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Synthesis and Characterization of the Bulky Thiolate Complexes $[Li(OEt_2)_3][Ti\{S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2\}_4]$ and $[Li(THF)_3(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)]$. Comparisons of M–SR and M–OR Bonding

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The syntheses and X-ray crystal structural characterizations of the homoleptic titanium(III) thiolate complex $[Li(Et_2O)_3][Ti(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$ (**1**) and the mononuclear lithium thiolate $[Li(THF)_3(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)]$ (**2**) are reported. The complexes are the first well-characterized homoleptic titanium thiolate and a monomeric lithium thiolate. The titanium complex has distorted-tetrahedral coordination at the metal, and the thiolate ligands are oriented to minimize steric interference of the bulky substituents. The Ti–S distances average 2.36 Å, and the STiS angles range from 101.8 (1) to 116.1 (1)°. The discrete cation in **1** is the previously unreported $[Li(Et_2O)_3]^+$ species. This has three ethers oriented in an approximate trigonal-planar fashion around lithium. The O–Li–O angles range from 115.4 to 128.2°, and the Li–O distances average close to 1.9 Å. Compound **2** is notable because it is monomeric in contrast to its alkoxide analogues, which are dimeric. The Li^+ ion in **2** has a distorted-tetrahedral geometry with an average Li–S distance of 2.454 (11) Å and average LiSC angle of 103.8 (3)°. Crystallographic data with Mo Kα (λ = 0.71069 Å) at 130 K: **1**, $TiS_4O_3C_{66}LiH_{107}$, M_r = 1129.9, orthorhombic $C222_1$, Z = 4, a = 17.104 (5) Å, b = 20.960 (10) Å, c = 20.788 (13) Å; **2**, $SO_3C_{30}LiH_{53}$, M_r = 500.7, triclinic $P\bar{1}$, Z = 4, a = 10.820 (2) Å, b = 17.841 (4) Å, c = 17.814 (4) Å, α = 62.25 (2)°, β = 89.77 (2)°, γ = 87.86 (2)°. For **1**, R = 0.053, and for **2**, R = 0.083.

Introduction

Thiolate ligands (^-SR) are a fundamental ligand type, and their metal complexes have attracted considerable interest because of their diverse nature and biological relevance.[1] Recently, sterically demanding thiolate ligands have been attracting increasing attention due to their ability to reduce the degree of aggregation in metal thiolates, giving a lower coordination number at the metal. For example, the complexes $[M(S\text{-}2,4,6\text{-}R_3C_6H_2)_2]$ (R = *i*-Pr, *t*-Bu; M = Ge, Sn, Pb) isolated by Lappert and co-workers have low degrees of aggregation and coordination numbers as low as 2 for the metal.[2] It was also demonstrated by the Koch, Millar, and co-workers that both the $^-S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2$ (TIPT = 2,4,6-triisopropylbenzenethiolate) and $^-S\text{-}2,3,5,6\text{-}Me_4C_6H$ (TMPT = 2,3,5,6-tetramethylbenzenethiolate) ligands were effective (among other factors) in preventing the auto redox reaction, $[M(SR)_4]^- + RS^- \rightarrow [M(SR)_4]^{2-} + {}^1/_2RSSR$, in certain transition metals.[3-5] This allowed the isolation of the stable Fe(III) ions $[Fe(TMPT)_4]^-$ and $[Fe(TIPT)_4]^-$ and the interesting, nearly square-planar, Co(III) ion in $[Co(TIPT)_4]^{-3}$. At the same time Dilworth and Zubieta used the TIPT ligand to obtain the molybdenum thiolates $Mo_2(TIPT)_6$ and $[Mo(CO)_2(TIPT)_3]^-$.[4] Other derivatives of TMPT and TIPT that have recently appeared in the literature are the ruthenium and osmium complexes $[M(TMPT)_4CH_3CN]$ and $[M(TIPT)_4CH_3CN]$[5], the complex $Mo(TIPT)_4$, which is of particular relevance,[6] and some gallium complexes.[7]

For the earlier transition metals however, thiolate complexes are much less studied. For example, there are no structures known for homoleptic thiolate complexes of either titanium or vanadium. For titanium the relatively few thiolate derivatives involve Ti(IV) species such as $Ti(SPh)_4$,[8] $Ti(\eta^5\text{-}C_5H_5)Cl_2SR$,[9] $Ti(\eta^5\text{-}C_5H_5)_2(SR)_2$,[10] and $[Ti(diars)Cl_2(S\text{-}t\text{-}Bu)_2]$.[11] With the exception of the last complex, which has been structurally characterized, it is thought that these are mostly associated through thiolate bridging in solution.

