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Synthesis, Structure, Hydrolysis, and Film Deposition Studies of Complexes of the Formula $[NbCl_4(S_2R_2)_2][NbCl_6]$

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Introduction

Early transition metal dichalcogenides are promising cathode materials for lithium batteries[1] and have been used as solid lubricants due to weak van der Waals interactions between adjacent layers in the lattice.[2] Recent emphasis on the development of thin film batteries requires cathodes fabricated in thin film form.[3] Accordingly, there has been considerable interest in film deposition processes that produce layered metal disulfide films.[4−7] We recently reported that alkanethiol adducts of the formula $TiCl_4(HSR)_2$ function as molecular precursors to high quality titanium disulfide films.[6] We reasoned that adducts derived from niobium pentachloride and organosulfur donors might function as precursors to niobium disulfide (NbS_2) films. Treatment of niobium pentachloride with organosulfides affords complexes of the formula $NbCl_5(R_2S)$,[8] although structures of such species have not been reported. We were particularly interested in monomeric complexes of the formula $NbCl_5(R_2S_2)$, since such species would contain the correct stoichiometry for NbS_2 films. However, $NbCl_5(R_2S_2)$ has not been described and there have been no reports of the reaction of niobium pentachloride with dialkyl disulfides. Several physical deposition processes for NbS_2 films have been reported,[9] but no chemical vapor deposition (CVD) processes for NbS_2 films have been described.

Herein we report a study of the reactions of niobium pentachloride with dimethyl disulfide and diisopropyl disulfide and evaluation of the resulting complexes as single source precursors to NbS_2 films. These disulfides react with niobium pentachloride to form ionic complexes of the formula $[NbCl_4(S_2R_2)_2][NbCl_6]$, which are hydrolyzed by traces of water to $\{[NbCl_4(S_2R_2)_2]\}_2[NbCl_5{\cdot}NbOCl_4{\cdot}NbOCl_4{\cdot}NbCl_5]$. The complexes $[NbCl_4(S_2(CH_3)_2)_2][NbCl_6]$ and $\{[NbCl_4(S_2(CH(CH_3)_2)_2]\}_2[NbCl_5{\cdot}NbOCl_4{\cdot}NbOCl_4{\cdot}NbCl_5]$ are the first structurally characterized niobium complexes bearing organic disulfide ligands.[10] Furthermore, $\{[NbCl_4(S_2(CH(CH_3)_2)_2]\}_2[NbCl_5{\cdot}NbOCl_4{\cdot}NbOCl_4{\cdot}NbCl_5]$ contains an unusual, architecturally interesting tetranuclear dianion. Finally, $[NbCl_4(S_2(CH(CH_3)_2)_2][NbCl_6]$ functions as a single-source precursor to mixed Nb_2O_5/NbS_2 films using CVD techniques.

Results and Discussion

Reaction of Niobium Pentachloride with Dialkyl Disulfides. Treatment of niobium pentachloride with one equivalent of dimethyl disulfide or diisopropyl disulfide in dichloromethane at ambient temperature afforded $[NbCl_4(S_2(CH_3)_2)_2][NbCl_6]$ (**1**, 86%) or $[NbCl_4(S_2(CH(CH_3)_2)_2][NbCl_6]$ (**2**, 72%), respectively, as orange and red powders (Scheme 1).

Sublimation of these crude products (80 °C/0.01 mmHg) yielded analytically pure, moisture-sensitive orange and red blocks of **1** and **2**, respectively. Powder samples of **1** and **2** showed identical spectroscopic features as sublimed **1** and **2**, but both complexes were extremely water sensitive in solution and were best purified by sublimation. Complexes **1** and **2** were fully characterized by spectroscopic and analytical techniques.

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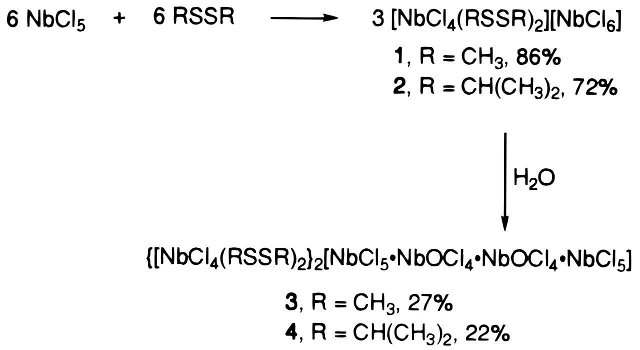
Scheme 1. Reaction of Niobium Pentachloride with Dialkyl Disulfides



The ^{1}H and ^{13}C{^{1}H} NMR spectra revealed intact alkyl groups with downfield shifts relative to the free ligands. For example, **1** showed resonances at δ 2.803 in the ^{1}H NMR spectrum, and 24.26 ppm in the ^{13}C{^{1}H} NMR spectrum. By comparison, free dimethyl disulfide showed resonances at δ 2.419 in the ^{1}H NMR spectrum, and 22.10 ppm in the ^{13}C{^{1}H} NMR spectrum. The molecular geometry of **1** was established by an X-ray structure determination (vide infra). Microanalytical data for **2** indicated a composition similar to that of **1**.

