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Group 5 Tetrathiometalates: Simplified Syntheses and Structures

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The tetrathiometalates $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$, previously known only in the form of intractable solids prepared at high temperatures, have been synthesized in the reaction system $M(OEt)_5/(Me_3Si)_2S/LiOMe$ (1:4:3) in acetonitrile solution at ambient temperature The species $[VS_4]^{3-}$ was prepared similarly from $VO(OMe)_3$. The initial product in these systems is $Li_3[MS_4]\cdot 4MeCN$ (M = V, Nb, Ta), as established by the structure of the niobium compound. $Li_3[NbS_4]\cdot 4MeCN$ crystallizes in orthorhombic space group *Fddd* with $a = 6.0772$ (6) Å, $b = 24.682$ (4) Å, $c = 25.683$ (4) Å, and $Z = 8$. Pure and stable products were obtained by recrystallization of the TMEDA adducts to afford $Li_3[MS_4]\cdot 2TMEDA$ (M = V (dark red), Nb (light yellow), Ta (colorless) (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine)). These compounds are isomorphous and crystallize in tetragonal space group $P\bar{4}n2$ with $a = 13.902\,(3)/13.983\,(6)/13.994\,(2)$ Å, $c = 6.0474\,(9)/6.152\,(3)/6.1633\,(5)$ Å, and $Z = 2$ for M = V/Nb/Ta. The crystal structures reveal discrete, essentially tetrahedral $[MS_4]^{3-}$ species with imposed D_{2d} symmetry and four S···S edges bridged by Li^+ in distorted tetrahedral coordination. Opposite edges are bridged by Li^+ to form a linear chain of $[MS_4]^{3-}$ units; two other edges are bridged by Li^+ coordinated to two MeCN ligands or one TMEDA ligand. The differences in colors of the three chromophores arise from a progressive high-energy shift of the first LMCT band ($1t_1 \rightarrow 2e$) in the series M = V (501, 561 nm), Nb (340 nm), Ta (300 nm). $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ are the simplest of the few discrete soluble chalcogenoniobates and -tantalates that have thus far been prepared; structures of these species are illustrated. The role of Li^+ in stabilizing and solubilizing the product compounds is considered, and unknown tetrathiometalates that might be obtained by the cation-stabilizing aspect of the methods used here are pointed out.

Introduction

The simplest and, thus far, most synthetically useful species in the rapidly expanding chemistry of soluble transition metal chalcogenides $[M_mQ_n]^{z-}$ (Q = S, Se, Te)[2-5] are the d^0 tetrathiometalates $[MS_4]^{z-}$.[6-12] These have been prepared with M = V,[7-10] Mo,[7,11] W,[7,11] and Re[7,9,12] by reaction of an appropriate oxometalate with H_2S in a strongly alkaline aqueous solution. Given that tractable salts of $[VS_4]^{3-}$ have been isolated[8-10]—the first of these over 100 years ago[8]—it is perhaps unexpected that the analogous group 5 species $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ do not present a similarly lengthy history. These species are, however, known in the solid state and were first recognized in the set of compounds M'_3MQ_4 (M = V, Nb, Ta; M′ = Cu(I),[13] Tl(I)[14]) that were prepared from the elements at 500–800 °C. Subsequently, the phases $Cu_3MS_{4-n}Se_n$ (M = Nb, Ta; *n* = 1–3) were also obtained at high temperatures.[15] In all of these insoluble phases, the $[MS_4]^{3-}$ ions are not discrete but are covalently linked to M(I) atoms in cubic structures similar to that of sulvanite (Cu_3VS_4), the first compound containing a tetrathiometalate whose structure was determined.[16] The compound $Ba_6(NbS_4)(NbOS_3)$ has been formed as a byproduct in high-temperature BaS/Nb/S reaction systems and identified crystallographically.[17] More recently, the compounds Cs_3MSe_4[18] and K_3MQ_4[19] (M = Nb, Ta; Q = S, Se) have been synthesized by high-temperature methods, typically at 1150 °C for 8 days. The solubility properties of these compounds have not been described. Consequently, none are of evident use for solution reaction chemistry.

The niobium and tantalum tetrathiometalates are of current interest and significance for two reasons. First, earlier attempts in this laboratory to prepare them from polynuclear oxometalates and H_2S were either unsuccessful or inconclusive. Another approach utilized the reaction system $M(OEt)_5/(Me_3Si)_2S/Et_4NCl$ (1:4:1.4) in acetonitrile but, rather than $[MS_4]^{3-}$, afforded the unique C_{5v} cages $[M_6S_{17}]^{4-}$ (M = Nb, Ta), illustrated in Figure 1, as Et_4N^+ salts in moderate yield.[2] We have also been unable to repeat the claimed preparation of $[NbO_2S_2]^{3-}$ from Nb_2O_5 and H_2S in aqueous base.[20] Thus, a different synthetic method is required. Second, the predominant route to heteronuclear MFe_3S_4 cubane-type clusters of the earlier transition elements[21] (M = V,[22] Mo and W,[23] Re[24]) is self-assembly in reaction systems containing $[MS_4]^{z-}$ as an obligatory component. Access to $NbFe_3S_4$ and $TaFe_3S_4$ clusters would appear to rest on the availability of the corresponding tetrathiometalates.

