Inorg. Chem. **1995**, *34*, 2267−2268

Synthesis and Structural Characterization of the $[Nb(O)(S_2)_2SH]^{2-}$, $[Nb(S)_3SH]^{2-}$, and $\{[Nb(S)_3]_2O\}^{4-}$ Anions. New Elementary Thio- and Oxothioniobates

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Received August 19, 1994

The coordination chemistry of V with either aliphatic or aromatic thiolate ligands is well established.[1] More recently the analogous chemistry with Nb and Ta also has received considerable attention.[2] Additions to this chemistry originating from our laboratory include the following: (a) the six-coordinate homoleptic complexes of Nb(IV,V) and Ta(V) with monodentate arenethiolate ligands,[3] (b) the mixed $^tBuS^-/S^{2-}$ complexes $[Nb(^tBuS)_4S]^-$ and $[Nb(^tBuS)_2(S)_2]^-$,[4] and (c) the $[M(^tBuS)(E)_3]^{2-}$ complexes[5] (E = S, M = Nb, Ta; E = Se, M = Nb). The last two types are alkyl derivatives of the $[M(E)_4]^{3-}$ chalcogenoanions. The $[M(E)_4]^{3-}$ anions, whether in extended solids (as the $NbSe_4$ units in K_3NbSe_4[6]) or in $Li_3[NbS_4]\cdot L_x$ (L = CH_3CN, $x = 4$; L = TMEDA, $x = 2$[7]) are stabilized by interacting countercations. The cation interactions that are needed for the sucessful isolation of the trianions apparently facilitate the partial "neutralization" of the excessive negative charge in the small, highly charged, $[MS_4]^{3-}$ complexes.[7]

The systematic synthesis of binary and tertiary Mo/S and Mo/S/O complexes has led to homologous series of complexes[8] that resulted in the development of functional group chemistry associated with specific chromophores in various chemical environments.[9] The corresponding solution chemistry of the M/S and M/S/O complexes (M = Nb, Ta) has not been developed as extensively. In this communication we report on the reactivity of the $[Nb(^tBuS)(S)_3]^{2-}$ anion, **I**, and the synthesis and structural characterization of new thio- and oxothiometalate anions of Nb(V) that appear well suited as synthons for future studies.

The reaction of either $(Ph_4P)_2$**I** or $(Et_4N)_2$**I** with elemental sulfur in DMF solution and in the presence of a stoichiometric amount of water (needed as a source of protons and O^{2-}) affords in 65% yield the yellow $[Nb(O)(S_2)_2(SH)]^{2-}$ anion, **II**, as crystalline $(Ph_4P)_2$**II**·2DMF[10a] or $(Et_4N)_2$**II**[10b] salts. In $(Et_4N)_2$**II** the S−H stretching vibration is found as a weak but sharp band at 2544 cm^{-1} and upon deuteration shifts to 1848 cm^{-1}. The ^1H NMR of **II** in CD_3CN solution shows the S−H proton resonance at −0.09 ppm. The reaction of $(Ph_4P)_2$**II**·2DMF with Et_3P in DMF solution at ambient temperature affords the diamagnetic $[Nb(HS)(S)_3]^{2-}$ anion, **III**, as the $(Ph_4P)_2$**III** salt[11] in 85% yield. The isolated byproducts of this reaction were Et_3PO and Et_3PS, positively identified by infrared spectroscopy. We were unable to detect the S−H vibration in **III** mainly due to interference by the Ph_4P^+ cation; however, the S−H proton resonance in the NMR spectrum is observed at 0.65 ppm. The presence of the proton in **III** also is indicated by the analytical data, the crystallographic detection of only two Ph_4P^+ cations, the presence of two sets of Nb−S bonds in **III**, and the similar electronic spectra of the perturbed NbS_4^{3-} anions in **III** (348 nm) and the $Li_3[NbS_4]\cdot 2TMEDA$ complex[7] (340 nm). The abstraction of the oxygen atom from the Nb═O group suggests that the Nb(V) ion undergoes reduction to a short-lived Nb^{III} species before it undergoes rapid reoxidation to the final Nb(V) product.