For alkali-metal thiolate derivatives the number of well-characterized derivatives is extremely small compared to those of alkylamide, alkoxide, or phosphide ligands. For lithium derivatives the structures of the complexes $[Li_2(THF)_4\{SCH(SiMe_3)_2\}_2]$ and $[Li_2(THF)_{3.5}\{SC(SiMe_3)_3\}_2]$ have been determined in this laboratory,[12] and a powder diffraction study of LiSMe[13] has been reported.

In this paper, as part of our continuing studies of sterically demanding amide, phosphide, alkoxide, and thiolate ligands, we report the first structure of a homoleptic titanium thiolate $[Li(Et_2O)_3][Ti(TIPT)_4]$ and a rare example of a monomeric lithium salt, the species $[Li(THF)_3(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)]$.

Experimental Section

General Procedures. All reactions were performed by using either modified Schlenk techniques (under N_2) or a Vacuum Atmospheres HE43-2 drybox (under Argon). Solvents were freshly distilled from drying agents and degassed immediately before use. Anhydrous $TiCl_3$ was purchased from Aldrich; $HSC_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6$ (TIPTH) and $HSC_6H_2\text{-}t\text{-}Bu_3\text{-}2,4,6$ (TBPTH) were synthesized by literature procedures.[14] All compounds gave satisfactory C and H elemental analyses. ESR spectra were recorded on a Bruker ER 200 D ESR using X-band microwave radiation (ν = 9.48 GHz) at liquid-helium temperatures.

$[Li(Et_2O)_3][Ti\{S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2\}_4]$ (1). A solution of (TIPT)Li from the addition of *n*-BuLi (3.3 mL of a 1.6 M solution) to TIPTH (1.24 g, 5.2 mmol) in ether (25 mL) was added dropwise to a suspension of $TiCl_3$ (0.21 g, 1.3 mmol) in ether (20 mL) at 0 °C. Overnight stirring gave a reddish orange solution and gray precipitate. The solution was filtered and the solvent removed under reduced pressure to yield a red solid. Addition of *n*-hexane (25 mL) at 10 °C gave an orange precipitate and red solution. The red filtrate was removed via a double-tipped needle and the orange precipitate redissolved in ether (20 mL) to give a reddish orange solution. Slow cooling to −20 °C afforded pale yellow crystals suitable for X-ray diffraction studies: yield 0.34 g, 23%; mp 280 °C dec; UV-vis (Et_2O) 458 and 300 nm.

$[Li(THF)_3S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2]$ (2). $2,4,6\text{-}t\text{-}Bu_3C_6H_2SH$ (1.0 g, 3.6 mmol) in THF (30 mL) was quantitatively converted into the lithium salt by the dropwise addition of an *n*-hexane solution of *n*-BuLi (2.2 mL, 1.6 M) at 0 °C. The stirred solution was warmed slowly to 25 °C and the

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Table I. Crystal Data and Summary of Data Collection and Refinement