Reactions Affording Hydrolysis Products. Treatment of niobium pentachloride with one equivalent of dimethyl disulfide or diisopropyl disulfide in dichloromethane at ambient temperature, followed by crystallization at −20 °C for 7 days in a Schlenk flask capped with a rubber septum, afforded $\{[NbCl_4(S_2(CH_3)_2)_2]\}_2[NbCl_5{\cdot}NbOCl_4{\cdot}NbOCl_4{\cdot}NbCl_5]$ (**3**, 27%) and $\{[NbCl_4(S_2(CH(CH_3)_2)_2]\}_2[NbCl_5{\cdot}NbOCl_4{\cdot}NbOCl_4{\cdot}NbCl_5]$ (**4**, 22%), respectively, as red plates and black-red plates (Scheme 1). Complexes **3** and **4** were fully characterized by spectroscopic and analytical techniques. NMR analyses of **3** and **4** revealed intact alkyl groups with downfield shifts relative to the free ligands and upfield of complexes **1** and **2**. The X-ray crystal structure of **4** was determined (vide infra). The microanalysis of **3** indicated a composition similar to that of **4**. Attempts to grow crystals of **1** from dichloromethane, even with rigorous exclusion of moisture (e.g., glass stopper on Schlenk flask, carefully dried solvent), always led to a mixture of orange crystals of **1** and red plates of **3**. A similar situation was observed upon attempting to crystallize **2** from dichloromethane (i.e., light red crystals of **2**, black-red plates of **4**). Thus, hydrolysis of **1** and **2** is exceptionally facile, and the products **3** and **4** crystallize extremely efficiently from dichloromethane solution.

Crystal Structures of 1 and 4. The X-ray crystal structures of **1** and **4** were determined in order to establish their molecular geometries. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2 and 3, and perspective views are presented in Figures 1−3. Further data are available in the Supporting Information.

The cation in **1** is an eight-coordinate dodecahedral $[NbCl_4]^+$ unit with the two dimethyl disulfide ligands bonded to the niobium atom in a η^2-fashion. The chlorine atoms in the cation exhibit an average niobium−chlorine bond length of 2.365 Å (range 2.356(2)−2.374(2) Å). The average length of the niobium−sulfur bonds is 2.647 Å (range 2.631(2)−2.667(2) Å). The sulfur−sulfur bond lengths are 2.060(3) (S(1)−S(2)) and 2.045(3) Å (S(3)−S(4)). The cis chlorine−niobium−chlorine angles average 92.86° and range from 89.49(7) to 95.00(9)°. The trans chlorine−niobium−chlorine angles are 154.18(7) (Cl(3)−Nb(1)−Cl(2)) and 154.23(7)° (Cl(1)−Nb(1)−Cl(4)). The sulfur−niobium−sulfur angles for each chelating ligand are 45.91(7)° (S(1)−Nb(1)−S(2)) and 45.36(6)° (S(3)−Nb(1)−S(4)). The hexachloroniobate anion is approximately octahedral. The niobium−chlorine bond lengths (range 2.179(5)−2.459(5) Å; av 2.319 Å) are very similar to those reported in the literature for this anion.[11] The cis chlorine−niobium−chlorine angles average 90.0° and range from 84.9(2) to 97.6(2)°. The trans chlorine−niobium−chlorine angles average 175.3° and range from 172.0(3)−177.51(13)°.

There are two independent molecules in the unit cell of **4**. Only the data for Nb(5) of the cation and Nb(1) and Nb(2) of the anion will be discussed here. The corresponding data for

Table 1. Experimental Crystallographic Data for **1** and **4**

	1	**4**
empirical formula	$C_4H_{12}Cl_{10}Nb_2S_4$	$C_{24}H_{64}Cl_{26}Nb_6O_2S_8$
fw	728.7	2120.39
space group	$P2_1/n$	$P2_1/c$
a (Å)	11.8960(10)	27.658(2)
b (Å)	12.4030(10)	14.3090(10)
c (Å)	15.2580(10)	19.8430(10)
β (deg)	100.6120(10)	110.8830(10)
V (A^3)	2212.8(3)	7337.2(8)
Z	4	4
T (K)	295(2)	295(2)
λ (Å)	MoKα (λ = 0.710 73 Å)	
ρ_{calcd} (g cm^{-3})	2.187	1.920
μ (mm^{-1})	2.607	2.107
$R(F)$ (%)^a	5.54	4.04
Rw(F) (%)^b	11.90	6.54

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $\mathrm{Rw}(F)^2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) for **1**

