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Chalcogenometalate Complexes of Nb^V and Ta^V. Synthesis and Structural Characterization of the Et_4N^+ Salts of the $[(E)_3M(S^tBu)]^{2-}$ Complexes (E = S, M = Nb, Ta; E = Se, M = Nb) and of $(Ph_4P)_2[(S)_3M(OMe)]$

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The rich chemistry of the readily accessible tetrathiometallate ions of the group VI elements $[MS_4]^{2-}$ (M = Mo, W) is well developed and forms the basis of the functional group Mo/S chemistry that has emerged in recent years.[1] In contrast the relative unavailability of group V tetrathiometalates (mainly of Nb and Ta prior to 1990) has been the reason for the relatively slow development of Nb/S or Ta/S chemistry. Indeed, a convenient "wet" synthesis of second and third row, group V tetrathiometalates, $[MS_4]^{3-}$ (M = Nb or Ta), was not known until lately[2] and the MS_4^{3-} anions were available only in products such as $M'_3(ME_4)$ (M′ = Cu(I), Tl(I); M = V, Nb, Ta: E = S, Se, Te)[4] or K_3Me_4[4] obtained from solid state, high temperature syntheses.

The recently reported[2] syntheses of the $[MS_4]^{3-}$ anions (M = Nb or Ta) are carried out in CH_3CN solution and employ simple alkoxide complexes of the pentavalent metal ions and the $(Me_3Si)_2S$ reagent. The replacement of the alkoxide ligands by S^{2-} is driven by the superior thermodynamic stability of the Me_3SiOR siloxane byproducts.

Previously we have reported[5] on the syntheses and structures of two new thiolate−thioniobate anions. In the trigonal bipyramidal $[Nb^V(S)(^tBuS)_4]^-$, **I**, and the tetrahedral $[Nb^V(S)_2(^tBuS)_2]^-$, **II**, complexes, the S^{2-} ligands have been generated as a result of C−S bond cleavage. These C−S bond cleavage reactions appear to follow two parallel pathways: (a) a heterolytic route that involves a *tert*-butylcarbonium ion, β-elimination, and generation of isobutene or (b) a homolytic route that involves *tert*-butyl free radicals and generates isobutane by proton abstraction from the CH_3CN solvent. The possibility that further C−S bond cleavage reactions or substitution of the RS^- ligands in **II** by S^{2-} may lead to an alternate, convenient synthesis of the $[NbS_4]^{3-}$ anion prompted the studies reported in this paper.

The Et_4N^+ "salts" of the $[M^V(S)_3(^tBuS)]^{2-}$ anions[6] (M = Nb (**III**), Ta (**IV**)) can be obtained as yellow crystals, in 67% and 33% yields, respectively, directly from the reactions of $NbCl_5$ or $TaCl_5$ with NaS^tBu in the presence of sulfur and Et_4NCl in CH_3CN solution. If, instead of sulfur, elemental selenium is used for the oxidation of the $^tBuS^-$ ligands the $(Et_4N)_2[Nb(Se)_3(S^tBu)]$ complex, **V**, is obtained in 30% yield.[7] The same complex also is obtained in the reaction of **I** with elemental selenium in 1:1 ratio in CH_3CN solution. The ^1H-NMR of **V** in CD_3CN solution shows the ^tBu resonance at 1.48 ppm. The exclusive formation of **V** and the absence of the $[Nb(Se)(S)_2(S^tBu)]^-$ anion as a coproduct suggest that in this reaction the oxidation of S^{2-} or $^tBuS^-$ by elemental selenium of a likely $[Nb(Se)(S)(S^tBu)_2]$ intermediate is fast and efficient and affords entirely **V**.

