Monomeric Oxo-Thiolate of Niobium Complex: The Synthesis and Structural Characterization of Square-Pyramidal $[Ph_4P][NbO(SPh)_4]$ Complex

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Transition metal complexes with aliphatic or aromatic thiolate ligands are of much current interest not only they exhibit structural diversity but also they can serve as precursors for corresponding transition metal sulfide complexes.[1,2] There have been enormous synthetic developments on the transition metal thiolate complexes with different types and nuclearity.[3,4] Despite these advances, the types and structural pattern of group V metal thiolate complexes have not been fully derived. The relative unavailability of starting materials and instability of resulting thiolate complexes have been the reason for this slow development of Nb-thiolate chemistry.

As with the new development of synthetic and characterization technologies, several research groups recently reported the synthesis and structural characterization of various niobium thiolate complexes including $[Nb(SCH_2CH_2S)_3]^-$, $[Nb(S)(SCH_2CH_2S)(SCH_2CH_2SCH_2CH_2S)]^-$, and $Li_4Nb_4S_2(SPh)_{12}$.[5,6] However, most of the researches on the chemistry of niobium thiolate complexes are toward complexes with homoleptic mono, bidentate thiolate ligands, and/or sulfido ligands. The oxo-thiolate niobium complexes have not been reported yet. We have been interested in obtaining niobium oxo-thiolate complexes since they would serve as a potential starting materials for niobium oxo-sulfide compounds.

In this communication we report on the synthesis and structural characterization of the first example of monomeric oxo-thiolate niobium complex, $[Ph_4P][NbO(SPh)_4]$ (I), from neutral $NbOCl_3L_2$, (L=CH_3CN, THF). $NbOCl_3L_2$ is synthesized by previous methods[7] using the reaction of $NbCl_5$ and $(Me_3Si)_2O$ in CH_3CN or THF. The reaction of $NbOCl_3(CH_3CN)_2$ with NaSPh in CH_3CN solution in 1 : 4 molar ratio proceeds readily at ambient temperature, under N_2 atmosphere, to give red solution of $[NbO(SPh)_4]^-$ anion (Eq. 1). Upon addition of organic cations such as $[(C_2H_5)_4N]Cl$ or $[(C_6H_5)_4P]Cl$, the solution becomes a bright red. The product can be isolated by slow addition of diethylether into CH_3CN solution as a gummy material. Recrystallization of this material from a THF/Hexane mixture gives red crystals of I in 80% yield.[8] The red crystals of I are very sensitive to air and moisture and must handle with care.

$$NbOCl_3(CH_3CN)_2+4NaSPh+Ph_4PCl \rightarrow [Ph_4P]+[NbO(SPh)_4]^- +4NaCl+2CH_3CN \qquad (1)$$

The synthesis of I is accomplished by simple ligand exchange reaction of chloride by thiophenolate group. The precipitation of NaCl facilitates the completion of the reaction. During the synthesis of $[Ph_4P]_2[Nb(SPh)_6]$ from $NbCl_5$ in the other study, niobium was reduced to +4 oxidation state with a concomitant oxidation of PhS^- to 1/2 PhSSPh.[9] However, in this study, we were not able to isolate reduced niobium oxo-thiolate species, $[NbO(SPh)_4]^{2-}$, even with the addition of excess amount of NaSPh. The oxidation and reduction behavior of anion in complex I is currently under study.

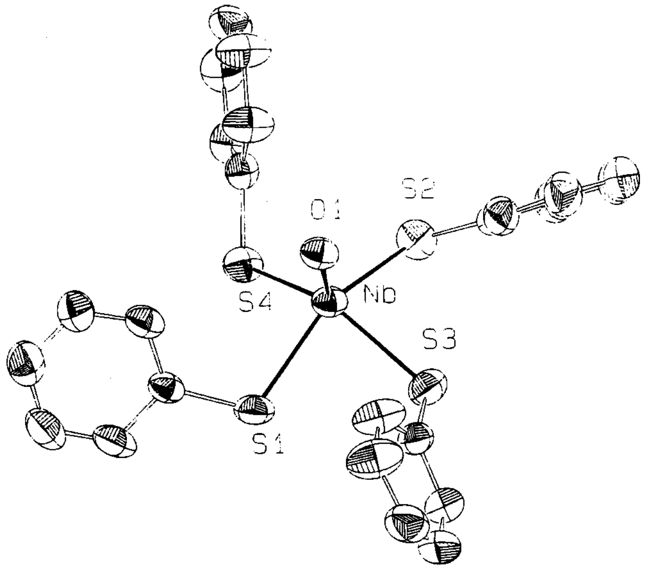

Figure 1. Structure and labeling of the anion in the $[Ph_4P][NbO(SPh)_4]$ complex. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

The structure of I has been determined,[10] and the ORTEP diagram of anion is shown in Figure 1.

