

Soluble Sulfides of Niobium(V) and Tantalum(V): Synthesis, Structures, and Properties of the Fivefold Symmetric Cages $[M_6S_{17}]^{4-}$

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The reaction system $(Me_3Si)_2S:Et_4NCl:M(OEt)_5 = 4:1.4:1$ in acetonitrile affords the Et_4N^+ salt of the hexanuclear anion $[M_6S_{17}]^{4-}$ with $M = Nb$ (black, 55%) and Ta (dark brown, 33%). The compounds $(Et_4N)_4[M_6S_{17}] \cdot 3MeCN$, $M = Nb$ (Ta), crystallize in monoclinic space group $P2_1/c$ with $a = 14.799$ (4) Å (14.799 (3) Å), $b = 11.909$ (4) Å (11.949 (3) Å), $c = 40.024$ (11) Å (40.084 (8) Å), $\beta = 97.74$ (2)° (97.57 (2)°), and $Z = 4$. The anions are isostructural and virtually isometric and provide examples of rare fivefold symmetry. They are configured as an open cage built by the fusion of 10 nonplanar M_2S_2 rhombs to form a M_6S_{10} framework. An apical M atom is located on the C_5 axis, which is perpendicular to successive planes of five μ_3 -S, five M (basal), and five μ -S atoms. Each M site has a terminal sulfide ligand at a short distance (2.18 Å) consistent with a $M=S$ bond. The remaining sulfur atom (S_b) is located on the C_5 axis inside the cage at weakly bonding distances from the apical (2.62–2.64 Å) and basal (2.89–3.01 Å) $M(V)$ atoms. The entire anion closely approaches C_{5v} symmetry. Detailed structural data are reported. Absorption spectra at 250–700 nm consist of four LMCT features with energy order $Nb < Ta$. The ^{93}Nb NMR spectrum of $[Nb_6S_{17}]^{4-}$ in acetonitrile solution at 335 K exhibits two resolved resonances whose $\sim 4.3:1$ intensity ratio indicates retention of the solid-state structure in solution. Extended Hückel calculations of $[Nb_6S_{17}]^{4-}$ reveal rather localized framework bonding, no significant $M-M$ interactions (distances 3.39–3.65 Å), terminal $M=S$ bonds, and a μ_6 -S description for S_b . This description follows from small but appreciable overlap populations between S_b and apical (0.23) and basal (0.11) Nb atoms. Analysis of the fragment Nb_6S_6 shows that the principal bonding interactions involve S s and p orbitals and Nb orbitals of a_1 and e_1 symmetry. The anion $[Nb_6S_{17}]^{4-}$ is calculated to be 1.90 eV more stable than the isolated fragments $[Nb_6S_{16}]^{2-}$ (C_{2v}) and S^{2-} . This stability results from formation of four additional filled bonding MO's upon insertion of S_b into the fragment cage, whose electron-deficient interior contains virtual orbitals capable of binding a suitable ligand.

Introduction

We have observed in the initial report² of the research to be described in full here, and elsewhere,³ that soluble salts of the metal sulfide anions $[M_xS_y]^{2-}$ constitute a relatively new and expanding class of transition-element compounds. Those with $M = Mo$ comprise the largest set, ranging in composition from $[MoS_4]^{2-}$ to $[Mo_7S_{13}]^{2-}$ ³⁻¹⁰ and containing one or more of the ligands sulfide, persulfide, or polysulfide. Most of these species are ultimately derivable from the simplest member of the set, $[MoS_4]^{2-}$. There is some evidence, in the form of two species with $M = W$,^{11,12} that an extensive set of polynuclear tungsten sulfides may be obtainable from $[WS_4]^{2-}$.⁴ The other two tetrathiometalates, $[ReS_4]^-$ and $[VS_4]^{3-}$,⁴ have been relatively little investigated¹³ and have not yet been shown to be precursors to polynuclear sulfides.