	1	**2**
formula	$LiTiS_4O_3C_{72}H_{122}$	$C_{30}H_{53}O_3SLi$
fw	1218.87	500.7
cryst syst	orthorhombic	triclinic
space group	$C222_1$ (No. 20)	$P\bar{1}$
conditions	hkl, $h + k = 2n$; $00l, = 2n$	none
cryst dimens, mm	0.125 × 0.275 × 0.50	0.25 × 0.40 × 1.10
cryst color and habit	pale yellow parallelepipeds	colorless plates
a, Å	17.104 (5)	10.820 (2)
b, Å	20.960 (10)	17.841 (4)
c, Å	20.788 (13)	17.914 (4)
α, deg		62.25 (2)
β, deg		89.77 (2)
γ, deg		87.86 (2)
Z	4	4
V, Å^3	7452 (6)	3058 (3)
d_{calcd}(130 K), g/cm^3	1.09	1.09
linear abs coeff, cm^{-1}	2.14	1.25
temp, K	130	130
scan speed, deg min^{-1}	9	60
scan width, deg	1	1.1
type of scan	ω	ω
ω offset for bckgds, deg	1	1
2θ range, deg	0–50	0–50
range of trmn fctrs	0.90–0.98	0.88–0.97
octants	$+h,+k,+l$	$+h,\pm k,\pm l$
variables	199	653
data/variable	16	9.2
no. of unique data	3610	7165
no. of data used in rfmt	3177 ($I > 2\sigma(I)$)	6038 ($I > 3\sigma(I)$)
$R(F)$	0.053	0.084
$R_w(F)$	0.057	0.091
w	$[\sigma^2(F)]^{-1}$	$[\sigma^2(F) + 0.0076F^2]^{-1}$
largest Δ/σ	0.071 for rotation of H around C(14)	−0.149 for rotation of H around C(8)

volume reduced 10 mL under reduced pressure. Addition of n-hexane (3 mL) followed by filtration through celite gave a yellow solution. Slow cooling to −20 °C gave colorless crystals of **2** suitable for X-ray analysis: yield 1.21 g, 61%; mp 208–211 °C.

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex P2$_1$ diffractometer equipped with a locally modified low-temperature device using Mo Kα radiation (λ = 0.71069 Å, graphite monochromator). Calculations were carried out on a Data General Eclipse computer using the SHELXTL package, version 4. The atomic form factors including anomalous scattering were from ref 15. Colorless crystals of $[Li(OEt_2)_3][Ti(TIPT)_4]$ were obtained by cooling a OEt_2/hexane solution to −20 °C. These were protected by hydrocarbon oil from air and moisture contamination. Crystals exposed to atmosphere for any length of time became reddish. A single crystal coated in oil was mounted on a glass fiber and quickly placed in the N_2 cold stream of the diffractometer. Lattice constants were determined by a least-squares fit of 22 centered reflections with 18° < 2θ < 29°. The data were corrected for Lorentz, polarization, and absorption effects.[15] The structure was solved by direct methods. The Ti, Li, and O(2) atoms were found to occupy 2-fold symmetry positions of the space group $C222_1$. Final refinement was carried out with isotropic thermal parameters for all atoms. Hydrogen atoms were included at positions calculated by using a riding model and given thermal parameters 1.2 times those of the corresponding carbons. Further details of data collection and refinement are in Table I.

Crystals of $[Li(THF)_3(S\text{-}2,4,6\text{-}t\text{-}Bu_3\text{-}C_6H_2)]$ were handled in a fashion identical with the treatment of **1**. Two of the six THF molelcules within the asymmetric unit were found to be disordered. The disordered atoms were modeled on the basis of Fourier peak heights and their site occupancies varied to allow for the best fit possible. They are labeled C(N) and D(N), and their occupancies vary as K and $1 - K$. Further details are given in Table II. In the final cycles of refinement all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated positions as before. Further details of data collection and refinement are in Table I. Atom coordinates for **1** and **2** are given in Table II.

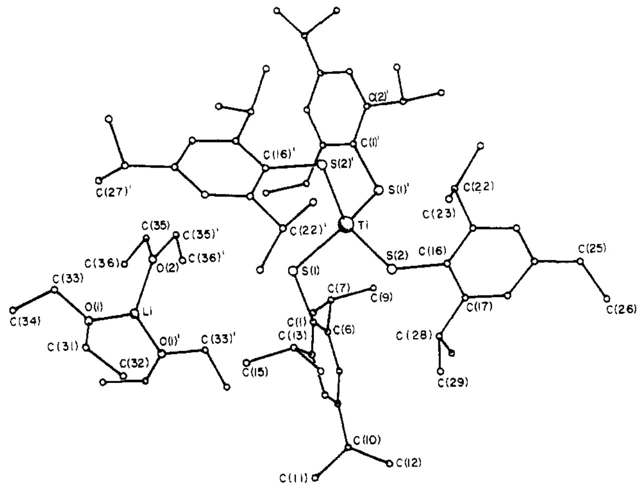

Figure 1. Computer-generated drawing of $[Li(OEt_2)_3][Ti(TIPT)_4]$ (**1**) with hydrogens omitted for clarity.