The reaction of $(Ph_4P)_2$**III** with dibenzyltrisulfide, BzSSSBz, in "wet" CH_3CN affords $(Ph_4P)_2$**II** in 65% yield.[12] The reaction of $(Et_4N)_2$**I** with Et_3N and H_2O in 2:2.5:1 molar ratio in CH_3CN solution afforded the yellow crystalline Et_4N^+ salt of the $[(S)_3Nb\text{-}O\text{-}Nb(S)_3]^{4-}$ dimer, **IV**, in 70% yield.[13] In the rigorous absence of water no reaction occurs between $(Et_4N)_2$**I** and Et_3N. The weak base Et_3N originally was used in this reaction in an attempt to obtain NbS_4^{3-}. It was expected to assist in the abstraction of a β proton from the Bu^tS^- ligand in **I**, that would lead to formation of isobutene and the concomitant cleavage of the C−S bond.

The structures of $(Et_4N)_2$**II**, $(Ph_4P)_2$**III**, and $(Et_4N)_4$**IV** have been determined[14] (Figure 1). In $(Et_4N)_2$**II**, the pentagonal pyramidal $[Nb(O)(S_2)_2(SH)]^{2-}$ anion (Figure 1) has the sulfur atoms located in the equatorial plane with the oxo ligand occupying the apical position and the Nb^V ion located 0.70 Å above the plane defined by the five S atoms. The Nb═O bond length at 1.729(9) Å is comparable to that reported for other similar molecules.[15] The $Nb(O)(S_2)_2$ unit in **II** is structurally similar to the $V(O)(S_2)_2$ unit in the pentagonal bipyramidal

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(10) (a) Anal. Calcd for $(Ph_4P)_2$**II**·2DMF, $NbS_5P_2O_3N_2C_{54}H_{55}$: C, 59.2; H, 5.02; N, 2.55 Found: C, 58.98; H, 5.06; N, 2.54. IR spectrum: Nb═O, 907 cm^{-1}; S−S, 515 cm^{-1} shoulder on cation peak at 526 cm^{-1}; S−H, 2544 cm^{-1}; Nb−S, 354, 345 (350) cm^{-1}; DMF (C═O), 1670 cm^{-1}. (b) Anal. Calcd for $(Et_4N)_2$**II**, $NbS_5ON_2C_{16}H_{41}$: C, 36.21; H, 7.79; N, 5.28. Found: C, 36.16; H, 8.10; N, 5.38. IR spectra: Nb═O, 909 cm^{-1}; S−S, 517 (496 w, sh) cm^{-1}; S−H, 2544 cm^{-1} or S−D, 1848 cm^{-1}; Nb−S, 354, 345 cm^{-1} (350 cm^{-1} unresolved).

(11) Anal. Calcd for $(Ph_4P)_2$**III**, $NbS_4P_2C_{48}H_{41}$: C, 63.99; H, 4.59. Found C, 63.07; H, 4.67. IR spectra: Nb═S/−SH, 462/447 cm^{-1}.

(12) The same reaction in "dry" CH_3CN affords a nearly equimolar mixture of the $[Nb^V(O)(S_2)_2(SH)]^{2-}$ and $[Nb^V(S)(S_2)_2(SH)]^{2-}$ anions. This crystalline material has been structurally characterized, and the disordered structure shows the two isostructural anions occupying the same site.

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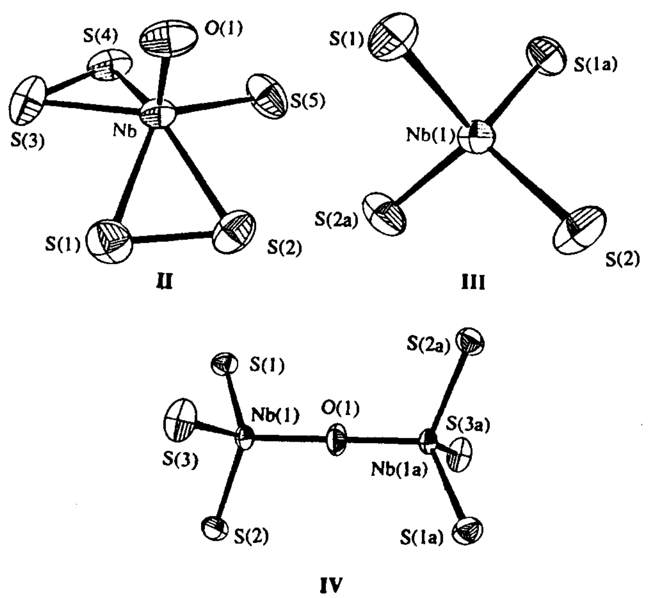