Nb(1)−Cl(1)	2.368(2)	S(1)−C(1)	1.790(9)
Nb(1)−Cl(2)	2.374(2)	S(2)−C(2)	1.800(7)
Nb(1)−Cl(3)	2.362(2)	S(3)−C(3)	1.800(8)
Nb(1)−Cl(4)	2.356(2)	S(4)−C(4)	1.820(8)
Nb(1)−S(1)	2.631(2)	Nb(2)−Cl(5)	2.352(2)
Nb(1)−S(2)	2.652(2)	Nb(2)−Cl(6)	2.327(2)
Nb(1)−S(3)	2.667(2)	Nb(2)−Cl(7)	2.304(6)
Nb(1)−S(4)	2.637(2)	Nb(2)−Cl(8)	2.179(5)
S(1)−S(2)	2.060(3)	Nb(2)−Cl(9)	2.295(5)
S(3)−S(4)	2.045(3)	Nb(2)−Cl(10)	2.459(5)

Cl(1)−Nb(1)−Cl(2)	89.49(7)	S(1)−Nb(1)−Cl(2)	125.19(6)
Cl(1)−Nb(1)−Cl(3)	94.50(8)	S(1)−Nb(1)−Cl(3)	80.25(7)
Cl(1)−Nb(1)−Cl(4)	154.23(7)	S(1)−Nb(1)−Cl(4)	83.07(8)
Cl(2)−Nb(1)−Cl(3)	154.18(7)	S(2)−Nb(1)−Cl(1)	82.67(6)
Cl(2)−Nb(1)−Cl(4)	95.00(9)	S(2)−Nb(1)−Cl(2)	80.98(6)
Cl(3)−Nb(1)−Cl(4)	92.41(9)	S(2)−Nb(1)−Cl(3)	124.83(7)
S(1)−Nb(1)−S(2)	45.91(7)	S(2)−Nb(1)−Cl(4)	73.04(7)
S(1)−Nb(1)−S(3)	141.79(7)	S(3)−Nb(1)−Cl(1)	81.91(6)
S(1)−Nb(1)−S(4)	155.14(7)	S(3)−Nb(1)−Cl(2)	82.66(6)
S(2)−Nb(1)−S(3)	157.55(6)	S(3)−Nb(1)−Cl(3)	72.70(6)
S(2)−Nb(1)−S(4)	141.28(6)	S(3)−Nb(1)−Cl(4)	123.82(7)
S(3)−Nb(1)−S(4)	45.36(6)	S(4)−Nb(1)−Cl(1)	125.74(6)
Nb(1)−S(1)−S(2)	67.56(7)	S(4)−Nb(1)−Cl(2)	74.42(6)
Nb(1)−S(2)−S(1)	66.53(7)	S(4)−Nb(1)−Cl(3)	82.65(7)
Nb(1)−S(3)−S(4)	66.54(7)	S(4)−Nb(1)−Cl(4)	79.76(7)
Nb(1)−S(4)−S(3)	68.10(7)	Cl(8)−Nb(2)−Cl(9)	94.5(3)
Nb(1)−S(1)−C(1)	114.8(4)	Cl(8)−Nb(2)−Cl(7)	93.5(3)
Nb(1)−S(2)−C(2)	115.5(3)	Cl(9)−Nb(2)−Cl(7)	172.0(3)
Nb(1)−S(3)−C(3)	117.1(3)	Cl(8)−Nb(2)−Cl(6)	84.9(2)
Nb(1)−S(4)−C(4)	115.1(3)	Cl(9)−Nb(2)−Cl(6)	88.3(2)
S(1)−S(2)−C(2)	103.1(3)	Cl(7)−Nb(2)−Cl(6)	91.5(2)
S(2)−S(1)−C(1)	104.6(4)	Cl(8)−Nb(2)−Cl(5)	97.6(2)
S(3)−S(4)−C(4)	104.6(3)	Cl(9)−Nb(2)−Cl(5)	92.1(2)
S(4)−S(3)−C(3)	102.9(3)	Cl(7)−Nb(2)−Cl(5)	87.7(2)
S(1)−Nb(1)−Cl(1)	73.72(7)	Cl(6)−Nb(2)−Cl(5)	177.51(13)
Cl(8)−Nb(2)−Cl(10)	176.3(2)	Cl(9)−Nb(2)−Cl(10)	86.8(3)
Cl(7)−Nb(2)−Cl(10)	85.3(3)	Cl(6)−Nb(2)−Cl(10)	91.7(2)
Cl(5)−Nb(2)−Cl(10)	85.90(14)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **4**[a]

