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Monomeric Niobium Persulfide Complexes: The Synthesis and Structural Characterization of Pentagonal-Pyramidal $[\mathrm{Ph_4P}]_2[\mathrm{Nb(E)(S_2)_2(SPh)}]$ (E = O, S) Complexes

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Introduction

The transition metal sulfides not only serve as models for industrial catalysts and biological systems[1−7] but also exhibit structural variety and characteristic reactivities.[8−12] Because of these features, current interest in coordination chemistry has been focused on the synthesis and characterization of various transition metal sulfide complexes and their precursors.[13−24] Among the transition metal sulfides, group V species have remained relatively unexplored. The relative unavailability of starting materials and instability of resulting complexes have been the reason for this slow development of group V, especially niobium, chemistry.

Over the past few years, we have been investigating inorganic niobium/sulfide chemistry, concentrating on the high oxidation states (IV−V) of metal.[25−27] Together with related efforts by others, an impressive pool of complexes has now been made available, spanning a variety of nuclearities and oxidation levels.[28−33] However, most of complexes obtained so far are limited to sulfide complexes and their thiolate precursors. Only few complexes that have an oxo ligand have been reported until recently, but their synthesis has been inadvertent.[35,36] In this report, the synthesis and structural characterization of new monomeric niobium persulfide complexes, $[\mathrm{Ph_4P}]_2[\mathrm{NbO(S_2)_2(SPh)}]$ (**I**) and $[\mathrm{Ph_4P}]_2[\mathrm{NbS(S_2)_2(SPh)}]$ (**II**), are described.

Experimental Section

All manipulations were performed using standard Schlenk line techniques and under a dinitrogen atmosphere. Dimethylformamide (DMF) was stored over $\mathrm{CaH_2}$ for 1 week and distilled under reduced pressure before use. Tetrahydrofuran (THF) and diethyl ether were distilled after being refluxed with sodium/benzophenone. Acetonitrile was distilled after being refluxed over $\mathrm{CaH_2}$ before use. Elemental sulfur was recrystallized in toluene before use, and $\mathrm{NaBH_4}$ was used as received. $[\mathrm{Et_4N}][\mathrm{NbO(SPh)}]_4$ and $[\mathrm{PPh_4}][\mathrm{NbO(SPh)}]_4$ were prepared according to a literature method.[27]

$[\mathrm{Ph_4P}]_2[\mathrm{NbO(S_2)_2(SPh)}]$ (I). A 250 mL Schlenk flask was charged with 3 g of $[\mathrm{PPh_4}][\mathrm{Nb(O)(SPh)_4}]$ (3.38 mmol), 0.11 g of elemental sulfur (3.43 mmol), 1.27 g of $\mathrm{PPh_4Cl}$ (3.39 mmol), 0.45 g of NaSPh (3.4 mmol), and a stirring bar. To this mixture was added 100 mL of $\mathrm{CH_3CN}$ via cannula with stirring at ambient temperature. The solution color turned from dark red to bright red, and finally orange. After 12 h, this solution was filtered through a fine-porosity fritted funnel, 100 mL of diethyl ether was added to the orange red filtrate, and then the solution stood at ambient temperature. Finally 2.8 g (84% yield) of orange crystals was obtained. Calcd for $\mathrm{NbS_5P_2OC_{54}H_{45}}$: C, 63.27; H, 4.39. Found: C, 63.01; H, 4.42. FT-IR (KBr disk): ν(Nb=O) 905 $\mathrm{cm^{-1}}$, ν(S−S) 525 $\mathrm{cm^{-1}}$.

The $\mathrm{Et_4N^+}$ salt was also obtained by a similar synthetic procedure in 80% yield. Calcd for $\mathrm{NbS_5N_2OC_{32}H_{45}}$: C, 55.32; H, 6.48; N, 4.03. Found: C, 55.45; H, 6.78; N, 4.12. FT-IR (KBr disk): ν(Nb=O) 908 $\mathrm{cm^{-1}}$, ν(S−S) 520 $\mathrm{cm^{-1}}$. ^{1}H NMR (d_6-DMSO): δ 1.18 (t, 24H, $\mathrm{CH_3}$ in cation), δ 3.21 (q, 16H, $\mathrm{CH_2}$ in cation), and 6.72−7.80 (m, 5H, SPh in ligand).