Figure 1. Structure and labeling of the anions in the $(Et_4N)_2[Nb(O)(S_2)_2(SH)]$ (**II**), $(Ph_4P)_2[Nb(S)_3(SH)]$ (**III**), and $(Et_4N)_4\{[Nb(S)_3]_2O\}$ (**IV**) complexes. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Mean values of selected distances and angles: for **II**, Nb−S$_2$, 2.230(6) Å; Nb−SH, 2.526(4) Å; Nb═O, 1.729(9) Å; S−S, 2.071(6), 2.085(9) Å; S$_2$−Nb═O, 106.4(5)°; for **III**, Nb−S$_t$, 2.257(1) Å; Nb−SH, 2.312(1) Å; S$_t$−Nb−S$_t$, 111.7(1)°; S$_t$−Nb−SH, 109.6(4)°; for **IV**, Nb−Nb, 3.831(1) Å; Nb−S$_t$, 2.261(5) Å; Nb−O, 1.916(1) Å; Nb−O−Nb, 180.0°; S$_t$−Nb−S$_t$, 108.9(1)°; S$_t$−Nb−O, 110.0(1)°.

$[V(O)(S_2)_2(bipy)]^-$ anion.[1a] The S−S distances in **II** at 2.071(6) and 2.085(9) Å are as expected for a η^2-S_2^{2-} ligand.[8a,16] The Nb(V)−S bond lengths with the η^2-S_2 ligands range from 2.452(4) to 2.467(5) Å and are shorter than the corresponding Ta−S bonds in the $\{[Ta(S_2)_2(S)]_2S\}^{2-}$ anion[17] (2.579(5) Å). Not unexpectedly the Nb^V−η^2-S$_2$ bonds in **II** are considerably longer than the corresponding Mo^{VI}−S bond lengths in the $[Mo(S_2)_2(O)]_2S\}^{2-}$ complex[18] (2.37(2) Å). The Nb−SH bond at 2.526(4) Å is significantly longer than the Nb−S^{t}Bu bonds in the $[Nb(E)_3S^tBu]^{2-}$ anions,[5] which range from 2.422(3) to 2.439(2) Å. The anion in **II** is electronically and structurally similar to the $[Mo(O)(S_2)_2(S)]$, $[Ta(S)(S_2)_2(S)]$, $[Nb(Se)(Se_2)_2(Se)]$, and $[W(S)(S_2)_2(S)]$ subunits in the known $\{[Mo(O)(S_2)_2]_2(S)\}^{2-}$,[18] $\{[Ta(S)(S_2)_2]_2S\}^{4-}$,[17] $[Nb_4Se_{22}]^{6-}$,[17] and $\{[W(S_2)_2(S)]_2S\}^{2-}$ [19] anions. The apparent stability of the SH ligand in **II** suggests that, SH complexes similar to **II** may be obtainable with other metals (Ta, W, Mo) by reduction of the available oligomeric precursor complexes that contain the M(E)(S$_2$)$_2$(S) structural units (E = S, O). Among examples of thiometalate anions that contain the SH$^-$ anion as a terminal ligand are included the $(S_3WSH)^-$ [20] and $[W_2S_{11}H]^-$ [21] anions. The possibility that the proton in **II** is located on a η^2-S^{2-} ligand can be ruled out by (a) the symmetric mode of chelation of the S_2^{2-} ligands to the Nb atom and (b) by the unusually long Nb−S(5) distance (Figure 1) that suggests a thiolate-like rather than a Nb═S bond.