Results and Discussion

The X-ray structure of $[Li(OEt_2)_3][Ti(TIPT)_4]$ (**1**) is the first to be reported for a four-coordinate Ti(III) thiolate complex. The crystallization of **1** as discrete cations and anions is in contrast to many bulky alkoxide and amido complexes where the alkali-metal ion is almost always an integral part of the metal complex. Recent examples of these are $[Li\{CoN(SiMe_3)_2(OC\text{-}t\text{-}Bu_3)_2\}]$[16] and $[Na(THF)_2Ti\{O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3\}_4]$ (**3**).[17] This feature is also somewhat odd in light of the well-documented propensity of SR ligands for bridging.[1]

The structure of **1** is illustrated in Figure 1. Relevant bond lengths and bond angles are given in Table III. The d^1 titanium atom is surrounded by a somewhat flattened tetrahedral array of four thiolate groups very similar to that seen in $Mo(TIPT)_4$.[6] The ion also possesses a crystallographically imposed 2-fold axis of symmetry. The two S(1)TiS(1)′ or S(2)TiS(2)′ planes however are not quite mutually perpendicular (dihedral angle, 98.4°) although the TiS_4 unit is indeed close to having D_{2d} symmetry. These distortions are presumed to be due to either crystal packing forces or a nondegenerate ground state. There do not appear to be any significant (<4.0 Å) interactions between the sulfurs and hydrogen on adjacent ligands that might explain the deviation from tetrahedral values.[18] Distortions have also been reported for the $M(SPh)_4^{2-}$ series (M = Cd, Zn, Ni, Co, Mn).[19]

It is also of interest to compare the Ti–O–C and Ti–S–C angles in the structure of the closely related alkoxide and thiolate complexes, **3** and **1**. In the case of **3** the Ti–O–C angles in the terminal alkoxide ligands are ca. 150° whereas in **1** they are much more acute at 110.6 and 113.8°. The wide angles seen in **3** and many other transition-metal alkoxides are thought to be due to oxygen–metal p–d π overlap. It could also be argued that the wide angles are due to the large steric requirement of the alkoxide ligands. However, large MOC angles are seen even with smaller alkoxides.[20] Similarly, only small variations in MSC angles are seen whether the organic substituent on the thiol is small or large. Clearly then, although some steric relief and lowering of the angles is expected through replacement of oxygen by sulfur, the difference

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a]