The selected bond distances and angles of anion in complex I are presented in Table I and are compared to corresponding data of the isostructural $[NbS(SPh)_4]^-$ anion.[11] The coordination geometry around the metal is square pyramidal which four sulfur atoms from thiolate ligands located in the equatorial plane with the oxo ligand occupying the apical position. The similar square pyramidal geometry was also found in $[NbS(SPh)_4]^-$ anion, in which the apical position is occupied by the terminal sulfido group. However, if the arylthiolate ligands around the metal are replaced by alkylthiolate ligands as in the case of $[NbS(S\text{-}tBu)_4]^-$ or $[NbO(S\text{-}tBu)_3Cl]^-$ anions, the niobium metal adopts trigonal bipyramidal geometry.[12,13] The structural differences between these complexes probably are due to the relative bulkiness of the S-tBu ligands. The Nb=O distance at 1.710 Å which is shorter than that reported for $[Nb^V(O)(S_2)_2SH]^{2-}$ (1.729 Å)[14] also suggests the strong π-interaction between the metal and oxo ligand. The average C-S bond distance is 1.771 Å which do not show significant difference from those in $[Nb(SPh)_6]^{2-}$.[9]

The infrared spectrum of $[Et_4N][NbO(SPh)_4]$ exhibits the

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Anion in Complex I and Isostructural $[NbS(SPh)_4]^-$, II

	I	II[a]
	Distances[b]	
M=Xt[c] (X=O,S)	1.710(3)	2.171(2)
M-S	2.454	2.441
range	2.451(2), 2.457(2)	2.440(2), 2.443(2)
	Angles[b]	
S-M-Xt	108.9	109.8
range	107.5(1), 110.8(1)	108.2(1), 110.9(1)
S-M-S	83.96	83.4
range	83.29(6), 84.52(6)	82.0(1), 84.4(1)
S-M-S	140.28(5), 143.93(6)	142.3(1), 138.4(1)

[a] From ref. 11. [b] Mean values of crystallographically independent, chemically equivalent structural parameters when more than two values are available. The number in parentheses represents the individual standard deviation. [c] Xt=terminal ligand at apical position.

characteristic stretching vibrational peak from a terminal Nb =O bond at 918 cm^{-1}. This value is significantly lower than that found in $NbOCl_3L_2$, where L is CH_3CN (960 cm^{-1}), but is higher than those of $[Nb(O)(S_2)_2SH]^2$ (907 cm^{-1})[14] or $\{NbO(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3\}$ (*ca* 895 cm^{-1}).[15] This can be explained by the ligand field strength effect or basicities of the ligands. The stronger the basicity of the ligand, the stronger the bond between the metal and the attached ligand. Therefore, Nb=O bond is weaken in the increasing order of the ligand basicity. This is consistent with X-ray data for Nb=O distances in earlier discussion. The Nb-S bond stretching vibrations from thiophenolate ligands are observed at 480 and 430 cm^{-1}, which is usual for most of metal thiolate complexes.

The reactivity characteristics of anion in complex I and the utility of the very reactive I as a precursor for the oxothioniobate compounds are currently under investigation in our laboratory.

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Supplementary Material Available. Tables S1-S5 containing listings of crystal data, positional parameters (including hydrogen atoms), thermal parameters, and selected distances and angles of $[Ph_4P][NbO(SPh)_4]$(I) (12 pages); Tables S6 listing structure factors of $[Ph_4P][NbO(SPh)_4]$(I) (14 pages). are available from one of Authors (SMK).

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8. Analytical data for I are as follows. Calcd. For $NbS_4NOC_{32}H_{40}$ (MW; 675.14): C, 56.9%, H, 5.92% N, 2.07%. Found. C, 55.01% H, 6.09% N, 2.30%. The ^1H NMR spectrum in CD_3CN solution shows a triplet resonance for methyl group in $[(CH_3CH_2)_4N]^+$ cation at 1.18 ppm and a multiplet between 6.97 and 7.39 ppm due to the aromatic protons in SPh^- ligands. The integration of NMR resonance peaks confirms that the complex I is diamagnetic which the oxidation state of Nb is +5.
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10. Crystal and refinement data: Red crystal of $[Ph_4P][NbO(SPh)_4]$THF (I) is triclinic, space group P1bar with a= 12.628(2) Å, b=14.056(3) Å, c=15.450(4) Å, α=72.31 (2), β=70.83 (2), γ=72.67 (2), and Z=2. Single X-ray diffraction data for the crystal of I was collected on Mac Science MXC3 diffractometer using Mo-Kα radiation. The solution of structure was carried out by a combination of heavy atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structure by full matrix least squares methods was based on 6310 unique reflections (2θ=45°, $I>2\sigma$). Anisotropic temperature factors were used for all non-hydrogen atoms with the exceptions of the disordered THF solvent molecules that were refined with isotropic temperature factors. At the current stage of refinement on 537 parameters with all atoms present in the asymmetric units, R=0.048, Rw=0.1371.
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