Given the existence of $[VS_4]^{3-}$ as its sparingly soluble but tractable NH_4^+ salt and our interest in developing routes to new $[M_xS_y]^{2-}$ species, our attention was drawn to the absence of reports of similarly tractable compounds of the other group 5⁵⁵ tetrathiometalates, $[NbS_4]^{3-}$ and $[TaS_4]^{3-}$. The existence of these anions is not in question, having been obtained in the forms Cu_3MS_4 ,¹⁴ Tl_3MS_4 ,¹⁵ and $Ba_6[NbS_4][NbS_3O]_3$.¹⁶ In these compounds the anions are recognizable but not discrete. For example, in the first two compounds the six edges of the $[MS_4]^{3-}$ tetrahedra are bridged by strong $M(I)-S$ interactions. Isostructural congeneric compounds of the heavier chalcogenides are also known.^{4,14,15} All compounds are polymeric and insoluble and are synthesized at elevated temperatures. We have been repeatedly unable to prepare the reported compound $(Me_4N)_3[NbO_2S_2]$ by the reaction of freshly precipitated Nb_2O_5 and H_2S in alkaline solution.¹⁷ The anion as formulated would be expected to be discrete. It would be analogous to $[VO_2S_2]^{3-}$, generated in alkaline solution from $[VO_4]^{3-}$ and H_2S ,¹⁸ and to $[MO_2S_2]^{2-}$ ($M = Mo, W$),⁴ whose individual nature in crystalline NH_4^+ salts has been demonstrated.^{19,20} These observations prompted the exploration of different methods for the formation of soluble Nb and Ta sulfides. One such method, the reaction of $M(OEt)_5$ ($M = Nb, Ta$) and $(Me_3Si)_2S$ in acetonitrile solution, has afforded the remarkable hexanuclear anions $[M_6S_{17}]^{4-}$, isolated as Et_4N^+ salts. These species possess an unprecedented fivefold symmetric cage structure, which is described in detail here together with the synthesis and properties of the compounds.

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen atmosphere with use of Schlenk techniques. Acetonitrile was distilled from CaH_2 . Niobium and tantalum pentaethoxides (Alfa)

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Table I. Summary of Crystal Data, Intensity Collections, and Structure Refinement Parameters for $(\text{Et}_4\text{N})_4[\text{M}_6\text{S}_{17}]\cdot 3\text{CH}_3\text{CN}$

	M = Nb	M = Ta
formula	$\text{C}_{38}\text{H}_{89}\text{N}_7\text{Nb}_6\text{S}_{17}$	$\text{C}_{38}\text{H}_{89}\text{H}_7\text{S}_{17}\text{Ta}_6$
mol wt	1746.70	2274.96
a , Å	14.799 (4)	14.799 (3)
b , Å	11.909 (4)	11.949 (3)
c , Å	40.024 (11)	40.084 (8)
β , deg	97.74 (2)	97.57 (2)
V , Å ³	6990 (3)	7027 (3)
cryst syst	monoclinic	monoclinic
Z	4	4
d_{calcd} (d_{obsd}^a), g/cm ³	1.66 (1.69)	2.15 (2.19)
space group	$P2_1/c$	$P2_1/c$
cryst dimens, mm	$0.60 \times 0.35 \times 0.20$	$0.57 \times 0.42 \times 0.15$
radiation	Mo $K\alpha$ ($\lambda = 0.71073$ Å)	
abs coeff, μ , cm ⁻¹	15.2	103.1
transmission factors (max/min)	0.754/0.506	0.940/0.146
scan speed, deg/min	2.0–29.3 ($\theta/2\theta$ scan)	2.0–29.3 ($\theta/2\theta$ scan)
scan range, deg	$1.2 + (2\theta_{K\alpha_2} - 2\theta_{K\alpha_1})$	$1.4 + (2\theta_{K\alpha_2} - 2\theta_{K\alpha_1})$
bkgd/scan time ratio	0.1	0.1
data collected	$3^\circ \leq 2\theta \leq 44^\circ$ ($+h,+k,\pm l$)	$3^\circ \leq 2\theta \leq 46^\circ$ ($+h,+k,\pm l$)
total reflcns	8621	9822
R_{merge}^b , %	3.61	1.77
unique data ($I > 3\sigma(I)$)	4783	6501
no. of variables	613	593
goodness of fit	1.16	1.23
R (R_w), % ^c	5.27 (5.41)	5.05 (5.06)