The Ph_4P^+ "salt" of **III** also can be obtained in 56% yield by the reaction of **II** with $^tBuS^-$ as a base in CH_3CN solution. The Lewis basic ligands in the syntheses of **III**−**V** facilitate cleavage of the C−S bond in the Nb-coordinated $^tBuS^-$ ligands by deprotonating a nascent ^tBu carbonium ion and forming isobutene. The same reaction with sodium methoxide, NaOMe, as a base affords the $[Nb(S)_3(OMe)]^{2-}$ anion that can be isolated in 33% yield[8] as yellow crystalline $(Ph_4P)_2[Nb(S)_3(OMe)]\cdot CH_3CN$, **VI**. It is assumed that in the latter synthesis the $[Nb^V(S)_3(^tBuS)]^{2-}$ complex that forms originally reacts further with the CH_3OH reaction byproduct to form **VI**. This assumption is based on the observation that **VI** also can be obtained by the reaction of **III** with methanol.

Examination of the contents of both the head space and the solutions following the syntheses of **III** and **VI** (by gas-chromatographic−mass-spectroscopic, GC−MS, analyses) revealed the presence of both ^tBuSH and isobutene with their characteristic fragmentation patterns. The solution from the synthesis of **VI** also showed methanol in the GC−MS analysis. The lack of $NC-CH_2CH_2-CN$, found previously[5] in the synthesis of **I** and **II**, suggests that a free radical mechanism is not a significant pathway in the syntheses of **III** and **VI** in CH_3CN solution.

The infrared spectra of **III**−**V** show the M=E vibrations at 476, 457, and 444 cm^{-1} for M = Nb and E = S, at 458 (m), 443 (s), and 433 (vs) cm^{-1} for M = Ta and E = S, and at 478, 460 and 418 cm^{-1} for M = Nb and E = Se. For **VI** the Nb=S vibrations are found as an unresolved band around 458 cm^{-1}. The electronic spectra of **III**, **IV**, and **VI** in CH_3CN solution[9] resemble the spectra reported for the tetrachalcogenoniobates) (274 and 340 nm for NbS_4^{3-} [2] and 518 nm for $NbSe_4^{3-}$ [10]).

Single crystals of **III**−**VI** were obtained by slow diffusion of diethyl ether into CH_3CN solutions of the complexes, and their crystal structures were determined by single-crystal X-ray

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(6) (a) Anal. Calcd for $NbS_4N_2C_{20}H_{49}$: C, 44.50; H, 9.17; N, 5.20. Found: C, 44.78; H, 9.15; N, 5.32. ^1H NMR (CD_3CN): 1.38 ppm. (b) Anal. Calcd for $TaS_4N_2C_{20}H_{49}$: C, 38.32; H, 7.88; N, 4.47. Found: C, 38.08; H, 7.62; N, 4.46. ^1H NMR (CD_3CN): 1.39 ppm.

(7) Anal. Calcd for $NbSe_3SN_2C_{20}H_{49}$: C, 35.35; H, 7.27; N, 4.12. Found: C, 35.35; H, 7.58; N, 4.18. ^1H NMR (CD_3CN): 1.48 ppm.

(8) Anal. Calcd for $NbS_3P_2NOC_{51}H_{46}$: C, 65.15; H, 4.93; N, 1.49. Found: C, 65.07; H, 4.98; N, 1.45. ^1H NMR (CD_3CN): methoxy methyl protons at 3.24 ppm.

(9) Electronic spectra in CH_3CN solution: for the $(Et_4N)_2[Nb(S)_3(S^tBu)]$ complex, **III**, 357, 270 nm; for the $(Et_4N)_2[Ta(S)_3(S^tBu)]$ complex, **IV**, 316 nm; for the $(Et_4N)_2[Nb(Se)_3(S^tBu)]$ complex, **V**, 400, 298 nm; for the $(Ph_4P)_2[Nb(S)_3(OMe)]$ complex, **VI**, 345, 268 nm.

(10) Omloo, W. P. F. A. M.; Jellinek, F.; Müller, A.; Diemann, E. *Z. Naturforsch.* **1970**, *B25*, 1302. In this reference the reflectance spectra of the Tl^{III} salts of $NbSe_4^{3-}$ and NbS_4^{3-} are reported. The latter is reported to be a red-brown compound with an absorption at 417 nm and is at variance with the more recent paper[2] that reports on a yellow NbS_4^{3-} with absorptions at 274 and 340 nm.