We have recently turned our attention again to reaction systems containing $M(OEt)_5$ and hexamethyldisilthiane. As reported recently, we have been successful in preparing soluble salts of $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ in acceptable yields.[25] Here we describe

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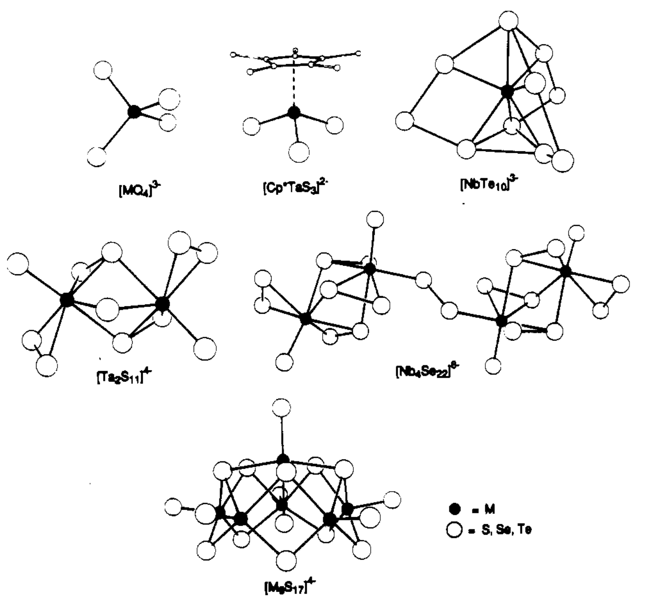

Figure 1. Structures of the discrete chalcogenoniobates and -tantalates $[MQ_4]^{3-}$ (M = Nb, Ta; Q = S, Se) (this work[18,19]), the $[Cp^*TaS_3]^{2-}$ fragment of $[Cp^*TaS_3Li_2(THF)_2]_2$,[32] $[NbTe_{10}]^{3-}$,[39] $[Ta_2S_{11}]^{4-}$,[40] $[Nb_6Se_{22}]^{6-}$,[40] and $[M_6S_{17}]^{4-}$.[2]

in detail the synthetic procedure and a closely related method for the preparation of $[VS_4]^{3-}$ and the full characterization by X-ray structural determinations and UV–visible absorption spectra.

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen atmosphere. Methanol was distilled from $Mg(OMe)_2$, acetonitrile from CaH_2, and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) from $LiAlH_4$ and were degassed before use. Hexamethyldisilthiane ($(Me_3Si)_2S$) was obtained from Aldrich, and $Nb(OEt)_5$ and $Ta(OEt)_5$ were from Aldrich or Strem.

$Li_3[MS_4]$·4MeCN (M = Nb (1), Ta). A mixture of 179 mg (4.71 mmol) of LiOMe in 20 mL of acetonitrile was treated with 1.32 mL (6.29 mmol) of $(Me_3Si)_2S$, and the resultant mixture was stirred until all solid dissolved. A solution of 1.57 mmol of $M(OEt)_5$ in 20 mL of ether was added, yielding an orange (M = Nb) or canary-yellow (M = Ta) solution and within ca. 5 min a white precipitate. The solution was stirred for 1.5 h, and the white microcrystalline solid was collected by filtration and dried in vacuo to afford the product in 66–70% yield. IR (KBr): 2271, 1360, 462 cm^{-1} (M = Nb); 2272, 1361, 440 cm^{-1} (M = Ta). These compounds were slightly soluble in acetonitrile. Washing with ether or acetonitrile causes a color change from white to red; the red species was not identified. These compounds are insufficiently stable for elemental analysis; composition is based on the X-ray structure of the M = Nb compound.

$Li_3[VS_4]$·2TMEDA (2). To a slurry of 90 mg (2.37 mmol) of LiOMe in 10 mL of acetonitrile was added 0.66 mL (3.15 mmol) of $(Me_3Si)_2S$. The mixture was stirred until all of the LiOMe dissolved. A solution of 126 mg (0.787 mmol) of $VO(OMe)_3$[26,27] in 10 mL of acetonitrile was added, yielding a dark red solution. The reaction mixture was stirred for 5 h; within 2 h, a violet solid precipitated. After removal of most of the solvent by cannula, 800 mg (6.88 mmol) of TMEDA was added, causing the solid to dissolve. Over 2 d, 40 mL of ether was introduced into this solution by vapor diffusion. The solid was collected, washed with ether, and dried in vacuo to afford 220 mg (64%) of product as dark red crystals. Anal. Calcd for $C_{12}H_{32}Li_3N_4S_4V$: C, 33.33; H, 7.46; Li, 4.82; N, 12.96; S, 29.66; V, 11.78. Found: C, 33.28; H, 7.54; Li, 4.73; N, 12.86; S, 29.76; V, 11.68. IR (KBr): ν_{VS} 477 cm^{-1}. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 346 (5400), 380 (sh, 4000), 501 (3600), 561 (sh, 2200) nm.

$Li_3[NbS_4]$·2TMEDA (3). To a slurry of 90 mg (2.37 mmol) of LiOMe in 10 mL of acetonitrile was added 0.66 mL (3.15 mmol) of $(Me_3Si)_2S$. The mixture was stirred until all of the LiOMe dissolved. A solution of 250 mg (0.786 mmol) of $Nb(OEt)_5$ in 10 mL of ether was added, yielding an orange solution and white precipitate. The mixture was stirred for 1.5 h and its volume reduced to ca. 2 mL by solvent removal by cannula. The residual mixture was dissolved by the addition of 548 mg (4.71 mmol) of TMEDA. Ether (25 mL) was slowly added, resulting in the separation of light yellow crystals. This material was collected, washed with ether, and dried in vacuo to afford the 200 mg (54%) of product. Anal. Calcd for $C_{12}H_{32}Li_3N_4NbS_4$: C, 30.38; H, 6.80; Li, 4.39; N, 11.81; Nb, 19.58; S, 27.03. Found: C, 30.46; H, 6.73; Li, 4.29; N, 11.87; Nb, 19.43; S, 27.15. IR (KBr): ν_{NbS} 435 cm^{-1}. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 274 (14 900), 340 (10 000).