Nb(5)−Cl(19)	2.3832(13)	S(4)−C(10)	1.858(5)
Nb(5)−Cl(20)	2.3689(12)	Nb(1)−Cl(1)	2.319(2)
Nb(5)−Cl(21)	2.3796(13)	Nb(1)−Cl(2)	2.3351(14)
Nb(5)−Cl(22)	2.3743(13)	Nb(1)−Cl(3)	2.3222(14)
Nb(5)−S(1)	2.6396(14)	Nb(1)−Cl(4)	2.274(2)
Nb(5)−S(2)	2.6919(14)	Nb(1)−Cl(5)	2.327(2)
Nb(5)−S(3)	2.6519(14)	Nb(2)−Cl(6)	2.4826(12)
Nb(5)−S(4)	2.6599(14)	Nb(2)−Cl(6′)	2.7224(11)
S(1)−S(2)	2.043(2)	Nb(2)−Cl(7)	2.3183(13)
S(3)−S(4)	2.038(2)	Nb(2)−Cl(8)	2.3437(12)
S(1)−C(1)	1.873(5)	Nb(2)−Cl(9)	2.3395(12)
S(2)−C(4)	1.852(5)	Nb(1)−O(1)	2.085(3)
S(3)−C(7)	1.854(5)	Nb(2)−O(1)	1.750(3)

Cl(19)−Nb(5)−Cl(20)	155.07(5)	S(1)−Nb(5)−Cl(20)	78.74(4)
Cl(19)−Nb(5)−Cl(21)	90.62(5)	S(1)−Nb(5)−Cl(21)	81.12(4)
Cl(19)−Nb(5)−Cl(22)	92.52(5)	S(1)−Nb(5)−Cl(22)	76.52(5)
Cl(20)−Nb(5)−Cl(21)	95.90(5)	S(2)−Nb(5)−Cl(19)	81.38(4)
Cl(20)−Nb(5)−Cl(22)	91.87(5)	S(2)−Nb(5)−Cl(20)	123.55(5)
Cl(21)−Nb(5)−Cl(22)	154.39(5)	S(2)−Nb(5)−Cl(21)	74.01(4)
S(1)−Nb(5)−S(2)	45.06(4)	S(2)−Nb(5)−Cl(22)	81.35(4)
S(1)−Nb(5)−S(3)	151.03(4)	S(3)−Nb(5)−Cl(19)	75.99(4)
S(1)−Nb(5)−S(4)	144.03(4)	S(3)−Nb(5)−Cl(20)	81.46(4)
S(2)−Nb(5)−S(3)	145.20(4)	S(3)−Nb(5)−Cl(21)	80.10(4)
S(2)−Nb(5)−S(4)	154.77(4)	Cl(4)−Nb(1)−Cl(1)	96.24(7)
S(3)−Nb(5)−S(4)	45.11(4)	Cl(4)−Nb(1)−Cl(2)	94.80(7)
Nb(5)−S(1)−S(2)	68.82(5)	Cl(4)−Nb(1)−Cl(3)	94.89(6)
Nb(5)−S(2)−S(1)	66.11(5)	Cl(4)−Nb(1)−Cl(5)	93.68(6)
Nb(5)−S(3)−S(4)	67.65(5)	Cl(3)−Nb(1)−Cl(1)	89.69(6)
Nb(5)−S(4)−S(3)	67.23(5)	Cl(3)−Nb(1)−Cl(2)	88.78(5)
Nb(5)−S(1)−C(1)	117.4(2)	Cl(3)−Nb(1)−Cl(5)	171.22(6)
Nb(5)−S(2)−C(4)	116.9(2)	Cl(2)−Nb(1)−Cl(1)	168.94(6)
Nb(5)−S(3)−C(7)	116.8(2)	Cl(2)−Nb(1)−Cl(5)	88.58(5)
Nb(5)−S(4)−C(10)	117.9(2)	Cl(1)−Nb(1)−Cl(5)	91.30(6)
S(1)−S(2)−C(4)	100.9(2)	Nb(1)−O(1)−Nb(2)	175.7(2)
S(2)−S(1)−C(1)	108.2(2)	O(1)−Nb(2)−Cl(6′)	171.12(10)
S(3)−S(4)−C(10)	103.8(2)	O(1)−Nb(2)−Cl(6)	93.87(10)
S(4)−S(3)−C(7)	105.2(2)	O(1)−Nb(2)−Cl(7)	101.54(10)
S(1)−Nb(5)−Cl(19)	126.11(5)	O(1)−Nb(2)−Cl(8)	94.85(10)
S(3)−Nb(5)−Cl(22)	125.28(5)	O(1)−Nb(2)−Cl(9)	95.87(10)
S(4)−Nb(5)−Cl(19)	81.93(4)	Cl(6′)−Nb(2)−Cl(6)	77.24(4)
S(4)−Nb(5)−Cl(20)	74.60(4)	Cl(6′)−Nb(2)−Cl(7)	87.34(4)
S(4)−Nb(5)−Cl(21)	124.97(5)	Cl(6′)−Nb(2)−Cl(8)	84.74(4)
S(4)−Nb(5)−Cl(22)	80.62(4)	Cl(6′)−Nb(2)−Cl(9)	83.87(4)
O(1)−Nb(1)−Cl(1)	85.08(9)	Cl(6)−Nb(2)−Cl(7)	164.59(5)
O(1)−Nb(1)−Cl(2)	83.89(9)	Cl(6)−Nb(2)−Cl(8)	86.95(4)
O(1)−Nb(1)−Cl(3)	86.37(9)	Cl(6)−Nb(2)−Cl(9)	87.14(4)
O(1)−Nb(1)−Cl(4)	178.18(10)	Cl(7)−Nb(2)−Cl(8)	91.73(5)
O(1)−Nb(1)−Cl(5)	85.02(9)	Cl(7)−Nb(2)−Cl(9)	91.22(5)
Cl(8)−Nb(2)−Cl(9)	168.08(5)		