In $(Ph_4P)_2$**III** the $[Nb(S)_3(SH)]^{2-}$ anion is located on a crystallographic 2-fold axis and consequently shows two symmetry independent Nb−S bonds at 2.257(1) and 2.312(1) Å. The Nb−SH bond in **III** at 2.312(1) Å is quite shorter than that in **II** and may be reflecting either the difference in geometry (and the less crowded Nb(V) ion in **III**) or a "sharing" of the H$^+$ between the two sulfur atoms related by the crystallographic 2-fold axis. A positionally disordered Nb−SH unit would be accounted for by half occupancy protons on the two S atoms that show the longer Nb−S bond cannot be ruled out. At 2.257(1) Å the two shorter Nb═S bonds (also related by the 2-fold axis) are somewhat longer than the Nb═S bonds in the $[Nb(S)_3S^tBu]^{2-}$ anion[5] (2.230(6) Å. The mean Nb−S bond in **III** at 2.285 Å is slightly longer than that reported[7] for $Li_3[NbS_4]\cdot L_x$. In the latter the Nb−S bonds also are perturbed with the four sulfido ligands interacting pairwise with the three Li$^+$ ions (range Li−S: 2.466(4)−2.512(1) Å). The oxo ligand of the tetraanion in **IV** is located on a crystallographic center of symmetry, and consequently the Nb−O−Nb bridge is strictly linear with the terminal sulfido ligands staggered in an idealized D$_3$d symmetry. a nearly linear $[V{-}O{-}V]^{+4}$ unit has been found in the structure of the $V_2O(SCH_2CH_2NMe_2)_4$ complex[1b]. The Nb═S bond in **IV** at 2.261(5) Å is similar to the one in **III**. The ion is isoelectronic and nearly isostructural to the $Mo^{VI}{}_2O_7{}^{2-}$ anion.[22] The corresponding isostructural $[Mo^{VI}{}_2OS_6]^{2-}$ anion is not known although the $[Mo^{VI}S_4Mo^{IV}(O)(S_2)]^{2-}$ anion[23] (an internal redox isomer of the hypothetical $[Mo^{VI}{}_2OS_6]^{2-}$) has been synthesized and structurally characterized. Preliminary indications and studies currently in progress show that the Nb/S and Nb/S/O complexes are not as prone to intramolecular electron transfer (internal redox) as their Mo counterparts and possess unique structural and reactivity characteristics.

Acknowledgment. The support of this work by a grant from the National Science Foundation (CHE-9307382) is gratefully acknowledged.

Supplementary Material Available: Tables S1a, S2a, and S3a containing listings of positional parameters, thermal parameters and selected distances and angles for **II**, **III**, and **IV**, a table giving a summary of distances and angles for **I**−**IV**, and a figure showing structural disorder in **II** (24 pages). Ordering information is given on any current masthead page.

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(13) Anal. Calcd for $(Et_4N)_4$**IV**; $Nb_2S_6ON_4C_{32}H_{80}$: C, 41.99; H, 8.8; N, 6.12. Found: C, 41.86; H, 8.28; N, 6.22. IR spectrum of the molecule shows the following vibrations: Nb−S, 444, 414 cm^{-1}; Nb−O−Nb, 727 cm^{-1}.

(14) Crystal and refinement data: Yellow crystals of $(Et_4N)_2[Nb(O)(S_2)_2SH]$, **II**, are monoclinic space group $P2_1/c$ with $a = 13.420(3)$ Å, $b = 10.262(3)$ Å, $c = 18.320(6)$ Å, $\beta = 90.98$ (2)° and $Z = 4$. Yellow crystals of $(PPh_4)_2[Nb(S)_3SH]$, **III**, are monoclinic, space group $C2/c$ with $a = 11.147(3)$ Å, $b = 19.624(5)$ Å, $c = 20.311(7)$ Å, $\beta = 91.24(3)$°, and $Z = 4$. Yellow crystals of $(Et_4N)_4[Nb(S)_3{-}O{-}Nb(S)_3]$, **IV**, are triclinic space group $P1$ with $a = 10.826(2)$ Å, $b = 11.476(3)$ Å, $c = 11.604(3)$ Å, $\alpha = 111.41(2)$°, $\beta = 103.00$ (2)°, $\gamma = 111.29(2)$°, and $Z = 1$. Single-crystal X-ray diffraction data for **II**, **III**, and **IV** were collected on a Siemens R3m diffractometer using Mo Kα radiation. The solutions of all structures were carried out by a combination of heavy atom Patterson techniques, direct methods, and Fourier techniques. The refinements of the structures by full-matrix least-squares methods were based on 1499 unique reflections ($2\theta_{max} = 45°$, $I > 2\sigma I$) for **II**, 3380 unique reflections ($2\theta_{max} = 52°$, $I > 3\sigma I$) for **III**, and 2743 unique reflections ($2\theta_{max} = 45°$, $I > 3\sigma I$) for **IV**. At the conclusion of refinement on 235 parameters for **II**, 329 parameters for **III**, and 205 parameters for **IV**, $R = 0.067$, 0.038, and 0.026 respectively for **II**, **III**, and **IV**.

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