The *pro-S* stereospecificity unearthed in E_1-catalyzed deprotonation agrees with the stereochemical convergency found for all PLP/PMP-dependent catalysis in which bond cleavage and formation have been demonstrated to occur only at the *si* face of C-4′ in the Schiff base complex.[19,20] Thus, despite the fact that E_1-mediated dehydration represents an unique offshoot of PMP-dependent catalysis, the stereochemical consistency of E_1 and all other PLP/PMP enzymes suggests that E_1 behaves as a normal vitamin B_6 dependent catalyst and C-3 deoxygenation follows the well-established PLP/PMP cofactor chemistry. This result also supports Dunathan's hypothesis that this class of enzymes, regardless of its catalytic diversity, evolved from a common progenitor.[19,21]

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Entry to the Solution Chemistry of Niobium and Tantalum Sulfides: Synthesis of Soluble Forms of the Tetrathiometalates $[MS_4]^{3-}$

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The tetrathiometalates $[MS_4]^{z-}$ are fundamental structural and reactive entities in transition-metal sulfide chemistry.[2] They serve as primary precursors for the synthesis of a diverse array of compounds ranging from small metal–sulfide anions to heterometal clusters.[2,3] The species $[VS_4]^{3-}$, $[MoS_4]^{2-}$, $[WS_4]^{2-}$, and $[ReS_4]^{1-}$ are generally prepared by action of H_2S on a strongly alkaline solution of the appropriate oxometalate[2] and have been obtained as soluble compounds. The existence of $[VS_4]^{3-}$, recently obtained as a soluble and stable Li^+ salt,[4] imples stability of $[MS_4]^{3-}$ (M = Nb, Ta), a matter confirmed by the high-temperature synthesis of $K_3[MS_4]$ from the elements (8 d, 1150 K).[5] These compounds are described as soluble in nonaqueous solvents, but characterization of solution species has not been reported. Low-temperature preparations of $[MS_4]^{3-}$ have been hampered by the lack of suitable oxometalate precursors, and as products of solution reactions these species have remained elusive. We report here facile *solution* syntheses of $[MS_4]^{3-}$.

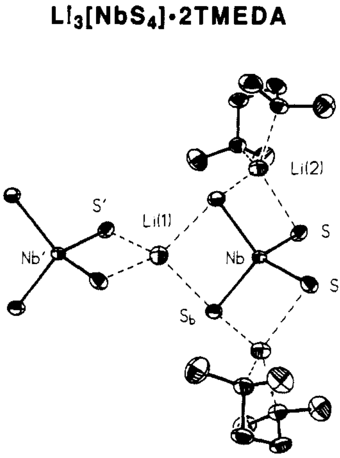
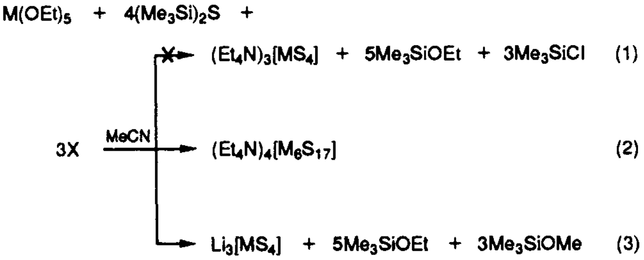


Figure 1. The structure of $Li_3[NbS_4]\cdot 2TMEDA$, showing 50% thermal ellipsoids and the atom-labeling scheme. The structure of $Li_3[TaS_4]\cdot 2TMEDA$ is isomorphous. Bond distances (Nb/Ta, Å): M–S, 2.274 (1)/2.280 (2); Li(1)–S, 2.512 (1)/2.518 (2); Li(2)–S, 2.465 (4)/2.40 (1). S–M–S bond angles (Nb/Ta, deg): 106.98 (4)/107.1 (1), bridged by Li(1); 106.92 (2)/104.0 (2), bridged by Li(2); 114.64 (3)/117.7 (2), unbridged.

Our first attempt to prepare $[MS_4]^{3-}$ (reaction 1, X = Et_4NCl) instead afforded the cages $[M_6S_{17}]^{4-}$ [6] (reaction 2), heretofore the only known soluble sulfides of Nb/Ta. However, anaerobic reaction 3 (X = LiOMe) generated after 3 h an orange-to-red supernatant and a precipitate, presumably $Li_3[NbS_4]\cdot 4MeCN$. Separation and dissolution of the latter in a solution of 6 equiv of *N,N,N′,N′*-tetramethylethylenediamine in acetonitrile followed by precipitation with ether afforded light-yellow $Li_3[MS_4]\cdot 2TMEDA$ (ca. 60%; M = Nb, Ta).[7] Compound identities were established by spectroscopy[8] and X-ray crystallography.[9]



The two compounds are isomorphous and isometric;[9] their structures are shown in Figure 1. The M = Nb/Ta atom resides on a position of 222 site symmetry, requiring D_{2d} anion symmetry with a distorted tetrahedral arrangement of sulfur atoms. Atom Li(1), also on a 222 site, interacts with four sulfur atoms from two adjacent anions, forming a linear polymeric chain. Symmetry-related atoms Li(2) bind to opposite pairs of sulfur atoms

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(7) Also, addition of THF to the M = Nb reaction mixture containing the precipitate resulted in a homogeneous solution; ether diffusion yielded pale yellow, readily desolvated $Li_3[NbS_4]\cdot 4MeCN$, which was identified crystallographically.