$Li_3[TaS_4]$·2TMEDA (4). This compound was prepared by the preceding method with use of $Ta(OEt)_5$. The initial reaction gave a light yellow solution and a white crystalline solid; the product was obtained as very light yellow, nearly colorless crystals. When the preceding preparation was conducted on a scale of ca. 80%, the product was obtained in 59% yield. Anal. Calcd for $C_{12}H_{32}Li_3N_4S_4Ta$: C, 25.62; H, 5.75; Li, 3.70; N, 9.96; S, 22.80; Ta, 32.16. Found: C, 25.43; H, 5.56; Li, 3.88; N, 9.78; S, 22.65; Ta, 32.46. IR (KBr): ν_{TaS} 435 cm^{-1}. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 241 (17 500), 249 (sh, 16 000), 300 (10 700).

Collection and Reduction of X-ray Data. With reference to Table I, diffraction-quality crystals of compounds **1**–**4** were readily obtained from the crude reaction mixtures by diffusion (**1** as pale yellow rectangular blocks, **2** as deep violet tetragonal blocks), layering (**3** as pale yellow crystals), or slow addition (**4** as white crystals) of ether. Crystals were transferred under a dinitrogen atmosphere into a layer of Paratone-N oil for microscopic inspection in air; this technique[28] is satisfactory for protection from atmospheric oxygen and moisture and solvent loss during crystal selection, although crystals of **1** were found to desolvate rapidly even under the oil layer. Suitable single crystals were selected and affixed, with the aid of the oil, to the tips of quartz capillary fibers; immediate transfer to a cold N_2 stream of a low-temperature goniometer froze the crystals to their mounts and provided protection from the atmosphere. Diffraction data were collected using graphite-monochromatized Mo Kα radiation on a Siemens R3m/v four-circle automated diffractometer equipped with a LT-2 cryostat operating at ca. 173 K. Following preliminary indexing, refined unit cell parameters were obtained by least-squares fits of machine-centered reflections (**1**, 50 with $25° \le 2\theta \le 35°$; **2**, 39 with $24° \le 2\theta \le 35°$; **3**, 50 with $16° \le 2\theta \le 35°$; **4**, 46 with $26° \le 2\theta \le 34°$). Data sets were processed and corrected for Lorentz and polarization effects with a locally modified version of XDISK (SHELXTL program suite, Siemens XRD Corp., Madison, WI). Empirical absorption corrections (PSICOR) were applied using azimuthal Ψ-scan data for **2** and **4**; for **1**, this correction was unsatisfactory and XABS was used instead. The intensities of three check reflections were monitored every 97 reflections with no significant decay observed over the course of the data collections. For crystals with noncentrosymmetric space groups (**2**–**4**), Friedel equivalents were collected and treated as independent data. Crystallographic data are provided in Table I.

Solution and Refinement of Structures. Atom scattering factors were taken from a standard source.[29] Initial solutions for **1** and **3** were obtained by direct methods. For **1**, systematic absences uniquely determined the space group to be *Fddd* (No. 70) and direct methods yielded the positions of the Nb and S atoms. For **3**, axial photographs and intensities of symmetry-equivalent reflections indicated 4/*mmm* Laue symmetry; systematic absences further narrowed the choice of space group to $P4_2nm$ (No. 102), $P\bar{4}n2$ (No. 118), or $P4_2/mnm$ (No. 136), with simple *E* statistics suggesting a noncentrosymmetric cell. The positions of all non-hydrogen atoms were obtained by direct methods in $P\bar{4}n2$; this choice as the proper space group was confirmed by refinement to convergence. Intensity data for **2** and **4** implied structures isomorphous with **3**; this was corroborated by successful refinements using the coordinates of **3** as a trial structure. Atoms not initially located by direct methods were found by successive Fourier or difference Fourier maps with intervening cycles of full-matrix least-squares refinement (CRYSTALS, with graphical interface provided by XP from SHELXTL). All non-hydrogen atoms were treated anisotropically, with the exception of Li(1) in **2** and both Li atoms in **4**. For **3**, all hydrogen atoms were located by difference maps and refined isotropically. In the final stages of the refinements of **2** and **4**, hydrogen

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Table I. Crystallographic Data[a] for $Li_3[NbS_4]\cdot 4MeCN$ (**1**) and $Li_3[MS_4]\cdot 2TMEDA$ (M = V (**2**), Nb (**3**), Ta (**4**))

	1	**2**	**3**	**4**
formula	$C_8H_{12}Li_3N_4NbS_4$	$C_{12}H_{32}Li_3N_4S_4V$	$C_{12}H_{32}Li_3N_4NbS_4$	$C_{12}H_{32}Li_3N_4S_4Ta$
fw	406.19	432.42	474.39	562.43
cryst syst	orthorhombic	tetragonal	tetragonal	tetragonal
space group	*Fddd*	$P\bar{4}n2$	$P\bar{4}n2$	$P\bar{4}n2$
Z	8	2	2	2
a, Å	6.0772 (6)	13.902 (3)	13.983 (6)	13.994 (2)
b, Å	24.682 (4)	13.902 (3)	13.983 (6)	13.994 (2)
c, Å	25.683 (4)	6.0474 (9)	6.152 (3)	6.1633 (5)
V, Å^3	3853.4 (9)	1169.0 (4)	1203 (1)	1206.9 (3)
ρ_{calcd} (ρ_{obsd}[b]), g/cm^3	1.40[c]	1.23 (1.20)	1.31 (1.29)	1.55 (1.55)
T, K	173	173	173	173
μ, mm^{-1}	1.05	0.78	0.85	4.90
R[d] (R_w[e]), %	3.23 (3.74)	5.74 (3.77)	2.23 (2.59)	4.35 (3.66)

[a] All data collected with graphite monochromatized Mo Kα radiation (λ = 0.710 69 Å) using ω-scans. [b] Determined by neutral buoyancy in hexane/CCl_4. [c] Rapid desolvation precluded density measurements. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum(w|F_o|^2)\}^{1/2}$, with the weighting scheme provided by a three-term Chebyshev polynomial: Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698.