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
Complex **1**									
Ti	0	1592 (1)	2500	17 (1)	C(16)	249 (3)	2265 (2)	975 (2)	19 (1)
S(1)	1026 (1)	996 (1)	2966 (1)	21 (1)	C(17)	639 (3)	1945 (2)	468 (2)	21 (1)
S(2)	683 (1)	2240 (1)	1762 (1)	22 (1)	C(18)	348 (3)	1998 (2)	−155 (2)	21 (1)
O(1)	3066 (2)	500 (2)	5661 (2)	39 (1)	C(19)	−322 (3)	2363 (2)	−299 (2)	20 (1)
O(2)	1480 (3)	0	5000	32 (1)	C(20)	−689 (3)	2662 (2)	211 (2)	20 (1)
Li	2587 (8)	0	5000	36 (3)	C(21)	−427 (3)	2620 (2)	848 (2)	20 (1)
C(1)	1768 (3)	817 (2)	2375 (2)	19 (1)	C(22)	−863 (3)	2974 (2)	1379 (2)	24 (1)
C(2)	2431 (3)	1220 (2)	2325 (2)	20 (1)	C(23)	−437 (3)	3587 (3)	1577 (3)	35 (1)
C(3)	3031 (3)	1048 (2)	1910 (2)	21 (1)	C(24)	−1715 (3)	3124 (3)	1223 (3)	31 (1)
C(4)	3018 (3)	481 (2)	1551 (2)	22 (1)	C(25)	−612 (3)	2408 (2)	−986 (2)	23 (1)
C(5)	2353 (3)	105 (2)	1595 (2)	23 (1)	C(26)	−24 (4)	2722 (3)	−1427 (3)	36 (1)
C(6)	1732 (3)	256 (2)	2002 (2)	22 (1)	C(27)	−850 (3)	1756 (3)	−1253 (3)	37 (1)
C(7)	1023 (3)	−182 (2)	2017 (2)	26 (1)	C(28)	1391 (3)	1570 (2)	578 (2)	23 (1)
C(8)	1242 (4)	−890 (3)	2098 (3)	46 (2)	C(29)	2089 (3)	2007 (3)	532 (3)	32 (1)
C(9)	529 (3)	−93 (3)	1407 (3)	29 (1)	C(30)	1482 (3)	989 (3)	135 (3)	33 (1)
C(10)	3718 (3)	285 (3)	1141 (2)	25 (1)	C(31)	3613 (5)	1010 (4)	5601 (4)	62 (2)
C(11)	4473 (3)	293 (3)	1526 (3)	31 (1)	C(32)	3887 (5)	1110 (4)	4941 (4)	70 (2)
C(12)	3812 (3)	709 (3)	540 (3)	30 (1)	C(33)	2732 (4)	454 (3)	6308 (3)	43 (1)
C(13)	2523 (3)	1816 (2)	2734 (2)	23 (1)	C(34)	3309 (4)	251 (3)	6804 (3)	52 (2)
C(14)	2861 (3)	2384 (3)	2365 (3)	35 (1)	C(35)	1010 (4)	546 (3)	4825 (3)	44 (1)
C(15)	3033 (4)	1653 (3)	3316 (3)	44 (1)	C(36)	1543 (4)	1083 (3)	4649 (3)	50 (2)
Complex **2**									
S(1)	6279 (1)	8471 (1)	1667 (1)	26 (1)*	C(26)	6141 (6)	9662 (4)	−1480 (4)	39 (2)*
S(2)	2323 (1)	1464 (1)	3470 (1)	27 (1)*	C(27)	3513 (6)	9299 (4)	−119 (4)	43 (3)*
O(1)	6559 (4)	7336 (3)	352 (3)	45 (2)*	C(28)	2323 (14)	9242 (9)	−596 (13)	48 (5)
O(2)	4297 (3)	8608 (2)	−93 (2)	32 (2)*	D(28)[b]	2211 (14)	9217 (9)	−313 (13)	60 (5)
O(3)	6812 (4)	9257 (2)	−678 (2)	35 (2)*	C(29)	2236 (9)	8329 (6)	−300 (7)	87 (3)
O(4)	2166 (3)	2574 (2)	4772 (2)	32 (2)*	C(30)	3578 (6)	8067 (4)	−290 (4)	45 (3)*
O(5)	2662 (3)	521 (2)	5664 (2)	30 (2)*	C(31)	2209 (5)	2544 (3)	2675 (3)	22 (2)*
O(6)	148 (3)	1319 (2)	5339 (2)	31 (2)*	C(32)	1042 (5)	2920 (3)	2263 (3)	24 (2)*