$[\mathrm{Ph_4P}]_2[\mathrm{Nb(S)(S_2)_2(SPh)}]$ (II). A 250 mL Schlenk flask was charged with 1.38 g of $[\mathrm{PPh_4}]_2[\mathrm{NbO(S_2)(SPh)}]$ (1.35 mmol), 0.1 g of $\mathrm{NaBH_4}$ (2.68 mmol), and a stirring bar. To this mixture was added 50 mL of DMF via cannula with stirring at ambient temperature. The solution color turned from orange to bright red. After 12 h, this solution was filtered through a fine-porosity fritted funnel, then 100 mL of diethyl ether was added to the red filtrate, and the solution stood at ambient temperature. The red orange crystals were isolated and dried under

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Table 1. Crystallographic Data for $[Ph_4P]_2[NbO(S_2)_2(SPh)]$ (**I**) and $[Ph_4P]_2[NbS(S_2)_2(SPh)]$ (**II**)

	I	**II**
formula	$NbS_5P_2OC_{54}H_{45}$	$NbS_6P_2C_{54}H_{45}$
fw	1025.05	1041.11
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No.2)	$P2_1/n$ (No.14)
a, Å	10.853(2)	10.821(5)
b, Å	10.976(1)	21.559(8)
c, Å	21.641(3)	21.273(7)
α, deg	103.58(1)	
β, deg	95.55(1)	95.55(1)
γ, deg	101.42(1)	
Z	2	4
V, Å^3	2428.3	4949
T, °C	20	20
λ, Å	0.710 69	0.710 73
ρ_{cacld}, g cm^{-3}	1.402	1.397
μ, cm^{-1}	5.68	5.97
R^a	0.042	0.065
$R_w{}^b$	0.096	0.135

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

vacuum. Finally 0.7 g (59% yield) of red orange crystals was obtained. Calcd for $NbS_6P_2C_{54}H_{45}$: C, 62.24; H, 4.32. Found: C, 62.18; H, 4.38. FT-IR (KBr disk): ν(Nb=S) 467 cm^{-1}, ν(S−S) 520 cm^{-1}.

X-ray Crystallography. Single-crystal X-ray diffraction data for both crystals are presented in Table 1. Diffraction data were collected at ambient temperature on a Bruker P4 four-circle diffractometer using Mo Kα radiation. Intensity data were collected by using a $\theta-2\theta$ step scan technique, and for all data sets the condition of the crystal was monitored by measuring 2 standard reflections. The solutions of both structures were carried out by a combination of heavy atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structures by full-matrix least-squares methods was based on 4541 unique reflections ($2\theta = 40$, $I > 2\sigma$) for **I**, and 5262 unique reflections ($2\theta = 45$, $I > 2\sigma$) for **II**. Anisotropic temperature factors were used for all non-hydrogen atoms in **I** and **II**. At the current stage of refinement on 568 parameters for **I** and 613 parameters for **II** with all atoms present in the asymmetric units, $R = 0.042$, $R_w = 0.096$ for **I** and $R = 0.065$, $R_w = 0.135$ for **II**.

Other Physical Measurements. ^{1}H NMR spectra (300 MHz) were obtained with a Varian Gemini 300 spectrometer. Infrared spectra were measured with a Shimadzu IR-470 spectrophotometer. CHN analyses were obtained with Thermoquest EA-1110 CHNS analyzer.

Results and Discussion

The Ph_4P^+ "salt" of the $[NbO(S_2)_2(SPh)]^{2-}$ anion can be obtained from the reaction of $[NbO(SPh)_4]^-$ with elemental sulfur in dimethylformamide (DMF) solution in a 1:1 molar ratio. The reaction proceeds readily at ambient temperature, under an N_2 atmosphere, to give an orange solution of the $[NbO(S_2)_2(SPh)]^{2-}$ anion with $[Ph_4P]^+$ as the cation (eq 1). In spite of efforts to derive other monomeric oxo−niobium sulfides by reaction of $[NbO(SPh)_4]^-$ with elemental sulfur, only $[NbO(S_2)_2(SPh)]^{2-}$ (1:1 to 1:4 in molar ratio) and unidentified insoluble polymeric oxo−niobium sulfides were obtained. When elemental sulfur was used in excess (more than 1:8 molar ratio), green powders which were assumed to be $[NbO(S_2)_2]^-$ could be obtained, but they have not been fully characterized yet.

$$[Ph_4P][NbO(SPh)_4] + 1{-}4S \rightarrow [Ph_4P]_2[NbO(S_2)_2(SPh)] + 3/2PhSSPh \quad (1)$$

To improve the yield we adopted an alternative synthetic route in which the Et_4N^+ (or Ph_4P^+) "salt" of $[NbO(S_2)_2(SPh)]^{2-}$ anion can be obtained in 80% yield from the reaction of $[NbO(SPh)_4]^-$ with elemental sulfur in CH_3CN solution in a 1:4 molar ratio in the presence of Et_4NCl (or Ph_4PCl) and NaSPh (eq 2).