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Table 1. Summary of Interatomic Distances (Å) and Angles (deg) in $(Ph_4P)[Nb(S)_2(S^tBu)_2]$ (**II**), $(Et_4N)_2[Nb(S)_3(S^tBu)]$ (**III**), $(Et_4N)_2[Ta(S)_3(S^tBu)]$ (**IV**), $(Et_4N)_2[Nb(Se)_3(S^tBu)]$ (**V**), and $(Ph_4P)_2[Nb(S)_3(OMe)]\cdot CH_3CN$ (**VI**)

	II[a]	**III**	**IV**	**V**	**VI**
		Distances[b]			
$M{=}S_t$[c]	2.184(3), 2.191(45)	2.230(6)	2.234(5)	2.313(3), 2.360(2)	2.239(3)
$M{-}S_L(O_L)$[d]	2.374(5), 2.380(4)	2.439(2)	2.425(3)	2.422(3)	1.938(8)
		Angles			
$S_t{-}M{-}E_t$	111.8(1)	111.6(9)	111.7(9)	111.4	111.3(4)
$S_t{-}M{-}S_L(O_L)$	109.5(5)	107.2	107.0	107.5	107.5(2)

[a] From ref 5. [b] Mean values of crystallographically independent, chemically equivalent structural parameters when more than two values are available. The number in parentheses represents the larger of the individual standard deviations or the standard deviation from the mean, $\sigma = [\sum_{i=1}^{N}(x_i - x)^2/N(N-1)]^{1/2}$. [c] S_t = terminal sulfido or selenido ligands. [d] S_L = S^tBu ligands.

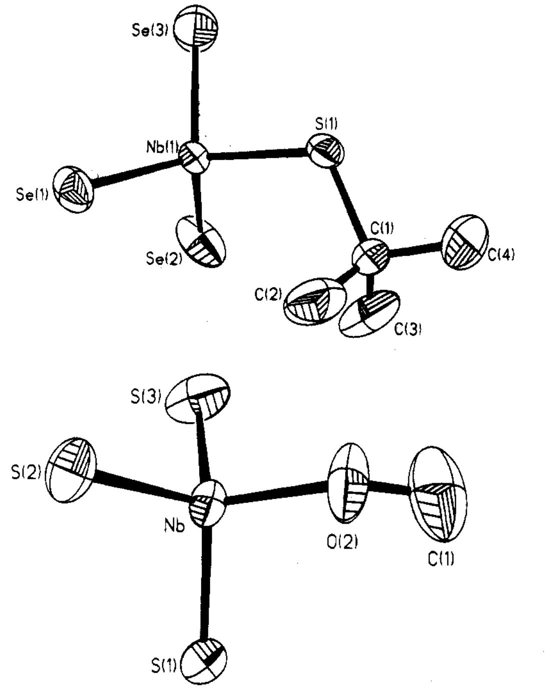

Figure 1. Structure and labeling of the anions in the $[(E)_3M(S^tBu)]^{2-}$ complexes (E = S, M = Nb, Ta; E = Se, M = Nb) and in $(Ph_4P)_2[(S)_3M(OMe)]$ Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