Table II. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (×10^2, Å^2) for $Li_3[NbS_4]\cdot 4MeCN$ (**1**)

atom	x	y	z	U[a]
Nb	1250	1250	1250	2.2
Li(1)	-3750	1250	1250	3.6
Li(2)	1250	2483 (3)	1250	3.9
S	-960 (1)	1793 (1)	1738 (1)	3.0
N	3309 (7)	2930 (2)	1677 (2)	5.6
C(1)	4743 (10)	3050 (2)	1924 (2)	5.9
C(2)	6650 (13)	3182 (3)	2247 (3)	9.2

[a] All atoms were refined anisotropically. Equivalent isotropic thermal parameters (U) were generated from $U = (U_1U_2U_3)^{1/3}$, where U_i are the principal axes of the anisotropic thermal ellipsoid.

atoms were placed at calculated positions 0.96 Å from, and with isotropic parameters 1.2 times those of, their parent carbon atoms. No hydrogen atoms were located or placed in **1**. The correct polarity of the noncentrosymmetric structures was determined by refinement of an enantiomorph-polarity parameter.[30] Final R values are given in Table I, and atomic coordinates are set out in Tables II and III; other crystallographic data are available elsewhere.[31]

Results and Discussion

Synthesis. Isolation of the polythiometalates $[M_6S_{17}]^{4-}$ (M = Nb, Ta) from reaction 1[2] suggested that modified, but similar,

$$6M(OEt)_5 + 17(Me_3Si)_2S + 4Et_4NCl \xrightarrow{MeCN} (Et_4N)_4[M_6S_{17}] \quad (1)$$

$$M(OEt)_5 + 4(Me_3Si)_2S + 3Et_4NCl \xrightarrow{MeCN} (Et_4N)_3[MS_4] \quad (2)$$

conditions might result in the synthesis of the tetrathiometalates $[MS_4]^{3-}$. In particular, the utility of the silicon–sulfur methodology, where silyl nucleophiles (e.g., RO^-, Cl^-) were used to unmask a latent sulfide source, was proven by the complete replacement of ethoxide with sulfide ligands. Although we have observed that stoichiometries exact for the production of tetrathiometalates in reaction 2 generate polythiometalates as the only isolable products, we decided to examine this reaction further on the basis of two mechanistic assumptions. Conceptually, reaction 2 may divert to the polythiometalate at two points: an alternative mechanistic pathway could shunt the intermediates *before* tetrathiometalate forms, or a decomposition pathway could be operative *after* initial generation of tetrathiometalate. We have observed that a mixture of $(Me_3Si)_2S$ and excess Et_4NCl in acetonitrile does not react at an appreciable rate; over a period of days, $(Me_3Si)_2O$ and was formed (presumably by hydrolysis with trace water), but no evidence of Me_3SiCl or Me_3SiS^- was found by NMR. Given this observation, a plausible sequence of events in reaction 1 might involve interaction of $(Me_3Si)_2S$ with coordinated ethoxide to afford an incompletely sulfided species, possibly $[MS(SSiMe_3)_3]_n$, owing to the unbalanced silyl:ethoxide ratio. Such a species might then comproportionate and/or react with chloride to afford the final polynuclear product. Alternatively, the reaction might initially produce some $[MS_4]^{3-}$, which then decomposes by reaction with other solution species to give polythiometalate. Possibilities include an incompletely sulfided complex and Et_4N^+. We have observed earlier that the ammonium salt of $[VS_4]^{3-}$, when in protic solvents, is stable only in strongly alkaline aqueous solution. All attempts to isolate more soluble salts by counterion metathesis with tetraalkylammonium ions have been unsuccessful,[9] probably due to reaction of $[VS_4]^{3-}$ with the β-CH_2 protons of the cation to afford alkene. This process, if occurring in reaction 2, would leave protons free to induce condensation of $[MS_4]^{3-}$ with elimination of H_2S.

Table III. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (×10^2, Å^2) for $Li_3[MS_4]\cdot 2TMEDA$ (M = V (**2**), Nb (**3**), Ta (**4**))

atom	x	y	z	U[a]
V	0	5000	2500	2.3
Li(1)	0	5000	-2500	4.1 (3)
Li(2)	-1498 (5)	3502 (5)	2500	2.6
S	-31 (1)	3748 (1)	396 (2)	3.0
N	-1567 (3)	2078 (3)	3424 (7)	3.0
C(1)	-1157 (4)	1958 (5)	5610 (12)	5.3
C(2)	-1070 (5)	1440 (4)	1900 (10)	4.6
C(3)	-2607 (4)	1882 (4)	3447 (11)	4.3
Nb	0	5000	2500	1.8
Li(1)	0	5000	-2500	3.6
Li(2)	-1522 (3)	3478 (3)	2500	3.0
S	-64 (1)	3694 (1)	301 (1)	2.6
N	-1607 (1)	2055 (2)	3446 (4)	2.8
C(1)	-1194 (3)	1929 (3)	5601 (7)	4.8
C(2)	-1109 (3)	1422 (2)	1915 (6)	4.4
C(3)	-2646 (2)	1871 (2)	3442 (7)	3.3
Ta	0	5000	2500	1.6
Li(1)	0	5000	-2500	3.1 (4)
Li(2)	-1511 (9)	3489 (9)	2500	3.1 (3)
S	-95 (2)	3693 (1)	302 (3)	2.4
N	-1611 (5)	2056 (6)	3455 (13)	2.8
C(1)	-1190 (8)	1913 (9)	5598 (18)	4.4
C(2)	-1105 (10)	1407 (8)	1930 (17)	4.3
C(3)	-2625 (7)	1875 (6)	3451 (17)	2.9

[a] Atoms with U values without esd's were refined anisotropically. Equivalent isotropic thermal parameters (U) were generated from $U = (U_1U_2U_3)^{1/3}$, where U_i are the principal axes of the anisotropic thermal ellipsoid.