Li(1)	6029 (9)	8397 (6)	345 (6)	31 (4)*	C(33)	933 (5)	3803 (3)	1787 (3)	26 (2)*
Li(2)	1788 (8)	1513 (6)	4783 (6)	31 (4)*	C(34)	1896 (5)	4331 (3)	1660 (3)	23 (2)*
C(1)	6688 (4)	7399 (3)	2412 (3)	23 (2)*	C(35)	3031 (5)	3940 (3)	1987 (3)	25 (2)*
C(2)	7958 (4)	7108 (3)	2582 (3)	23 (2)*	C(36)	3245 (5)	3078 (3)	2456 (3)	26 (2)*
C(3)	8240 (5)	6241 (3)	3019 (3)	28 (2)*	C(37)	4599 (5)	2731 (3)	2727 (3)	28 (2)*
C(4)	7346 (5)	5644 (3)	3339 (3)	25 (2)*	C(38)	5543 (5)	3438 (4)	2279 (4)	41 (3)*
C(5)	6126 (5)	5941 (3)	3267 (3)	25 (2)*	C(39)	4843 (5)	2377 (4)	3678 (4)	39 (3)*
C(6)	5777 (4)	6802 (3)	2830 (3)	23 (2)*	C(40)	4927 (5)	2051 (4)	2432 (4)	40 (3)*
C(7)	4374 (5)	7037 (3)	2845 (3)	27 (2)*	C(41)	1748 (5)	5300 (3)	1176 (4)	31 (2)*
C(8)	4219 (5)	7700 (4)	3170 (4)	35 (2)*	C(42)	2109 (7)	5677 (4)	1759 (4)	52 (3)*
C(9)	3625 (5)	6272 (4)	3435 (4)	36 (2)*	C(43)	2616 (6)	5649 (4)	406 (4)	41 (2)*
C(10)	3771 (5)	7376 (4)	1966 (3)	31 (2)*	C(44)	420 (5)	5608 (4)	857 (4)	38 (2)*
C(11)	9064 (5)	7704 (4)	2303 (4)	31 (2)*	C(45)	−115 (5)	2404 (3)	2305 (3)	25 (2)*
C(12)	9236 (6)	8109 (4)	1339 (4)	46 (3)*	C(46)	−694 (5)	2031 (4)	3185 (3)	33 (2)*
C(13)	8890 (5)	8397 (4)	2582 (4)	40 (3)*	C(47)	231 (5)	1695 (4)	2072 (4)	32 (2)*
C(14)	10291 (5)	7227 (4)	2715 (5)	47 (3)*	C(48)	−1127 (5)	2972 (4)	1671 (4)	38 (2)*
C(16)	8424 (6)	4474 (4)	3164 (4)	42 (3)*	C(49)	3038 (7)	2684 (4)	5306 (4)	46 (3)*
C(15)	7733 (5)	4699 (3)	3783 (3)	31 (2)*	C(50)	3103 (8)	3600 (4)	5023 (4)	57 (3)*
C(17)	8563 (6)	4504 (4)	4552 (4)	38 (2)*	C(51)	2534 (9)	4023 (4)	4169 (5)	80 (4)*
C(18)	6607 (6)	4134 (3)	4108 (4)	40 (2)*	C(52)	1708 (5)	3397 (4)	4134 (4)	35 (2)*
C(19)	7126 (9)	7258 (4)	−317 (4)	64 (3)*	C(53)	3832 (5)	184 (4)	5575 (4)	34 (2)*
C(20)	7195 (13)	6395 (8)	−170 (8)	43 (4)	C(54)	4697 (5)	341 (4)	6147 (4)	41 (3)*
D(20)[b]	6494 (19)	6415 (8)	−210 (9)	45 (5)	C(55)	3859 (6)	223 (4)	6881 (4)	44 (3)*
C(21)	6705 (9)	5884 (4)	771 (5)	71 (4)*	C(56)	2571 (5)	254 (4)	6556 (3)	37 (2)*
C(22)	6261 (12)	6485 (7)	1028 (7)	33 (3)	C(57)	−489 (6)	532 (4)	5725 (5)	52 (3)*
D(22)[b]	6895 (14)	6493 (8)	1125 (8)	44 (4)	C(58)	−1780 (6)	748 (4)	5460 (4)	51 (3)*
C(23)	8094 (5)	9423 (4)	−805 (4)	39 (3)*	C(59)	−1994 (7)	1607 (5)	5389 (7)	82 (5)*
C(24)	8191 (7)	10107 (4)	−1733 (4)	49 (3)*	C(60)	−716 (5)	1962 (4)	5285 (4)	35 (2)*
C(25)	7108 (6)	9931 (4)	−2152 (4)	41 (3)*					