[a] Only the data for Nb_5, Nb_1, and Nb_2 are reported. The corresponding data for Nb_6, Nb_3, and Nb_4 are identical within experimental error.

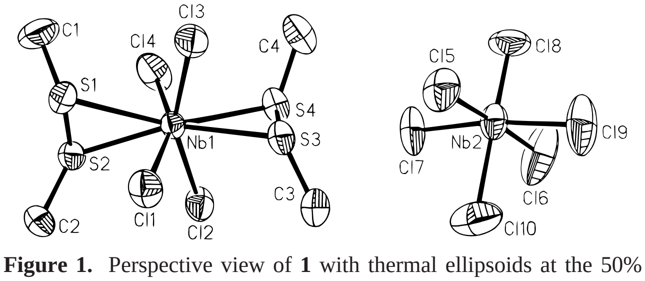


Figure 1. Perspective view of **1** with thermal ellipsoids at the 50% probability level.

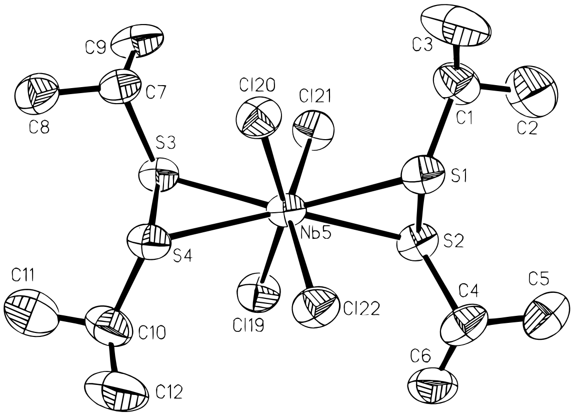


Figure 2. Perspective view of the cation of **4** with thermal ellipsoids at the 50% probability level.

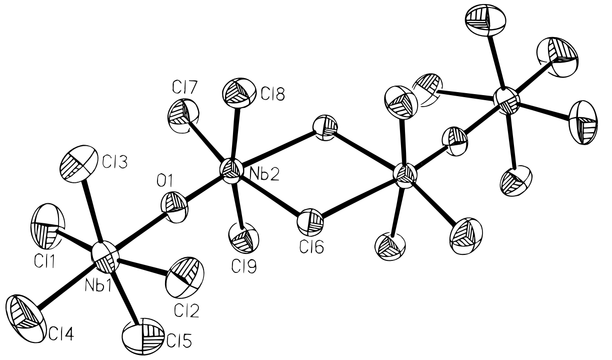


Figure 3. Perspective view of the anion of **4** with thermal ellipsoids at the 50% probability level.

Nb(6), Nb(3), and Nb(4) are identical within experimental error, and are available in the Supporting Information. The cation in **4** has the same eight-coordinate dodecahedral coordination sphere that exists in **1**. The chlorine atoms in the cation exhibit an average niobium−chlorine bond length of 2.3765 Å (range 2.3689(12)−2.3832(13) Å), which is slightly longer than that of **1**. The average length of the niobium−sulfur bonds is 2.661 Å (range 2.6396(14)−2.6919(14) Å) and is also slightly longer than that of **1**. The lengthening of these bonds is probably due to the bulkier nature of the isopropyl moieties on the sulfurs in **4**, compared to the methyl groups in **1**. The sulfur−sulfur bond lengths (S(1)−S(2), 2.043(2), and S(3)−S(4), 2.038(2) Å) are similar to those in **1**. The cis chlorine−niobium−chlorine angles (av 92.72°; range 90.62(5)−95.90(5)°) and the trans chlorine−niobium−chlorine angles (Cl(21)−Nb(5)−Cl(22), 154.39(5), and Cl(19)−Nb(5)−Cl(20), 155.07(5)°) are also similar to the angles in **1**. The sulfur−niobium−sulfur angles for each chelating ligand are S(1)−Nb(5)−S(2), 45.06(4), and S(3)−Nb(5)−S(4), 45.11(4)°. All of the angles surrounding the cation in **4** are identical to those in **1** within experimental error. The anion of **4** crystallized as a $[Nb_2OCl_9]^{-1}$ unit which dimerized with a chlorine bridge to form a centrosymmetric species containing four octahedral niobium atoms. The Nb(1)−O(1)−Nb(2) angle is nearly linear (175.7(2)°). The Nb(1)−O(1) bond length (2.085(3) Å) is appropriate for a single bond. The niobium−chlorine bond that is trans to the niobium−oxygen single bond (Nb(1)−Cl(4) 2.274(2) Å) is shorter than the mutually trans niobium−chlorine bonds (range 2.319(2)−2.3351(14) Å; av 2.326 Å). This suggests that the trans influence of a niobium−chlorine bond is stronger than that of the niobium−oxygen single bond. The short Nb(2)−O(1) bond

