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Synthesis of a Homoleptic Niobium(V) Thiolate Complex and the Preparation of Niobium Sulfide via Thio "Sol–Gel" and Vapor Phase Thin-Film Experiments

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Reaction of [Nb(NMe_2)$_5$] with 10 equiv of 2,6-$Me_2C_6H_3SH$ in toluene results in the formation of red crystals of [Nb($SC_6H_3Me_2$-2,6)$_5$]. Crystal structure analysis of [Nb($SC_6H_3Me_2$-2,6)$_5$] showed that the niobium center adopts a distorted trigonal bipyramidal geometry. Niobium disulfide, NbS_2, has been successfully prepared via a thio "sol–gel" process using [Nb($SC_6H_3Me_2$-2,6)$_5$] as the metal source. In contrast, vapor phase thin-film studies revealed that [Nb($SC_6H_3Me_2$-2,6)$_5$] functions as a single-source precursor to NbS films.

Introduction

Early transition metal disulfide films have attracted interest because of their applications as cathode materials for lithium batteries and as solid lubricants.[1,2] Bulk metal disulfides (MS_2) have been prepared by direct reaction of the elements,[3] solid-state metathesis reactions,[4] and solution phase metathetical reactions of MCl_x ($x = 4$, M = Ti, Mo; $x = 5$, M = Nb) with Li_2S.[5] Recently, bulk TiS_2 was prepared from the thio "sol−gel" reaction of either titanium alkoxides[6,7] or thiolates[8] with H_2S. Bulk NbS_2 has also been prepared from the thio "sol−gel" reaction of [Nb(OEt)$_5$] with H_2S in toluene.[7]

There have been a number of reports describing the preparation of TiS_2 thin films via dual-[9,10] and single-source[11−14] chemical vapor deposition (CVD). In contrast, CVD routes for niobium disulfide (NbS_2) films are limited[15] although a number of physical deposition processes for the preparation of NbS_2 films have been reported.[16] The single-source precursor [$NbCl_4$(S_2{CH(CH_3)$_2$}$_2$)][$NbCl_6$] resulted in the formation of mixed Nb_2O_5/NbS_2 films via CVD. The titanium thiolate complexes [Ti(S−t-Bu)$_4$][12] and [Ti(S−t-Bu)$_3$(NEt_2)][14] function as molecular precursors to TiS_2 thin films. Therefore, the aim of this work was to develop a homoleptic thiolate derivative of niobium, of the type [Nb(SR)$_5$], that might function as a precursor to NbS_2 thin films in a manner similar to the aforementioned titanium thiolate complexes. Homoleptic thiolate derivatives of niobium have only been studied to a limited extent.[17] We were also interested in extending the thio "sol−gel" route to the formation of NbS_2 using niobium thiolates.

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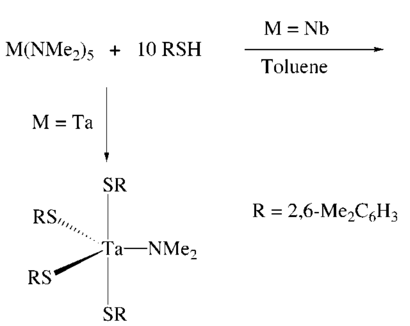
Scheme 1



Herein, we describe the synthesis and structural characterization of the first neutral homoleptic niobium thiolate complex, namely [$Nb(SC_6H_3Me_2\text{-}2,6)_5$]. Vapor phase thin-film and thio "sol−gel" experiments using the single-source precursor [$Nb(SC_6H_3Me_2\text{-}2,6)_5$] to prepare niobium sulfides (thin-film and bulk), are also described.