With these considerations in mind, reactions 3 and 4 of Scheme I were explored. These reactions, conducted by *first* allowing 3

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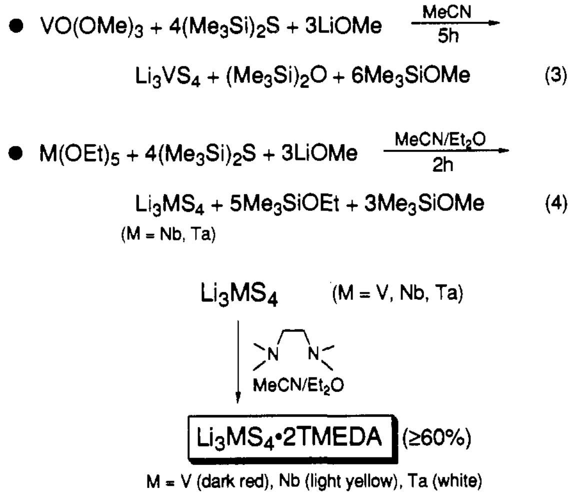
(31) See paragraph at end paper concerning supplementary material.

Scheme I. Synthesis of $[MS_4]^{3-}$ (M = V, Nb, Ta)



$$\bullet\ VO(OMe)_3 + 4(Me_3Si)_2S + 3LiOMe \xrightarrow[5h]{MeCN} Li_3VS_4 + (Me_3Si)_2O + 6Me_3SiOMe \quad (3)$$

$$\bullet\ M(OEt)_5 + 4(Me_3Si)_2S + 3LiOMe \xrightarrow[2h]{MeCN/Et_2O} Li_3MS_4 + 5Me_3SiOEt + 3Me_3SiOMe \quad (4)$$

equiv of LiOMe to react with 4 equiv of $(Me_3Si)_2S$, followed by addition of the metal alkoxide in ether, were found to proceed smoothly, precipitating $Li_3[MS_4]\cdot4MeCN$. These products are extremely sensitive to solvent loss and subsequent decomposition and are too unstable to be analyzed. The tetrasolvate formulation is based on the structure of the M = Nb compound (vide infra). Highly pure and stable products were obtained by recrystallization of TMEDA adducts, affording $Li_3[MS_4]\cdot2TMEDA$ in ca. 60% yields (Scheme I).

Replacement of Et_4NCl with LiOMe in reactions 3 and 4 addresses the problems perceived in reaction 2. The methoxide ion, a powerful silyl nucleophile, ensures that three Si–S bonds are cleaved rapidly and irreversibly. The importance of this step has been demonstrated. If LiOMe and $M(OEt)_5$ (M = Nb, Ta) are combined in MeCN/THF (THF solubilizes that tetrathiometalate product), a heterogeneous mixture is obtained. Addition of $(Me_3Si)_2S$ results in a rapid darkening of the solution from colorless to blue, then green, orange, and finally dark red, with slow dissolution of LiOMe. Although diffusion of ether into this solution in the M = Nb system yields some $[NbS_4]^{3-}$ salt, the dark color indicates the formation of polythiometalate species, likely $[M_6S_{17}]^{4-}$, the Et_4N^+ salts of which are red-black solids that form dark red solutions. In contrast, the addition of $M(OEt)_5$ to a homogeneous solution of $LiSSiMe_3/(Me_3Si)_2S$ (3:1) (obtained by the heterogeneous reaction of LiOMe and $(Me_3Si)_2S$) results in only a slower, milder darkening, to produce transparent red solutions. Indeed, by substitution of ether for THF in the solvent system, the side reaction is largely arrested, with the $[MS_4]^{3-}$ salt precipitating as it forms and the supernatant remaining a light orange (M = Nb) or yellow (M = Ta). Taken together, these results suggest that an alternative reaction path becomes operative if the tetrathiometalate is not rapidly generated and removed from solution.

Structures. Selected bond distances and angles are given in Table IV. The crystal structure of the initially precipitated product $Li_3[NbS_4]\cdot4MeCN$ is depicted in Figure 2. It consists of discrete, essentially tetrahedral $[NbS_4]^{3-}$ ions that interact with lithium ions by edge-bridging. The Nb and Li(1) atoms occur at sites of 222 symmetry. Two of the S···S edges are bridged by Li (2,2′) atoms, whose distorted tetrahedral coordination is completed by two acetonitrile molecules. The Li(1) atom interacts with the S···S_a edge and also with an edge in another $[NbS_4]^{3-}$ ion, resulting in a linear chain of bridged $[NbS_4]^{3-}$ units. The compounds $Li_3[MS_4]\cdot2TMEDA$ (M = V, Nb, Ta) are isomorphous (Table I), and the M = Nb and Ta compounds are practically isometric (Table IV). The crystal structures, shown in Figure 3, are strictly analogous to that of $Li_3[NbS_4]\cdot4MeCN$. The M and Li(1) atoms reside at 222 symmetry sites; four edges of distorted tetrahedral (D_{2d}) $[MS_4]^{3-}$ are bridged, two by Li(2,2′) which are chelated by TMEDA. The Li(1) atom bridges the edges of two anions, forming linear chains. The larger distortion of Li(2,2′) stereochemistry from tetrahedral in this set of compounds presumably arises from the bite distance constraints of the TMEDA chelate ring.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) in $Li_3[NbS_4]\cdot4MeCN$ (**1**) and $Li_3[MS_4]\cdot2TMEDA$ (M = V (**2**), Nb (**3**), Ta (**4**))