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(11) For examples, see: Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Acta Crystallogr., Sect. C (Cryst. Struct. Commun.)* **1990**, *46*, 1624. Schafer, H. N.; Burzlaff, H.; Grimmeiss, A. M. H.; Weiss, R. *Acta Crystallogr., Sect. C (Cryst. Struct. Commun.)* **1992**, *48*, 795. Therrien, B.; Beauchamp, A. L. *Acta Crystallogr., Sect. C (Cryst. Struct. Commun.)* **1993**, *49*, 1303. Dubgen, R.; Muller, U.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1980**, *471*, 89. Siewart, B.; Koeliner, G.; Ruhlandt-Senge, K.; Schmock, F.; Muller, U. *Z. Anorg. Allg. Chem.* **1991**, *593*, 160.

length (1.750(3) Å) implies that the bond has significant π-character and is therefore a multiple bond. The niobium−chlorine bond that is trans to this niobium−oxygen multiple bond (Nb(2)−Cl(6′), 2.7224(11) Å) is significantly longer than the terminal equatorial niobium−chlorine bonds (range 2.3183(13)−2.3437(12) Å; av 2.334 Å) and is longer than the other bridging niobium−chlorine bond (Nb(2)−Cl(6), 2.4826 Å). Such bond lengthening shows the substantial trans influence of the niobium−oxygen multiple bond and demonstrates the asymmetric nature of the chlorine bridge.

The $[NbCl_4(R_2S_2)_2]^+$ cation has not been structurally characterized previously. However, the structurally characterized complex, $[C_4ClPh_4]_2[NbCl_5{\cdot}NbOCl_4{\cdot}NbOCl_4{\cdot}NbCl_5]$, which contains an anion of the same formulation as that in **4**, has been described.[12] Although some angles differ slightly, the gross structure of the anion in complex **4** is similar to that reported for $[C_4ClPh_4]_2[NbCl_5{\cdot}NbOCl_4{\cdot}NbOCl_4{\cdot}NbCl_5]$ within experimental uncertainty. Complexes with the hexachloroniobate(V) anion have been documented in many structural studies.[11]

Deposition of Films from 2. A significant goal of this work was to develop single-source precursors to NbS_2 films. The hydrolyzed species **3** and **4** were not chosen as precursors due to the low yields and to avoid oxygen incorporation in the films. Evaluation of **1** as a single-source precursor did produce niobium sulfide films, but the depositions were patchy, not reproducible, and the film morphology was poor. Films deposited using **2** were of a higher quality. Film fabrication and analysis are discussed in this section.

Depositions were conducted at 500 °C as described in the Experimental Section using **2** as a single-source precursor in a CVD reactor that has been previously described.[13] Films that resulted were dark gold and specular. The X-ray powder diffraction spectra of the films deposited at 500 °C displayed broad reflections at $2\theta = 13.8°$ (100%), 14.5° (67%), and 31.3° (16%). While identification of the phases is tenuous based upon these data, the reflections are consistent with a mixture of Nb_2O_5 ($2\theta = 13.8°$, JCPDS #22-1196) and NbS_2 ($2\theta = 14.5$ and 31.3°, JCPDS #38−1367).[14] The X-ray photoelectron spectrum of a film deposited at 500 °C (sputtered for 45 min, at which time the elemental composition became constant) afforded an overall composition of approximately $Nb_{2.0}O_{3.2}S_{2.4}$. Ionizations resulting from carbon and chlorine were not observed, indicating that $\leq 5\%$ of these elements were present in the film. The niobium 3d region revealed the $Nb3d_{5/2}$ ionization at 207.2 eV and the $Nb3d_{3/2}$ ionization at 209.8 eV. The energy of the $Nb3d_{5/2}$ ionization is similar to a reported binding energy for Nb_2O_5 (207.3 eV[15]), and is consistent with a niobium(V) oxidation state. A scanning electron micrograph of the film using the highest possible magnification of our instrument revealed a featureless surface.