Results and Discussion

Treatment of [$Nb(NMe_2)_5$] with 10 equiv of 2,6-$Me_2C_6H_3$-SH in toluene at room temperature resulted in the isolation of red crystalline **1**. Analytical and spectroscopic data for **1** were consistent with the formation of the neutral homoleptic thiolate complex [$Nb(SC_6H_3Me_2\text{-}2,6)_5$], **1** (Scheme 1). A single-crystal structure determination showed the complex to have distorted trigonal bipyramidal geometry with the two axial Nb−S bonds folded essentially symmetrically over one of the equatorial Nb−S linkages (Figure 1). Despite the substantial axial distortion [S(1)−Nb−S(2) 155.18(3)°], the equatorial NbS_3 is planar to within 0.007 Å; there are, however, major departures from trigonal planar geometry for the equatorial angles which range from 107.57(3)° [S(4)−Nb−S(5)] to 127.11(3)° [S(3)−Nb−S(5)]. There is no differentiation between the axial and equatorial Nb−S bond lengths which range between 2.3609(9) and 2.4289(8) Å (Table 1), the longest distance being associated with the equatorial Nb−S(3) linkage, though the reason for this is not immediately apparent. The angles at sulfur range between 106.9(1)° and 127.3(1)°. So far as we are aware, there are no directly comparable 5-coordinate homoleptic niobium thiolate species whose structures have been reported, the most closely related examples[18] being the 6-coordinate salts [$Nb(SPh)_6]^{2-}$ and [$Nb(S\text{-}p\text{-}C_7H_7)_6]^{-}$ where overall the Nb−S bond lengths are ca. 0.1 Å longer than those seen in **1**. There have, we believe, been only three structurally characterized examples of 5-coordinate niobium complexes with all sulfur donors,[19] and of these, only one has a trigonal bipyramidal geometry.[19a] In this latter complex, the tetrakis(*tert*-butylthiolato)-thio-niobium(V) anion has equatorial Nb−S(t-Bu) distances that range between 2.365 and 2.407 Å, values comparable to those observed in **1**. The closest 5-coordinate structural analogue is the trigonal bipyramidal tantalum(V) complex tetrakis(2,3,5,6-tetramethylbenzenethiolato)-tantalum(V)[20] which exhibits directly comparable distortions in the coordination geometry with the axial Ta−S bonds subtending an angle of 156.7° and the equatorial S−Ta−S angles ranging between 105.1° and 129.4°; the Ta−S distances are in the range 2.329−2.401 Å with again no differentiation between axial and equatorial lengths. It is interesting to note that the all oxygen analogue of **1**, pentakis-(2,6-dimethylphenoxide-O)-niobium,[21] has a distinctly less distorted trigonal bipyramidal geometry with nearly collinear axial substituents [177.0°] though with equatorial interaxial angles in the range 113.1° to 126.6°. We have previously observed an axial distortion similar to that in **1** in the trigonal bipyramidal tantalum complex [$Ta(SC_6H_3Me_2\text{-}2,6)_4(NMe_2)$] where one of the equatorial sites is occupied by a dimethylamino ligand, though in this instance the axial Ta−S bonds are both tilted symmetrically away from the equatorial Ta−N bond.[14] The packing of molecules of **1** is dominated by intermolecular $\pi-\pi$ stacking interactions involving four of

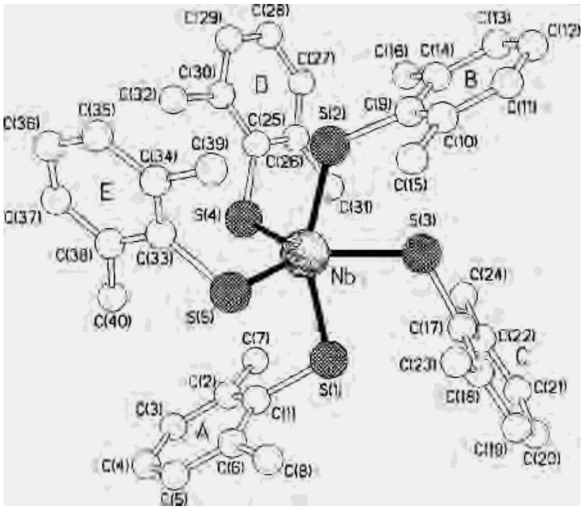


Figure 1. Molecular structure of **1**.

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

Nb−S(1)	2.3961(8)	Nb−S(2)	2.3708(9)
Nb−S(3)	2.4289(8)	Nb−S(4)	2.3609(9)
Nb−S(5)	2.3707(8)	S(1)−C(1)	1.780(3)
S(2)−C(9)	1.778(3)	S(3)−C(17)	1.773(4)
S(4)−C(25)	1.782(3)	S(5)−C(33)	1.790(3)
S(4)−Nb−S(5)	107.57(3)	S(4)−Nb−S(2)	93.91(3)
S(5)−Nb−S(2)	101.87(3)	S(4)−Nb−S(1)	101.16(3)
S(5)−Nb−S(1)	92.31(3)	S(2)−Nb−S(1)	155.18(3)
S(4)−Nb−S(3)	125.32(3)	S(5)−Nb−S(3)	127.11(3)
S(2)−Nb−S(3)	77.08(3)	S(1)−Nb−S(3)	78.12(3)
C(1)−S(1)−Nb	107.28(11)	C(9)−S(2)−Nb	127.27(12)
C(17)−S(3)−Nb	118.53(11)	C(25)−S(4)−Nb	117.20(11)
C(33)−S(5)−Nb	106.88(10)		