[a] Asterisks indicate equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Certain carbons of the THF molecule are disordered. The atoms labeled "D" are the disordered counterparts to those carbons atoms. Refinement was carried out with variable thermal parameters and occupancies. These are listed as follows for the C's (D's are 1 − *K*): C(20), *K* = 0.50 (1); C(22), *K* = 0.50 (1); C(28), *K* = 0.45 (2).

in the angles appears to be electronic rather than steric in origin. A partial explanation may arise from the fact that in simple two-coordinate oxygen compounds (e.g. H_2O) both lone pairs are in orbitals very close in energy whereas in the heavier two-coordinate chalcogens the lone pairs are much more disparate energetically. One sulfur lone pair is in an essentially p orbital whereas the other is in an orbital with much more s character. As a result it is possible that the d orbitals may interact efficiently with only one of these lone pairs, leaving the remaining lone pair stereochemically active and favoring the more bent arrangement. Supporting evidence for this view of the bonding comes from the doubly bridging metal thiolates $-M(\mu\text{-SR})M-$, the vast majority of which are pyramidal[1] at sulfur whereas alkoxide-bridged species are almost always planar at oxygen.[21] Also, in the case of triply bridging thiolates one of the M–S distances is invariably longer than the other two.[1]

The Ti–S bond lengths, ca. 2.36 Å, are in excellent agreement with the recently published tables of crystal radii (Shannon) based

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(21) Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 541.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg)

	Complex **1**		
Ti-S(1)	2.363 (1)	S2-C(16)	1.798 (4)
Ti-S(2)	2.359 (1)	Li-O(1)	1.912 (7)
S1-C(1)	1.806 (5)	Li-O(2)	1.894 (14)
S(1)-Ti-S(2)	101.8 (1)	Ti-S(2)-C(16)	113.8 (2)
S(1)-Ti-S(2)′	113.9 (1)	O(1)-Li-O(2)	115.4 (4)
S(1)-Ti-S(1)′	116.1 (1)	O(1)-Li-O(1)′	129.3 (8)
S(2)-Ti-S(2)′	109.6 (1)	O(2)-Li-O(1)′	115.4 (4)
Ti-S(1)-C(1)	110.6 (2)		
	Complex **2**		
S(1)-Li(1)	2.449 (11)	Li(1)-O(2)	1.988 (10)
S(2)-Li(2)	2.459 (12)	Li(1)-O(3)	1.974 (9)
S(1)-C(1)	1.788 (4)	Li(2)-O(4)	1.942 (12)
S(2)-C(31)	1.785 (4)	Li(2)-O(5)	1.950 (8)
Li(1)-O(1)	1.952 (12)	Li(2)-O(6)	1.993 (10)
Li(1)-S(1)-C(1)	103.1 (3)	O(2)-Li(1)-O(3)	97.9 (4)
Li(2)-S(2)-C(32)	104.5 (3)	S(2)-Li(2)-O(4)	113.7 (4)
S(1)-Li(1)-O(1)	116.9 (4)	S(2)-Li(2)-O(5)	104.3 (5)
S(1)-Li(1)-O(2)	113.9 (5)	S(2)-Li(2)-O(6)	127.5 (5)
S(1)-Li(1)-O(3)	118.5 (5)	O(4)-Li(2)-O(5)	114.1 (6)
O(1)-Li(1)-O(2)	104.4 (6)	O(4)-Li(2)-O(6)	99.6 (5)
O(1)-Li(1)-O(3)	102.7 (5)	O(5)-Li(2)-O(6)	97.0 (4)

on metal sulfides. This revised estimate differs from previous crystal radii tables based on metal oxides, which afforded a slightly shorter Ti-S distance of 2.34 Å.[22] Similar M-S bond lengths have been reported in the species [Ti(diars)Cl_2(S-*t*-Bu)$_2$].[10]