The results of the film deposition studies demonstrate that precursors derived from the reaction of niobium pentachloride with dialkyl disulfides do not constitute good source compounds for the deposition of high purity NbS_2 films. Instead, a mixture of oxide and sulfide phases was obtained. The oxygen observed in the films may originate from the glass substrates. Due to the low volatility of **2**, the films were always thin (probably $\leq$ 1000 Å). Hence, we were unable to grow films with sufficient thickness to avoid oxygen migration from the substrate. The films did not lose their metallic sheen over several months, implying that NbS_2 is stable toward degradation by ambient atmosphere. It is very likely that neutral niobium(V) complexes bearing dialkyl disulfide ligands will be substantially more volatile than **1** and **2** and should be markedly improved precursors to NbS_2 films. We are using the lessons learned from this study to prepare new precursors to NbS_2 and other early transition metal dichalcogenide films.

Experimental Section

General Considerations. All manipulations were performed under argon using either drybox or Schlenk line techniques. Dichloromethane was distilled over calcium hydride. Chloroform-*d* was dried over 4 Å molecular sieves. Niobium pentachloride, dimethyl disulfide, and diisopropyl disulfide were purchased (Aldrich Chemical Co.) and used as received.

^1H and $^{13}C\{^1H\}$ NMR spectra were obtained at 300 and 75 MHz, respectively, in chloroform-*d*. Infrared spectra were recorded using Nujol mulls. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN). Melting points are uncorrected. Single-crystal diffraction data were collected at ambient temperature on a Siemens/Bruker P4−CCD diffractometer with the SMART collection software and SAINT processing. For each structure, a hemisphere of data was collected with 10 s frames at 0.3° between each frame. X-ray photoelectron spectroscopy was performed on a Surface Science model SSX-100 spectrometer using Al Kα radiation. Samples were calibrated against the C1s binding energy (284.6 eV) of residual pump oil in the analysis chamber.

Preparation of $[NbCl_4(S_2(CH_3)_2)_2][NbCl_6]$ (1). A 150-mL Schlenk flask was charged with niobium pentachloride (0.772 g, 2.86 mmol), dichloromethane (30 mL), and a stir bar and was fitted with a rubber septum. Dimethyl disulfide (0.515 mL, 5.72 mmol) was added via syringe to form a turbid orange-red solution. The mixture was stirred for 18 h at ambient temperature and then was filtered through a 2-cm pad of Celite. The volatile components were removed by vacuum to afford **1** as an orange powder (0.901 g, 86% based on niobium pentachloride). Orange block crystals were obtained by sublimation of the crude powder at 80 °C/0.01 mmHg: mp 82−85 °C; IR (Nujol, cm^{-1}) 3026 (m), 2995 (m), 2922 (m), 2914 (m), 1398 (m), 1306 (s), 1297 (s), 1156 (w), 956 (s), 870 (m, br), 772 (w); ^1H NMR ($CDCl_3$, 21 °C, δ) 2.803 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 24.26 (s). Anal. Calcd for $C_4H_{12}Cl_{10}S_4Nb_2$: C, 6.59; H, 1.66; Cl, 48.65. Found: C, 6.24; H, 1.57; Cl, 46.16.

Preparation of $[NbCl_4(S_2(CH(CH_3)_2)_2][NbCl_6]$ (2). In a fashion similar to the preparation of **1,** niobium pentachloride (0.997 g, 3.69 mmol) and diisopropyl disulfide (1.18 mL, 7.403 mmol) were reacted to afford **2** as a red powder (1.112 g, 72% based on niobium pentachloride): mp 65−70 °C; IR (Nujol, cm^{-1}) 2870 (m), 1456 (s), 1367 (m), 1307 (w), 1237 (m), 1229 (m), 1150 (m), 1050 (s), 934 (w), 852 (vs), 838 (vs), 723 (m); ^1H NMR ($CDCl_3$, 21 °C, δ) 4.203 (sept, $J = 6.6$ Hz), 1.521 (d, $J = 6.3$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 46.10 (s), 27.24 (s). Anal. Calcd for $C_{12}H_{28}Cl_{10}S_4Nb_2$: C, 17.14; H, 3.36. Found: C, 16.95; H, 3.23.

Preparation of $\{[NbCl_4(S_2(CH_3)_2)_2]\}_2[NbCl_5{\cdot}NbOCl_4{\cdot}NbOCl_4{\cdot}NbCl_5]$ (3). A 150-mL Schlenk flask was charged with niobium pentachloride (0.642 g, 2.376 mmol), dichloromethane (25 mL), and a stir bar and was fitted with a rubber septum. Dimethyl disulfide (0.21 mL, 2.33 mmol) was added via syringe to form a turbid red solution. The mixture was stirred for 18 h at ambient temperature and then was filtered through a 2-cm pad of Celite. The Schlenk flask containing the filtrate was capped with a rubber septum that had been previously punctured several times with an 18-gauge syringe needle. The solution was chilled to −20 °C. After 7 days, the solvent was decanted to afford **3** as striated red plates (0.20 g, 27%): mp 82−87 °C (dec); IR (Nujol, cm^{-1}) 3035 (m), 3025 (m), 3007 (m), 2871 (vs), 1465 (vs), 1398 (s),

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1303 (s), 1264 (s), 1169 (w), 1153 (w), 1080 (w), 958 (s, br), 872 (vs, br), 733 (vs), 703 (m), 687 (w), 669 (w); ^{1}H NMR ($CDCl_3$, 21 °C, δ) 2.520 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 24.86 (s). Anal. Calcd for $C_8H_{24}Cl_{26}O_2S_8Nb_6$: C, 5.09; H, 1.28. Found: C, 5.05; H, 1.38.