crystallographic studies[11] (Figure 1). The mean Nb=S bond in **III** at 2.231(6) Å (Table 1) is longer than the Nb=S bonds in either **II** at 2.187(4) Å or in the pentagonal bipyramidal $NbS(SCNEt_2)(S_2CNEt_2)_2$ at 2.178(3) and 2.180(2) Å.[12] However it is significantly shorter than the same bond in the $[NbS_4]^{3-}$ anion at 2.274 Å. The Nb=S bond distances in **II**, **III**, and $[NbS_4]^{3-}$ show a nearly monotonic increase in length and reflect the effects of both an increase of negative charge as well as a weakening of the Nb−S dπ−pπ bonding with the S^{2-} ligands from **II** to $[NbS_4]^{3-}$. The Nb=S in **VI** is essentially the same as that in **III**. The unperturbed Nb=Se bond in **V** at 2.333 Å is short by comparison to the bonds in K_3NbSe_4 [4b] that range from 2.387(1) to 2.403(1) Å and the bonds in the $K_2CuNbSe_4$ extended solid that contains edge-shared $NbSe_4^{3-}$ tetrahedra. In the latter two compounds the Se ligands either bridge between Nb(V) ions or interact with metal counterions in the lattice. In the seven-coordinate, distorted pentagonal bipyramidal, $NbSe_7$ core subunits of $K_3CuNb_2Se_{12}$ the Nb=Se bonds range from 2.407(3) to 2.928(3) Å.[13]

The difficulty in obtaining the MS_4^{3-} anions (M = Nb, Ta) as quaternary organic cation salts and the possible stabilizing role of the alkali metal ion have been discussed previously in connection with the synthesis and characterization of solvated Li_3MS_4 salts.[2] In **III** the "neutralization" of excessive negative charge in the small highly charged NbS_4^{3-} anion becomes possible by the interactions of this anion with the $^tBu^+$ carbocation not unlike the apparent stabilization effected by the Li^+ ions in the Li_3MS_4 salts.[2]

The vast majority of mononuclear Nb(V) complexes that contain sulfur ligands, and no more than one S^{2-} ligands are found with coordination numbers of five,[14] six,[15] or seven.[16] The tetrahedral geometry of the ME_4 cores in **II**−**VI** is not unexpected and represents the structural arrangement of four ligands that minimizes repulsions between the S^{2-} ligands. The existence of $[Nb^V(S)(^tBuS)_4]^-$, **I**, with a trigonal bipyramidal structure,[5] suggests that the coordinatively unsaturated complexes **II** to **VI** may add ligands to form five-coordinate complexes with possibly trigonal bipyramidal structures. Such structures with *all* of the S^{2-} ligands axially or equatorially arranged would be subject to minimal interligand repulsions and should be stable particularly when highly charged species such as the hypothetical $[Nb^V(S)_3(^tBuS)_2]^{-3}$ derivative of **III** is stabilized by interactions with Li^+ or other alkali metal ions.

The chemistry of the alkylated group V chalcogenido anions and derivatives presently is under investigation in our laboratory.

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Supplementary Material Available: Tables S1a−S4a, containing crystal and refinement data, positional parameters, thermal parameters, and selected distances and angles of **III**−**VI**, respectively (37 pages). Ordering information is given on any current masthead page.

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(11) The structures of **III**−**VI** have been determined by X-ray crystallography with *R* values of 0.047, 0.057, 0.046, and 0.051, respectively. Crystal and refinement data have been deposited as supplementary material.

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(15) For examples see: (a) $[M(SR)_6]^-$ (R = aromatic groups; M = Nb, Ta), Koo, S.-M.; Bergero, R.; Salifoglou, A.; Coucouvanis, D. *Inorg. Chem.* **1990**, *29*, 4844−4846. (b) $[M(S_2C_6H_4)_3]^-$ (M = Nb, Ta), Martin, J. L.; Takats, J. *Inorg. Chem.* **1975**, *14*, 1358 and references therein.

(16) For examples see: (a) $NbS(SCNEt_2)(S_2CNEt_2)_2$, ref 12. (b) $NbS(S_2CNEt_2)_3$, Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3811. (c) $NbO(S_2CNEt_2)_3$, Dewan, J. C.; Kepert, D. L.; Raston, C. L.; Taylor, D.; White, A. H.; Maslen, E. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2082. (d) $NbCl_3(S_2CNEt_2)_2$, Canich, J. A. M.; Cotton, F. A. *Inorg. Chim. Acta* **1989**, *159*, 163.