(8) λ_{max} (ϵ_M) (acetonitrile): 274 (ν_2, 14900), 340 (ν_1, 10000) nm ($[NbS_4]^{3-}$); 241 (ν_2, 17500), 249 (ν_2, sh, 16000), 300 (ν_1, 10700) nm ($[TaS_4]^{3-}$). ^{93}Nb NMR (CD_3CN/TMEDA, $(Et_4N)[NbCl_6]$ external reference): 1214 ppm, $\Delta H_{1/2} \approx 2000$ Hz). ν_{MS} (KBr) 458 (Nb), 435 (Ta) cm^{-1}.

(9) X-ray data were collected on a Nicolet P3F diffractometer with Mo Kα radiation. Structures were solved by direct methods or Patterson synthesis. Crystallographic data are given as a, b, c; α, β, γ; space group, Z, $2\theta_{min/max}$, unique data ($F_o^2 \geq 3\sigma(F_o^2)$), R (%). $Li_3[NbS_4]\cdot 2TMEDA$ (180 K): 13.983 (6), 13.983 (6), 6.152 (3) Å; $P\bar{4}n2$, 2, 3.0°/50.0°, 880, 2.23. $Li_3[TaS_4]\cdot 2TMEDA$ (180 K): 13.994 (2), 13.994 (2), 6.163 (1) Å; $P\bar{4}n2$, 2, 3.0°/55.0°, 1026, 6.10. $(Me_4N)_3[NbFe_2S_4Cl_4]\cdot DMF$ (180 K): 11.639 (2), 15.788 (3), 19.560 (3) Å; 70.11 (1)°, 89.59 (2)°, 86.83 (2)°; $P\bar{1}$, 4, 3.0°/50.0°, 9450, 3.23. $(Et_4N)_3[TaFe_2S_4Cl_4]$ (298 K): 13.212 (4), 18.515 (5), 18.039 (4) Å; 90°, 111.09 (2)°, 90°; $P2_1/n$, 4. The structure of this compound was only partially refined owing to extreme cation disorder; however, the refinement demonstrated that the anion is isostructural with $[NbFe_2S_4Cl_4]^{3-}$.

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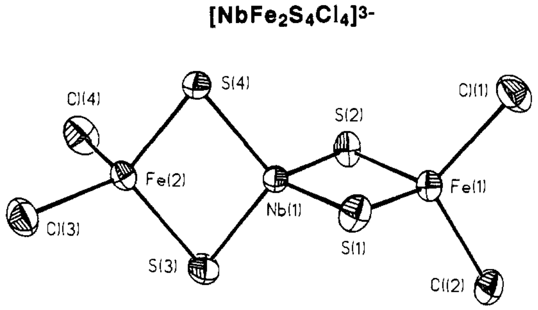

Figure 2. The structure of $[NbFe_2S_4Cl_4]^{3-}$, showing 50% thermal ellipsoids and the atom-labeling scheme. The following mean values are averaged over the two inequivalent anions. Bond distances (Å): Nb–S, 2.290 (4); Fe–S, 2.327 (5); Nb–Fe, 2.842 (8); Fe–Cl, 2.272 (3). Bond angles (deg): Fe–Nb–Fe, 176.16 (6); S(1)–Nb–S(2), 105.0 (2); Nb–S–Fe, 76.0 (2); S–Fe–S, 102.7 (3); Cl–Fe–Cl, 108.2 (6). $[TaFe_2S_4Cl_4]^{3-}$ is isostructural with this cluster.

of one $[MS_4]^{3-}$ anion and are chelated by one TMEDA molecule each. Relative to idealized T_d anion symmetry, Li^+ binding decreases S–M–S angles while the angle unbridged by Li^+ is considerably expanded. The unique Nb–S distance is slightly longer than those in K_3NbS_4 (2.241 (8)–2.258 (8) Å[5]). When compared to the shortest M–S bridge bonds in $[M_6S_{17}]^{4-}$ (M–μ_2S: mean 2.414 (4) Å (Nb), 2.405 (6) Å (Ta)[6]), it is clear that $[MS_4]^{3-}$ bond lengths correspond to multiple bonds,[10] a consistent property of all d^0 tetrathiometalates.