Preparation of $\{[NbCl_4(S_2(CH(CH_3)_2)_2]\}_2[NbCl_5\cdot NbOCl_4\cdot NbOCl_4\cdot NbCl_5]$ (4). In a fashion similar to the preparation of **3**, niobium pentachloride (0.606 g, 2.24 mmol) and diisopropyl disulfide (0.36 mL, 2.26 mmol) were reacted to afford **4** as deep red plates (0.175 g, 22% based on niobium pentachloride): mp 71 °C (dec); IR (Nujol, cm^{-1}) 2871 (s), 1454 (s), 1447 (w), 1413 (w), 1384 (m), 1367 (s), 1264 (w), 1229 (m), 1149 (m), 1100 (w), 1048 (vs), 935 (w), 884 (w), 870 (w), 737 (w), 596 (s), 571 (vs); ^{1}H NMR ($CDCl_3$, 21 °C, δ) 3.365 (m, J = 6.6 Hz), 1.430 (d, J = 6.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 44.31 (s), 22.55 (s). Anal. Calcd for $C_{24}H_{56}Cl_{26}O_2S_8Nb_6$: C, 13.65; H, 2.67; Cl, 43.64. Found: C, 13.67; H, 2.62; Cl, 43.45.

Crystal Structure Determination of 1. A red crystal (0.15 × 0.14 × 0.12 mm) of **1** was sealed in a thin-walled glass capillary in under argon for use in the diffraction experiment. After data collection, 12 125 total raw reflections were harvested from the frames with 2θ ranging from 4 to 56°. Absorption corrections were not applied because no correction significantly improved the data. 4735 reflections were obtained after averaging (R_{int} = 0.09). The structure was solved and refined on F^2 with the programs SHELXS and SHELX-93.[16] Hydrogen atoms were placed in calculated positions and all other atoms were anisotropically described. The asymmetric unit contains one cation and one anion. The hexachloroniobate(V) ion was badly disordered in an equatorial plane. To model this disorder, two axial chlorides (Cl(5) and Cl(6)) were included at full occupancy, while eight equatorial chlorides were placed at 0.5 occupancy. The final R-values including all data were R1 = 0.12 and wR2 = 0.14. Table 1 lists the crystallographic parameters.

Crystal Structure Determination of 4. Crystals of **4** were obtained as red plates. A fragment (0.36 × 0.24 × 0.16 mm) was sealed in a thin-walled glass capillary under an argon atmosphere. 39 346 reflections were integrated from the 1390 frames collected with 2θ ranging from 2 to 56°. Absorption corrections were applied with the program SADABS, and 15 086 reflections were obtained after averaging (R_{int} = 0.06). The structure was solved and refined on F^2 with the programs SHELXS and SHELX-93.[16] Hydrogen atoms were placed in calculated positions and all other atoms were anisotropically described. The asymmetric unit contains two-half dianions and two independent cations. Both independent dianions occupy inversion centers, but all atoms occupy general positions in the cell. The final R values including all data were R1 = 0.10 and wR2 = 0.078. Table 1 lists the crystallographic parameters.

Film Deposition Using 2. Depositions were conducted at 500 °C using **2** as a single-source precursor in a tube furnace apparatus that has been previously described.[13] Samples of **2** that were used as precursors did not show any resonances in the ^{1}H NMR beyond those expected, indicating a purity of >99%. Corning 7059 glass, prepared by wiping with a Kimwipe until visually clean, served as the film substrate. To perform the deposition, **2** (ca. 1 g) was sublimed at 10^{-2} mmHg into the furnace. Complex **2** was vaporized by positioning the deposition tube such that the end of the tube was at the edge of the furnace. The precursor sublimed quantitatively over the substrate in about 20 min. Due to the nature of the hot-walled reactor, both the tube and the substrate were coated with a dark gold-colored film. The deposition area extended only about 5 cm from the vial containing **2**. Accordingly, the substrate was positioned as close to the vial containing **2** as possible. The resultant films were specular and dark gold-colored. The films were thin, as judged by visual inspection. For film details of the film characterization, see the text and Supporting Information.

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Supporting Information Available: X-ray diffraction and X-ray photoelectron spectra of films prepared from **2** deposited on Corning 7059 glass with a substrate temperature of 500 °C (4 pages). X-ray crystallographic files, in CIF format, for complexes **1** and **4** are available on the Internet only. Access and ordering information is given on any current masthead page.

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