The cation of **1**, [Li(Et_2O)$_3$], has a distorted-trigonal-planar geometry. It possesses a crystallographically imposed 2-fold axis of symmetry along LiO(2) and is therefore planar at Li. The deviations from idealized 120° angles are probably due to packing forces. The greater bulk of Et_2O relative to THF is reflected in the [Li(Et_2O)$_3$]$^+$ stoichiometry. This has not been observed for THF-solvated Li^+, Li(THF)$_4^+$ being the most common species. The electronic absorption spectrum of **1** shows a broad intense absorption at 300 nm and a weak shoulder at 458 nm. The ESR spectrum of solid **1** at 50 K shows a typical rhombic pattern with tentative g value assignments at $g_z = 1.976$, $g_y = 1.954$, and $g_x = 1.924$.[23] Similar peaks possibly due to hyperfine coupling to ^{47}Ti or ^{49}Ti were also observed but were insufficiently resolved to make an unambiguous assignment.

The structure of [Li(THF)$_3$(S-2,4,6-*t*-$Bu_3C_6H_2$)] (**2**) is illustrated in Figure 2. Important bond distances and angles are given in Table III. The most conspicuous feature of the structure is its monomeric nature. This is in sharp contrast to the dimeric alkoxide structure [Li(Et_2O){O-2,6-*t*-Bu_2-4-MeC_6H_2}]$_2$[24] (**4**) and the dimeric thiolates [Li_2(THF)$_{3.5}${SC($SiMe_3$)$_3$}$_4$] (**5**) and [Li_2(THF)$_4${SCH($SiMe_3$)$_2$}$_4$] (**6**).[12] A possible explanation for the monomeric structure of **2** is that the 2,4,6-*t*-$Bu_3C_6H_2$ group is more sterically demanding than the bis- and tris(trimethylsilyl)methane groups in **5** and **6**.

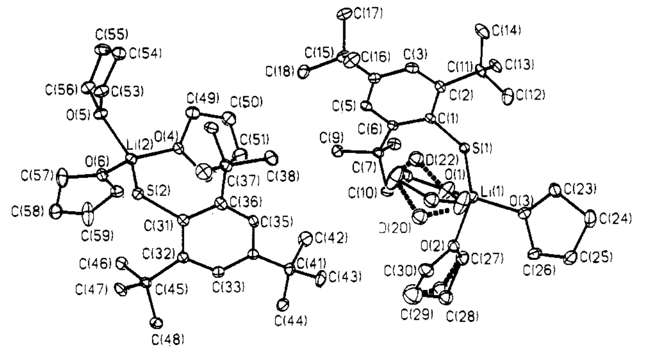

Figure 2. Computer-generated thermal ellipsoid drawing of **2** (probability level 30%). Disordered pairs of atoms are labeled C(N) and D(N) with the bonds to the latter indicated by dashes.

The Li-S bond length of ca. 2.45 Å is similar to the distances found in the dimers **5** and **6**. This unexpected similarity between bridging (in **5** and **6**) and terminal Li-S distances (in **2**) may be due to differing coordination numbers as well as steric factors. For example, in **6** the lithiums are nearer to three- than four-coordinate, since one of the THF's on each Li is almost dissociated. Lengthening of one of the Li-O distances in **4** was also observed. Thus, it can be argued that the coordination number of Li in **5** and **6** is effectively less than 4, which would lead to a shortening of the Li-S lengths. Similarly, the very large substituent on sulfur in **2** combined with coordination of three THF molecules on Li may lead to a slight lengthening of the Li-S bond over the predicted value of 2.4 Å. The result is that the Li-S distances in **2**, **4**, and **5** are all about 2.45 Å.

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Supplementary Material Available: Tables S1a,b and S2a,b, giving bond distances and angles, Tables 3b and S4a,b, listing anisotropic thermal parameters (complex **2** only) and hydrogen coordinates (11 pages); listings of structure factors (55 pages). Ordering information is given on any current masthead page.

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[22] Shannon, R. D. In *Structure and Bonding in Crystals*; O'Keeffe, M. K., Navrotsky, A., Eds.; Academic: New York, 1981; Vol. II, p 53.

[23] Veit, R.; Gireud, J.-J.; Kahn, O.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 4175.

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