,III}(OAr)_4]$ species is 0.13 Å [24]. The Ti–S distance in **1** is substantially longer than the V–S bond (2.218(2)) in $[V^{IV}(S-t-bu)_4]$ [44] and the M–S bonds in the second and third row transition metal compounds $[M^{IV}(S-t-Bu)_4]$ with Mo–S (2.235(3) Å) [42] and $[M^{IV}(S-2,4,6-i-Pr_3C_6H_2)_4]$ Mo–S (2.262(1) Å) [40], Ru–S (2.23(6) Å) [32]. Only part of the cited differences results from the periodic contraction in atomic radius as one moves across a row in the Periodic Table. Shannon has extensively analyzed the differences in M–S and M–O distances using data compiled from both solid-state and molecular compounds [56]. M–S distances that are predicted using the crystal radii of transition metals which are based on metal–oxides data are frequently larger than the experimental values. This discrepancy increases as one moves across the transition series. Shannon's data and the data from the incomplete series of $M^{IV}(XR)_4$ compounds (Table 6) suggest that the periodic trends in M–O and M–S bonding are opposite, with M–O bonding maximizing the early transition metals and M–S bonding increasing as one moves from the early transition metals toward the center in the Periodic Table. For example, we have found evidence for significant metal thiolate π -bonding character in the chemistry of Ru and Os $M^{IV}(SR)_4L$ compounds [53,57].

The structural chemistry described in this paper is reflected in the reactivity of the compounds. The oxophilic nature of the early transition metals is well established. The following ligand exchange reaction provides a chemical measure of M–S versus M–O bonding: $[M(OAr)_4] + 4RSH = [M(SR)_4] + 4HOAr$. This reaction which readily proceeds for Fe(III) does not take place for Ti(IV) or W(IV) [41,58]. The π -donation which is prominent in the bonding of alkoxide and phenolate ligands to high valent early transition

metals is not as important in related thiolate complexes. This situation may be a mixed blessing; although the early transition metal thiolate bonding will be weaker, the metal centers will remain electron deficient and therefore are apt to possess increased reactivity properties.

4. Supplementary material

Tables of atomic coordinates and bond distances and angles are available on request from the authors. The structural information has been deposited with the Cambridge Structural Database.

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