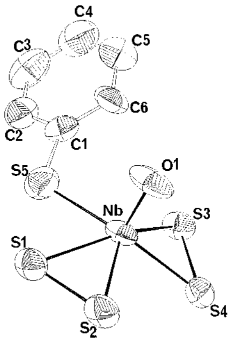

Figure 1. Structure and labeling of the anion **I** in the $[Ph_4P]_2[NbO(S_2)_2(SPh)]$ complex. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

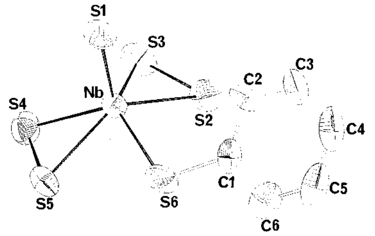

Figure 2. Structure and labeling of the anion **II** in the $[Ph_4P]_2[NbS(S_2)_2(SPh)]$ complex. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

$$[Et_4N][NbO(SPh)_4] + 4S + Et_4NCl + NaSPh \rightarrow [Et_4N]_2[NbO(S_2)_2(SPh)] + 4PhSSPh + NaCl \quad (2)$$

In the synthesis of complex **I**, it can be assumed that elemental sulfur oxidizes two of the coordinated SPh ligands with a concomitant generation of the $S_2{}^{2-}$ ligand. The $S_2{}^{2-}$ ligand generated coordinates to the metal center which retains the terminal oxo and one of the thiolate ligands. A similar ligand redox reaction has been reported by Christou's group in the synthesis of the structurally analogous $[Me_3(Bz)N]_2[V(S)_2(S_2)\text{-}SPh]$ complex (eq 3).[34]

$$VCl_3 + 7SPh^- + 3S \rightarrow [V(S)_2(S_2)SPh]^{2-} + 3PhSSPh \quad (3)$$

The isostructural $[NbO(S_2)_2SH]^{2-}$ anion also has been prepared by Coucouvanis' group from the reaction of $[Nb(^tBuS)(S)_3]^{2-}$ with elemental sulfur in the presence of water.[35] In the synthesis of the $[NbO(S_2)_2SH]^{2-}$ anion, they proposed that the initial step is the replacement of SH by OH in H_2O and subsequent redox reaction between S^0 and S^{2-} to generate the $S_2{}^{2-}$ group or vice versa.[36]

From the reaction of $[Ph_4P]_2[NbO(S_2)_2(SPh)]^{2-}$ with $NaBH_4$ in CH_3CN solution at ambient temperature, the $[NbS(S_2)_2(SPh)]^{2-}$ (**II**) anion as the Ph_4P^+ "salt" was obtained unexpectedly. The reducing agent $NaBH_4$ was used to reduce the Nb(V) center, which subsequently led to a dimeric complex. Instead, the S^{2-} anion might be generated from the reduction of $S_2{}^{2-}$ by the reducing reagent $NaBH_4$ and eventually replace the terminal oxo ligand. The reaction mechanism is currently under investigation.

The structures of **I** and **II** have been determined, and the ORTEP diagram of the anion is shown in Figures 1 and 2.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Anion Complexes **I**, **II**, and Isostructural $[NbO(S_2)_2(SH)]^{2-}$, **III**

	I	**II**	**III**[a]
	Distance[b]		
M=E$_t$[c] (E = O in **I**, **III**, E = S in **II**)	1.715(4)	2.184(4)	1.729(9)
M−S	2.469	2.439	2.460
range	2.456(2), 2.477(2)	2.412(4), 2.462(4)	2.452(4), 2.467(5)
M−SR	2.551(2)	2.492(4)	2.526(4)
S−S in S_2^{2-}	2.054(3), 2.076(2)	2.102(7), 2.013(6)	2.071(6), 2.085(9)
	Angles[b]		
S−M−E$_t$	105.30	108.01	106.4(5)
range	102.11(14), 108.7(2)	104.0(2), 109.9(2)	
S−M−S in S_2^{2-}	49.43(5), 49.21(6)	48.46(14), 51.3(2)	
S−M−SR	87.38(6), 73.32(6)	84.7(2), 73.12(14)	
S−M−S between S_2^{2-}	85.72(6)	84.5(2)	

[a] From ref 34. [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] E$_t$ = terminal oxo and sulfido ligand at apical position.