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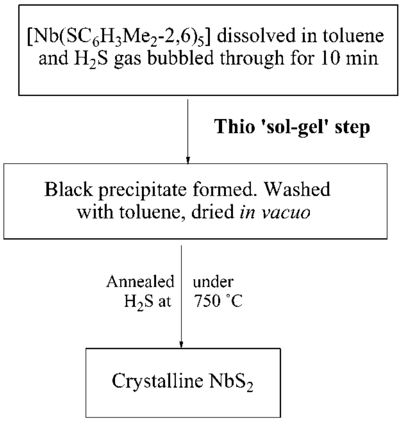
Scheme 2



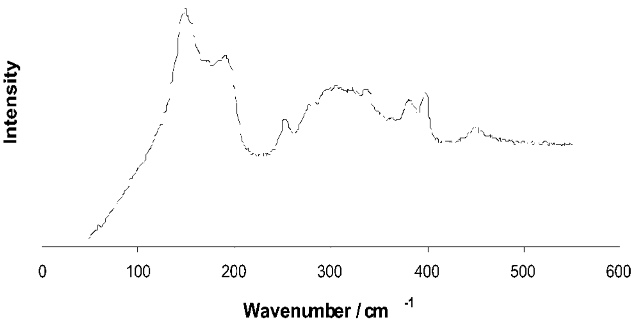


Figure 2. Raman spectrum of NbS_2 prepared from the thio "sol−gel" reaction of **1** with H_2S.

the five 2,6-dimethylphenyl ring systems (see Figure S1 in the Supporting Information).

It is interesting to note that the corresponding reaction between $[Ta(NMe_2)_5]$ and 10 equiv of 2,6-$Me_2C_6H_3SH$ resulted in the formation of $[Ta(SC_6H_3Me_2\text{-}2,6)_4(NMe_2)]$ rather than the anticipated product $[Ta(SC_6H_3Me_2\text{-}2,6)_5]$.[14] Thus, even in the presence of excess thiol, full substitution of all the dimethylamide ligands had not occurred. This is in contrast to the formation of **1** where complete substitution of the amide ligands by thiolate groups has taken place. However, it should be noted that elemental analysis of **1** showed the presence of a small amount of nitrogen (0.47%) suggesting that not all of the dimethylamide ligands had been eliminated. This was confirmed by ^1H NMR, which showed the presence of a small peak at 2.69 ppm, corresponding to NMe_2. These results indicate that either **1** was contaminated with unreacted $[Nb(NMe_2)_5]$ or a species analogous to the tantalum complex, for example, $[Nb(SC_6H_3Me_2\text{-}2,6)_4(NMe_2)]$, was also present. Attempts to improve the yield of compound **1** either by the addition of excess thiol to **1** or by carrying out the reaction between $[Nb(NMe_2)_5]$ and excess 2,6-$Me_2C_6H_3SH$ under reflux were unsuccessful. In addition, efforts to sublime compound **1** in order to grow crystals resulted in decomposition. The ^1H NMR of **1** also showed the presence of toluene of solvation. This was confirmed by the fact that the C and H analyses of **1** were slightly higher than expected.

With a view to preparing bulk NbS_2 from compound **1**, a thio "sol−gel" reaction was carried out, according to Scheme 2.

Thus, the reaction between **1** and H_2S in toluene at room temperature resulted in the formation of a black precipitate. An example of the overall reaction proposed for the thio "sol−gel" process between $[Nb(SR)_5]$ and H_2S is shown in eqs 1 and 2.

$$[Nb(SR)_5] + nH_2S \rightarrow [Nb(SR)_{5-n}](SH)_n + nRSH \quad (1)$$

$$2[Nb(SR)_{5-n}](SH)_n \rightarrow [(RS)_{4-n}(SH)_{n-1}Nb{-}S{-}Nb(SH)_{n-1}(SR)_{4-n}]_m + mH_2S \quad (2)$$