	1	**2**	**3**	**4**
M–S	2.274 (1)	2.157 (1)	2.2742 (7)	2.279 (2)
Li(1)–S	2.4978 (8)	2.470 (1)	2.5119 (7)	2.519 (2)
Li(2)–S	2.506 (6)	2.427 (7)	2.466 (4)	2.42 (1)
Li(2)–N	1.997 (6)	2.060 (8)	2.077 (5)	2.09 (2)
M–Li(1)	3.04	3.02	3.08	3.08
M–Li(2)	3.044 (8)	2.945 (9)	3.010 (6)	2.99 (2)
S–M–S(a)	107.57 (4)	107.71 (6)	106.98 (4)	107.1 (1)
S–M–S(b)	113.10 (4)	112.36 (9)	114.63 (3)	116.5 (1)
S(a)–M–S(b)	107.81 (4)	108.39 (8)	106.92 (3)	105.0 (1)
M–S–Li(1)	78.96 (2)	81.31 (3)	79.81 (2)	79.75 (6)
M–S–Li(2)	79.0 (1)	79.7 (2)	78.7 (1)	79.0 (3)
Li(1)–S–Li(2)	118.53 (5)	119.05 (8)	119.66 (4)	120.9 (1)
S–Li(1)–S(a)	94.51 (3)	89.68 (5)	93.39 (3)	93.43 (8)
S–Li(1)–S(b′)	119.77 (3)	121.84 (7)	121.46 (3)	123.2 (1)
S–Li(1)–S(c′)	115.14 (3)	118.56 (7)	114.76 (3)	113.2 (1)
N–Li(2)–N′	113.0 (5)	89.1 (4)	88.2 (3)	87.2 (8)

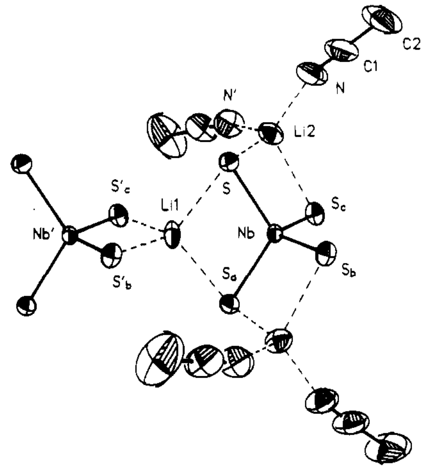


Figure 2. Crystal structure of $Li_3[NbS_4]\cdot4MeCN$ showing the atom-labeling scheme and 50% probability ellipsoids. The Nb and Li(1) atoms are located on 222 symmetry sites; primed and unprimed atoms are symmetry-related.

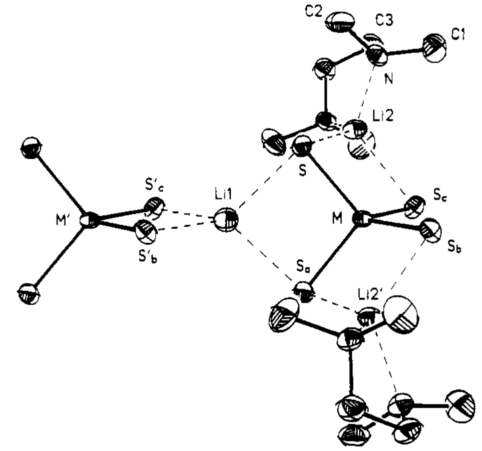


Figure 3. Crystal structure of the isomorphous compounds $Li_3[MS_4]\cdot2TMEDA$ (M = V, Nb, Ta) showing the atom-labeling scheme and 50% probability ellipsoids (M = Nb). The M and Li(1) atoms are located on 222 symmetry sites; primed and unprimed atoms are symmetry-related.

In all compounds, the $[MS_4]^{3-}$ ions have crystallographically imposed D_{2d} symmetry and thus three independent bond angles

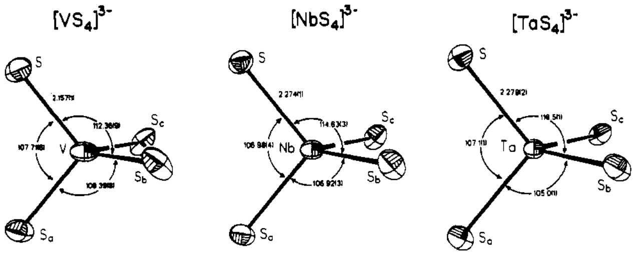


Figure 4. Structures of the anions $[MS_4]^{3-}$ as found with imposed D_{2d} symmetry in the compounds of Figure 2. Independent bond distances (Å) and angles (deg) are indicated.