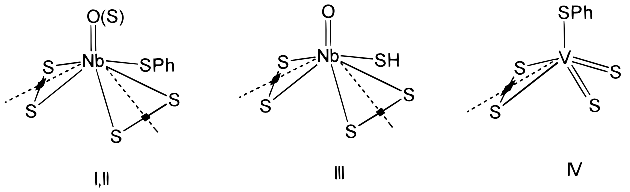

Figure 3. The pseudotetrahedral geometries of three structurally related anions: $[NbO(S_2)_2(SPh)]^{2-}$ (**I**), $[NbS(S_2)_2(SPh)]^{2-}$ (**II**), $[NbO(S_2)_2SH]^{2-}$ (**III**), and $[V(S)_2(S_2)SPh]^{2-}$ (**IV**).

The selected bond distances and angles of the anion in complexes **I** and **II** are presented in Table 2 and are compared to corresponding data of the isostructural $[NbO(S_2)_2(SH)]^{2-}$ (**III**) anion.[35] The coordination geometries around the metal for both complexes are pentagonal pyramidal consisting of five sulfur atoms from two persulfide ligands and a thiolate ligand in the equatorial plane with the terminal oxo ligand, for **I**, and sulfido ligand, for **II**, in the apical position. A similar pentagonal-pyramidal geometry was also found in the **III** anion, in which one of the equatorial positions is occupied by an SH group. In the case of the vanadium complex,[34] the central vanadium metal in the $[V(S)_2(S_2)SPh]^{2-}$ anion has a square-pyramidal geometry in which the persulfide ligand, terminal sulfide ligand, and thiophenolate ligand are located in equatorial positions and the remaining terminal sulfido group occupies the apical position. The geometries of the three structurally similar anions can also be described as tetrahedral with the S_2^{2-} occupying one of tetrahedral sites (Figure 3).

The Nb=O distance of 1.715 Å in $[NbO(S_2)_2(SPh)]^{2-}$, which is similar to that of the starting complex, $[NbO(SPh)_4]^-$, indicates the strong π interaction between the metal and the oxo ligand. However, the M−S distance between niobium(V) and the thiolate ligand in complex **I** is slightly longer (2.551 Å) than that (2.454 Å) in $[NbO(SPh)_4]^-$. This is probably due to the weakening of metal−thiolate bonding by the coordination of persulfide groups, which are better electron donors. The S−S distances of 2.054(3) and 2.067(2) Å in **I** are as expected for a η^2-S_2^{2-} ligand, and other bond lengths and angles are comparable to those reported for similar molecules.[35,37,38] The Nb=S distance of 2.184 Å in the $[NbS(S_2)_2SPh]^{2-}$ complex is shorter than those of $[Nb(S)_3(^tBuS)]^{2-}$ (2.230 Å)[32] and $[Nb(S)_3(SH)]^{2-}$ (2.257 Å).[36] This decrease in length reflects stronger Nb−S dπ−pπ bonding in complex **II** than that in the latter two complexes. The increase in bond angle from S−Nb−O$_t$ (105.30°) to S−Nb−S$_t$ (108.01°) may be explained by the steric crowding effect around the metal center as described before.

The infrared spectrum of $[NbO(S_2)_2SPh]^{2-}$ exhibits the characteristic stretching vibration from a terminal Nb=O bond at 905 cm^{-1}. This value is similar to that found in isostructural $[NbO(S_2)_2SH]^{2-}$ (907 cm^{-1}). In the $[NbS(S_2)_2SPh]^{2-}$, the stretching vibration of the terminal Nb=S is observed at 467 cm^{-1}. The S−S bond stretching vibration of complex **I** with the Et_4N^+ "salt" is also observed at 525 cm^{-1}, but is not observed in complex **II** due to its superposition on that from the Ph_4P^+ cation. The Nb−S bond stretching vibrations from thiophenolate ligands are observed at 480 and 430 cm^{-1}, which are typical values for most of the metal thiolate complexes.[25−27,32,33]

Preliminary indications and studies currently in progress show that complex **I** exhibits reactivity toward small organic nucleophiles similar to that found in its Mo counterparts and can be used as a precursor for the synthesis of new Nb/S/O complexes.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $[Ph_4P]_2[NbO(S_2)_2(SPh)]$ (**I**) and $[Ph_4P]_2[NbS(S_2)_2(SPh)]$ (**II**). This material is available free of charge via the Internet at http://pubs.acs.org.

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