Powder XRD of the precipitate[22] showed it to be amorphous. It was therefore decided to anneal the amorphous precipitate under H_2S gas at 750 °C. The conditions were chosen on the basis of related conversions of amorphous precipitates (formed by the thio "sol−gel" reaction of $[Nb(OEt)_5]$ and H_2S) to crystalline NbS_2 as reported previously.[7] A black solid formed after annealing at 750 °C, and the powder XRD of this material showed that a single phase of crystalline NbS_2 had formed with a typical crystallite size from X-ray line broadening of 970 Å. The X-ray powder pattern of the NbS_2 obtained was indexed, and the lattice parameters were found to be $a = 3.334(8)$ Å and $c = 17.88(1)$ Å which are in good agreement with literature values ($a = 3.335$ Å and $c = 17.86$ Å).[23] EDAX data also confirmed that the Nb/S ratio was 1/2 over a number of spots. A Raman spectrum was taken and is shown in Figure 2. Peaks were observed at 150, 192, 252, 381, 398, and 450 cm^{-1}. Unfortunately, we have been unable to find a Raman spectrum of NbS_2 in the literature for comparison. However, the spectrum obtained is similar to that obtained for another sample of NbS_2 prepared by a different route.[24] By scanning electron microscopy (SEM), the annealed material shows the presence of agglomerates of hexagonal platelets $\sim 1\ \mu m$ in diameter.

The thermogravimetric analysis (TGA) results of **1** at 10 °C/min from 20 to 500 °C, under N_2, are shown in Figure 3. The decomposition of **1** has an onset temperature of 90 °C and is completed at 367 °C. The TGA of **1** shows a total weight loss of 72%, which is less than the calculated value of 79.8% for the formation of NbS_2. This behavior indicates an incomplete decomposition to NbS_2 up to 500 °C has occurred. Preliminary vapor phase thin-film studies of **1** were investigated, the details of which are given in the Experimental Section. Compound **1** produced a black film on the inside of the hot wall glass tube, which was analyzed by EDAX/SEM and Raman spectroscopy. The EDAX data for the film deposited from **1** showed a 1/1 ratio of Nb/S over a number of spots. These data suggest that NbS has been formed rather than NbS_2. It is possible that a mixture of NbS_2 and Nb_2O_5 has formed; however, the Raman spectrum of

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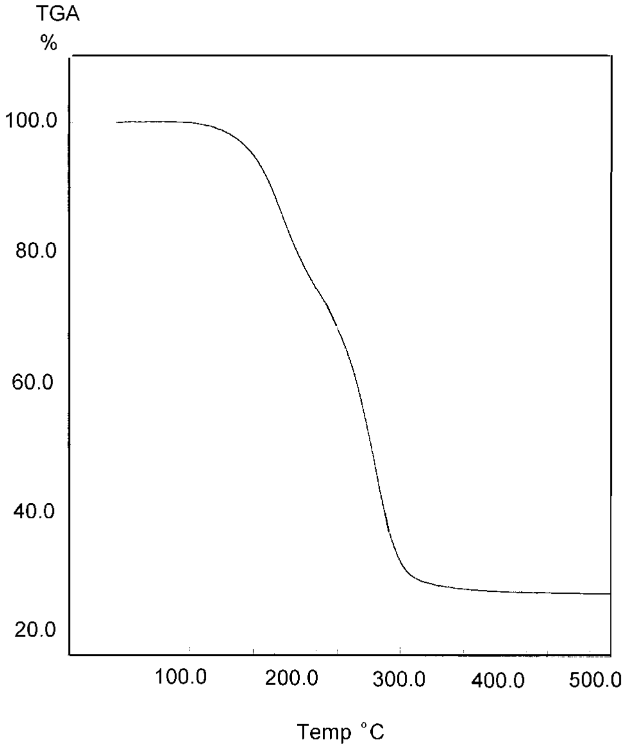

Figure 3. TGA of **1** under N_2.

Table 2. Crystallographic Data for Compound **1**

data	**1**
chemical formula	$C_{40}H_{45}S_5Nb$
fw	779.0
space group	$P\bar{1}$ (no. 2)
T (°C)	−70
a (Å)	10.609(1)
b (Å)	10.797(1)
c (Å)	19.087(1)
α (deg)	81.73(1)
β (deg)	82.98(1)
γ (deg)	61.96(1)
V (Å^3)	1905.8(2)
Z	2
ρ_{calcd} (g cm^{-3})	1.357
λ (Å)	1.54178
μ (mm^{-1})	5.33
R1[a]	0.037
wR2[b]	0.091

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

the thin-film does not show the presence of Nb_2O_5. By SEM, the niobium sulfide film shows an island-growth mechanism with an island size of 0.2 μm.