and one independent bond distance. Structures of these ions in the $Li_3[MS_4]\cdot2TMEDA$ series are presented in Figure 4. All edges are bridged by lithium ions except symmetry-related $S\cdots S_b$ and $S_a\cdots S_c$. Bond angles reflect the bridging interactions and decrease in the order $S–M–S_b$ (116.5°) > $S_a–M–S_b$ (107.1°) > $S–M–S_a$ (105.0°), with the angles for $[TaS_4]^{3-}$ quoted as examples. In all four compounds, the unbridged angle is the largest and the angles involved in the $Li(1)–S,S_a,S'_b,S'_c$ interactions that generate the linear chains are the smallest. The V–S distance is indistinguishable from the mean value in the ammonium salt.[9] In the two compounds examined here, Nb–S distances are identical and only slightly longer than the mean value in the potassium salt (2.250 (7) Å).[19] Similarly, the Ta–S distance is the same as that in the Cp^*TaS_3 fragment (Figure 1) of $[Cp^*TaS_3Li_2(THF)_2]_2$.[32]

The Li–S bond distances are in the range 2.42–2.52 Å and thus are comparable to the most closely related of such distances, those involving the Cp^*TaS_3 fragment for which the mean value is 2.48 (4) Å.[32] These interactions are readily disrupted. The compounds $Li_3[MS_4]\cdot4MeCN$ are sparingly soluble in acetonitrile but are soluble in THF; the compounds $Li_3[MS_4]\cdot2TMEDA$ are soluble in acetonitrile and THF. The solubility of both sets of compounds in the two solvents is significantly increased in the presence of excess TMEDA.

Absorption Spectra. The previously reported absorption spectra of $[VS_4]^{3-}$, $[MoS_4]^{2-}$, $[WS_4]^{2-}$, and $[ReS_4]^{1-}$ are dominated by a series of intense, relatively sharp LMCT bands[7,9,10] that extend into the visible region, giving rise to deeply-colored solutions. The spectra of the $Li_3[MS_4]\cdot2TMEDA$ series of compounds in acetonitrile solutions are presented in Figure 5. While the $[VS_4]^{3-}$ solution is purple-red, the $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ chromophores are light yellow and nearly colorless, respectively. Initial[34] and more recent[35,36] considerations of the absorption spectra of tetrahedral $[MS_4]^{z-}$ agree that the lowest energy band (ν_1) is assigned as $1t_1 \rightarrow 2e$. Theoretical calculations of the electronic structure of $[MoS_4]^{2-}$ indicate the second band (ν_2) is $3t_2 \rightarrow 2e$.[35,36] If these assignments are extrapolated to the $[MS_4]^{3-}$ series (for which there are no theoretical results), the first four features in the $[VS_4]^{3-}$ spectrum reflect a significant splitting of the $^1T_2$ excited states (2130 cm^{-1} in ν_1, 2580 cm^{-1} in ν_2). Indeed, the spectrum of this ion is definitely sensitive to the cation and the medium,[7,9,10,34b] and no spectrum has been reported in which the ν_2 transition is not split. In the present case, the origin of the splitting is very probably ion-pair association between the anion and $Li(TMEDA)^+$, which in the crystal lowers the anion symmetry to D_{2d}.

The spectra of $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ are strongly blue-shifted compared to that of $[VS_4]^{3-}$. Energies of the ν_1 transitions of $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ are displaced by ca. 10 000 and 14 000 cm^{-1}, respectively, with reference to the mean ν_1 energy of $[VS_4]^{3-}$, accounting for the dramatic color differences. Band splitting is discernible only for ν_2 of $[TaS_4]^{3-}$ (1300 cm^{-1}), in accord with the more pronounced tendency of the smaller $[VS_4]^{3-}$ to form ion pairs. LMCT band shifts to higher energy in the order V ≪ Nb < Ta[37] are entirely consistent with the concept of optical electronegativity.[38] Indeed, the $[MS_4]^{3-}$ set is the only one in which Q → M charge-transfer features have been observed in three isoelectronic complexes of the same group.

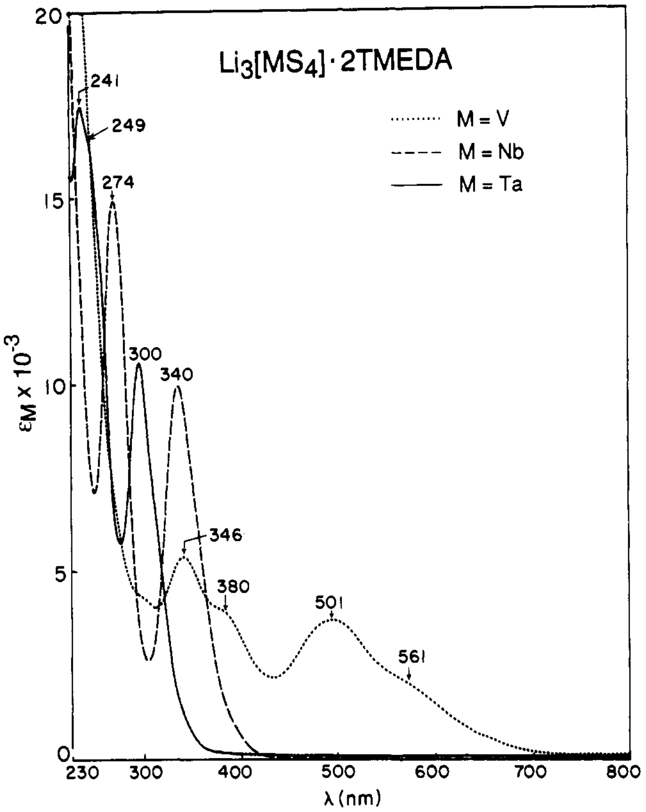


Figure 5. UV–visible absorption spectra of $Li_3[MS_4]\cdot2TMEDA$ in acetonitrile solutions. Band maxima are indicated.