The compounds $Li_3[MS_4]\cdot 2TMEDA$ are freely soluble in strongly polar solvents such as DMF and Me_2SO, are somewhat soluble in THF and acetonitrile, and are very soluble in the latter two solvents in the presence of ca. 4 equiv of TMEDA/M. Anaerobic solutions lacking protic impurities are stable for days. Unlike other tetrathiometalates, $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ are not intensely colored but form pale yellow solutions in solvents such as THF and acetonitrile with patterns of narrow absorption bands characteristic of $[MS_4]^{z-}$ chromophores. The two lowest-energy LMCT bands (ν_1, ν_2) occur in the UV region in the energy order Ta > Nb;[8] ν_1, likely $1t_1 \rightarrow 2e$,[12] is solvent dependent and is split in THF solution (335, 376 nm, Nb; 295, 329 nm, Ta). In comparison, the red-purple $[VS_4]^{3-}$ chromophore absorbs into the visible but also with a split ν_1 band (523, 560 (sh) nm, Me_2SO).[4] The spectra indicate retention of tetrahedral structures of $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ in solution and define the optical electronegativity series V > Nb > Ta.

The different outcomes of reactions 2 and 3 are dependent on reactant X. In reaction 3, we propose that the stronger silyl nucleophile MeO^- reacts irreversibly and completely with $(Me_3Si)_2S$ to afford the silyl methyl ether and $Me_3SiS^-Li^+$,[13] which then attacks $M(OEt)_5$ to give the silyl ethyl ether and $[MS_4]^{3-}$. Inasmuch as Et_4NCl does not react with $(Me_3Si)_2S$ in acetonitrile over 1 week at room temperature, $[M_6S_{17}]^{4-}$ probably arises from direct reaction of the silyl sulfide with $M(OEt)_5$. That the cage product is sulfide poor with respect to initial mole ratios suggests incomplete reaction of the sulfiding agent and/or decomposition of initial products via sulfide loss. Also, Li^+ may have a stabilizing effect on $[MS_4]^{3-}$ by ion-pair interactions, as are quite apparent in the crystal structures of $Li_3[MS_4]\cdot 2TMEDA$.[14]

The potential of $[MS_4]^{3-}$ as precursors for cluster synthesis is evident from the reaction of these species (generated in situ) with 2 equiv of $FeCl_2$ or $[FeCl_4]^{2-}$. From orange-red acetonitrile solutions crystalline R_4N^+ salts (R = Me, Et) of $[MFe_2S_4Cl_4]^{3-}$ are readily isolated in moderate yields. The compound $(Me_4N)_3[NbFe_2S_4Cl_4]\cdot DMF$ crystallizes with two metrically similar anions in the asymmetric unit. $[NbFe_2S_4Cl_4]^{3-}$, shown in Figure 2, is a linear trinuclear cluster (Fe–Nb–Fe 176.16 (6)°) which approaches D_{2d} symmetry and is isostructural with $[TaFe_2S_4Cl_4]^{3-}$[9] and with previously reported $[VFe_2S_4Cl_4]^{3-}$[15] and $[MFe_2S_4Cl_4]^{2-}$ (M = Mo,[16] W,[16] Re[17]). Complexation results in only a small increase (0.02 Å) in the mean Nb–S bond length.

The ready accessibility of soluble forms of $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$ provides entry to what should be a diverse solution reaction chemistry of these ions. One manifestation of this is formation of the clusters $[MFe_2S_4Cl_4]^{3-}$ which, as was $[VFe_2S_4Cl_4]^{3-}$,[16] may themselves be precursors to the unknown heterometal MFe_3S_4 cubane-type clusters. We also anticipate that the synthetic methodology of reaction 3 may be applied to other transition metals to yield previously unknown $[MS_4]^{z-}$ species with as yet unexplored reactivities. These are areas of our continuing research.

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Supplementary Material Available: Positional and thermal parameters of $Li_3[MS_4]\cdot 2TMEDA$ and $(Me_4N)_3$-$[NbFe_2S_4Cl_4]\cdot DMF$ (17 pages). Ordering information is given on any current masthead page.

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[10] These M–S bond distances are as much as ca. 0.1–0.2 Å longer than those at Nb/Ta atoms with a single terminal sulfide,[6,11] a feature qualitatively rationalized in terms of 4 strongly π-bonding ligands in a tetrahedral arrangement vs one such ligand in other stereochemistries.

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Tailored Cationic Palladium(II) Compounds as Catalysts for Highly Selective Linear Dimerization of Styrene and Linear Polymerization of *p*-Divinylbenzene

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An important advantage in using transition-metal compounds as catalysts is the ability to tailor their activity and selectivity by a rational choice of ligands. We had earlier reported[1] that the palladium(II) species $[Pd(MeCN)_4](BF_4)_2$ (**1**) was an active catalyst for the polymerization of styrene (typical MW: 70 000) and the di- and trimerization of α-methylstyrene to the corresponding indan derivatives at room temperature. The usual cationic mechanism was invoked for these transformations.[1] Herein, we report that the replacement of the weakly coordinating MeCN ligands in **1** by more strongly ligating and bulkier pyridine and phosphine derivatives results in the formation of highly selective catalysts for selective linear dimerization of styrene and linear polymerization of *p*-divinylbenzene. The new catalyst systems differ from most existing systems[2] for the cationic oligomerization and polymerization of styrene derivatives in several important ways. Specifically, (a) no indan derivative or higher oligomers are formed from styrene;[2] (b) only styrene reacts when a mixture of styrene and α-methylstyrene is employed, although

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