In summary, we have synthesized and structurally characterized the first neutral homoleptic niobium thiolate. The formation of NbS_2 via the novel thio “sol−gel” process suggests that this route could be extended to the formation of a range of metal sulfides. Further studies are in progress; for example, we are currently looking at the influence of temperature, H_2S, and the thio “sol−gel” step on the product obtained. In addition, more detailed CVD studies will be carried out.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a MBraun Unilab glovebox. All solvents were distilled from appropriate drying agents prior to use (sodium, toluene and hexanes; potassium, THF; CaH_2, CH_2Cl_2). All other reagents were procured commercially from Aldrich and used without further purification. [$Nb(NMe_2)_5$] was prepared according to literature procedures.[25] Microanalytical data were obtained at University College London.

Physical Measurements. NMR spectra were recorded on Brüker AMX300 or DRX500 spectrometers at UCL. The NMR spectra are referenced to CD_2Cl_2, which was degassed and dried over molecular sieves prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ (0.00 ppm). Mass spectra (CI) were run on a micromass ZABSE instrument, and IR spectra, on a Nicolet 205 instrument. Melting points were obtained in sealed glass capillaries under argon and are uncorrected. Thermolysis studies were performed in a Carbolite tube furnace. EDXA/SEM results were obtained on a Hitachi S570 instrument using the KEVEX system. Raman spectra were acquired on a Renishaw Raman System 1000 using a helium−neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. TGA of the compounds were obtained from the Thermal Methods Laboratory at Birkbeck College (ULIRS). Melting points were obtained in sealed glass capillaries under nitrogen and are uncorrected.

Synthesis of 1. The dropwise addition of 2,6-$Me_2C_6H_3SH$ (0.66 mL, 4.98 mmol) to a pale yellow solution of $Nb(NMe_2)_5$ (0.16 g, 0.511 mmol) in toluene (20 mL) at room temperature resulted in a color change to dark red. The reaction mixture was allowed to stir for 2 h, after which the solvent was removed in vacuo. The resulting dark red oil was redissolved in CH_2Cl_2 (15 mL) and filtered through Celite. Concentrating this solution to 2 mL and cooling to −20 °C for 24 h resulted in the formation of **1** in a 50% yield. Calcd for $C_{40}H_{45}S_5Nb$: C, 61.6; H, 5.77; N, 0.00. Found: C, 63.8; H, 6.84; N, 0.47. ^{1}H NMR (CD_2Cl_2): δ 2.19 (s, toluene), 2.37 (s, 24H, S 2,6-$(CH_3)_2C_6H_3$), 2.69 (s, NCH_3), 6.80−7.01 (m, 12H, 2,6-$(CH_3)_2$-SC_6H_3 and toluene).

Thio “Sol−Gel” Reaction. Compound **1** (0.300 g) was dissolved in toluene (30 mL) to give a red solution. H_2S gas was bubbled through the solution at room temperature, and a black precipitate formed immediately. The H_2S gas was allowed to bubble through the mixture for 10 min, after which the black solid was allowed to settle. The solvent was removed by syringe, and the residue was washed twice with 20 mL of fresh toluene. The solid was dried in vacuo (10^{-3} mmHg) for 2 h resulting in a black precipitate. The black precipitates were annealed under H_2S at 750 °C for 6 h using a furnace. A black solid resulted which was reanalyzed by powder XRD, EDXA/SEM, and Raman spectroscopy.

Vapor Phase Thin-Film Experiments. A sample of compound **1** (0.300 g) was loaded into a glass ampule (40 cm length × 9 mm diameter) in the glovebox. The ampule was then placed in a furnace such that 30 cm was inside the furnace and the end containing the sample protruded by 4 cm. The ampule was heated to a temperature of 450 °C under dynamic vacuum, except for the section of the tube containing the sample. The ampule was slowly drawn into the furnace over a period of a few minutes until **1** started to melt. Once all of the compound had decomposed, the furnace was allowed to cool to room temperature. A black film resulted on the inside wall of ampule where the tube was in the furnace.

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The film was analyzed by EDAX/SEM, UV−vis, and Raman spectroscopy.

X-ray Structure Determination of 1. Table 2 provides a summary of the crystallographic data for compound **1** (CCDC 186823).

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Supporting Information Available: Figure S1, showing the $\pi-\pi$ stacking interactions between adjacent molecules in the crystals of **1**, and an X-ray crystallographic file in CIF format for the structure of **1**. The material is available free of charge via the Internet at http://pubs.acs.org.

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