Niobium and Tantalum Chalcogenometalates. With the structure proofs for $[MS_4]^{3-}$, there are now five discrete chalcogenometalates of these elements. The others, whose structures are illustrated in Figure 1, are $[NbTe_{10}]^{3-}$,[39] $[Ta_2S_{11}]^{4-}$,[40] $[Nb_4Se_{22}]^{6-}$,[40] and $[M_6S_{17}]^{4-}$.[2] While, strictly speaking, $[Cp^*TaS_3Li_2(THF)_2]_2$[32] is not a chalcogenometalate, its $[Cp^*TaS_3]^{2-}$ components, discrete except for the Li–S bridging interactions between them, represent the closest approach to the $[TaS_4]^{3-}$ ion prior to its synthesis. A general feature of the group 5 tetrathiometalates is the longer bond lengths than those of terminal M═S bonds in other compounds of vanadium,[41] niobium,[2,40,42]

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(33) The spectra of these four ions have been presented in a single plot.[9]

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and tantalum.[2,40,43] This follows simply on symmetry grounds, as the π-bond order in a tetrahedral d^0 complex cannot exceed the 1.5–2 range whereas, in the pseudotetragonal arrangements usually encountered in the other complexes, a bond order maximum of 3 is possible.

Other Tetrathiometalates. It is probable that the regime of stable $[MS_4]^{z-}$ species will involve the elements of groups 4–8 inasmuch as they display the oxidation states known to be capable (V–VII) or potentially capable (IV) of stabilizing four strongly nucleophilic sulfide ligands. Of this collection, tetrathiometalates of six of the fifteen elements have now been prepared. Species of chromium, manganese, and iron are improbable owing to the conflicting demand of high metal oxidation state and the ease of reducibility of that state. Of the remaining six, one or both of the ions $[TcS_4]^{-,2-}$ appear viable, as does $[RuS_4]^{2-}$ and (more likely) $[OsS_4]^{2-}$. One of the apparent factors contributing to the successful solution preparations of the group 5 species $[MS_4]^{3-}$ is the presence of Li^+, which serves to stabilize these small, highly charged nucleophiles. This same tactic of using a cation appropriate to stabilization *and* solubility might apply in preparing the group 4 tetrathiometalates $[MS_4]^{4-}$. (Here the high ion charge might even require a divalent metal such as Mg^{2+}.) In this context, it is observed that other small, highly charged $[MS_4]^{z-}$ species (M = Fe,[44] Ge,[45] Sn[46]) have been stabilized in the solid state by immersion in a sea of cations,[44] together with some contribution from hydrogen bonding. Conceivably, the synthesis of soluble salts and stability in solution could be achieved by the approach introduced in this work.[47]

Finally, the compounds $Li_3[MS_4]\cdot 4MeCN$ serve as valuable synthetic precursors. The linear clusters $[MFe_2S_4Cl_4]^{3-}$ (M = Nb, Ta) have been prepared from them,[25] and we have recently demonstrated by a structural determination the formation of the triply bridged cluster $[Nb_2Fe_6S_8(SEt)_9]^{3-}$ containing $NbFe_3S_4$ cubane units. Future reports will deal with cluster formation from the group 5 tetrathiometalates.

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Supplementary Material Available: Crystallographic data for the compounds in Table I, including tables of intensity collections, positional and thermal parameters, and interatomic distances and angles (10 pages). Ordering information is given on any current masthead page.

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(42) Nb=S ≈ 2.09–2.20 Å: (a) Do, Y.; Holm, R. H. *Inorg. Chim. Acta* **1985**, *104*, 33. (b) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1985**, 1821. (c) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1358.

(43) Ta=S ≈ 2.18–2.23 Å: (a) Peterson, E. J.; Von Dreele, R. B.; Brown, T. M. *Inorg. Chem.* **1978**, *17*, 1410. (b) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1984**, 845.

(44) Na_5FeS_4: Klepp, K. O.; Bronger, W. *Z. Anorg. Allg. Chem.* **1986**, *532*, 23. This phase, prepared at 970 °C, contains discrete tetrahedral $[FeS_4]^{5-}$ ions surrounded by cations; it is the extreme case of cation stabilization of a small, highly charged anion.

(45) $Na_4GeS_4\cdot 14H_2O$: Krebs, B.; Jacobsen, H.-J. *Z. Anorg. Allg. Chem.* **1976**, *421*, 97.

(46) (a) $Na_4SnS_4\cdot 14H_2O$: Pohl, S.; Schiwy, W.; Weinstock, N.; Krebs, B. *Z. Naturforsch.* **1973**, *28B*, 565. (b) Na_4SnS_4: Jumas, J. C.; Vermot-Gaud-Daniel, F.; Philipott, E. *Cryst. Struct. Commun.* **1973**, *2*, 157.

(47) We do not insist that $[MS_4]^{3-}$ salts with quaternary organic cations cannot be prepared. In recent experiments, we have observed that acetonitrile solutions initially containing $NaSSiMe_3/(Me_3Si)_2S$ (3:1), Et_4NCl, and $M(OEt)_5$ (M = Nb, Ta) yield yellow solutions and precipitates. Absorption spectra reveal the diagnostic bands of $[MS_4]^{3-}$ as the (dominant) product, with no other bands present. Thus, $[MS_4]^{3-}$ is stable in solutions containing Et_4N^+,[48] although Na^+ probably plays an important stabilizing role. To date, we have been unable to *isolate* crystals of an $[MS_4]^{3-}$ salt containing quaternary counterions.

(48) A stable solution of the tricaprylmethylammonium salt of $[VS_4]^{3-}$ (toluene/DMF, 98:2 v/v) has been reported: Halbert, T. R.; Hutchings, L. L.; Rhodes, R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 6437.