^a Determined by flotation in $\text{CCl}_4/\text{CH}_2\text{Br}_2$. ^b $R_{\text{merge}} = [\sum N_i \sum_{j=1}^{N_i} (F_j - \bar{F}_j)^2 / \sum (N_i - 1) \sum_{j=1}^{N_i} F_j^2]^{1/2}$, where N_i is the number of reflections in a given set, F_j is one member of the set, and \bar{F}_j is the mean. ^c $R = (\sum ||F_o| - |F_c||) / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}$. $w = [\sigma^2(|F_o|) + g(|F_o|)^2]^{-1}$ with $g = 0.0014$ for Nb and Ta.

and hexamethyldisilthiane (Petrarch Systems) were used without further purification.

$(\text{Et}_4\text{N})_4[\text{Nb}_6\text{S}_{17}]\cdot 3\text{CH}_3\text{CN}$. A mixture of 3.18 g (10 mmol) of Nb(OEt)₅ and 2.32 g (14 mmol) of Et_4NCl in 250 mL of acetonitrile was stirred at $\sim 50^\circ\text{C}$ for 20–25 min. To the warm mixture was added with stirring 7.14 g (40 mmol) of $(\text{Me}_3\text{Si})_2\text{S}$. After it was cooled to room temperature, the mixture was stirred for 4–12 h, during which time it became dark brown. The mixture was filtered to remove some insoluble material. Addition of 135 mL of anhydrous ether to the filtrate and cooling at -20°C caused separation of a black crystalline solid. This material was recrystallized from acetonitrile to give 1.60 g (55%) of product as black crystals. Anal. Calcd for $\text{C}_{38}\text{H}_{89}\text{N}_7\text{Nb}_6\text{S}_{17}$: C, 26.13; H, 5.14; N, 5.61; Nb, 31.91; S, 31.21. Found: C, 25.84; H, 5.19; N, 5.42; Nb, 32.02; S, 31.03. IR spectrum (mull): 483 (vs), 377 (m), 335–329 (d, s) cm⁻¹. Absorption spectrum (acetonitrile): λ_{max} 255 (sh) (ϵ_M 70 600), 302 (42 700), 385 (16 100), 470 (sh, 8500) nm.

$(\text{Et}_4\text{N})_4[\text{Ta}_6\text{S}_{17}]\cdot 3\text{CH}_3\text{CN}$. The preceding procedure on the same molar scale was used. Differences include 350 mL of acetonitrile as reaction solvent, 210 mL of ether added to the reaction mixture filtrate, and purification by two recrystallizations from acetonitrile. The pure product was obtained as 1.25 g (33%) of dark brown crystals. Anal. Calcd for $\text{C}_{38}\text{H}_{89}\text{N}_7\text{S}_{17}\text{Ta}_6$: C, 20.06; H, 3.94; N, 4.31; S, 23.96; Ta, 47.72. Found: C, 19.71; H, 3.61; N, 4.22; S, 23.50; Ta, 47.69. IR spectrum (mull): 471 (vs), 356 (m), 331 (s), 311 (s) cm⁻¹. Absorption spectrum (acetonitrile): λ_{max} 228 (sh) (ϵ_M 83 400), 268 (64 000), 346 (22 400), 390 (sh, 12 900) nm.

The two compounds are sensitive to dioxygen and moisture and should be handled accordingly.

X-ray Data Collection and Reduction. Black (M = Nb) and dark brown (M = Ta) crystals of $(\text{Et}_4\text{N})_4[\text{M}_6\text{S}_{17}]\cdot 3\text{CH}_3\text{CN}$, obtained by slow cooling of concentrated acetonitrile solutions, were sealed in glass capillaries under an Ar atmosphere. Diffraction experiments were performed with a Nicolet R3M four-circle automated diffractometer with a Mo X-ray tube equipped with a graphite monochromator. Data collection parameters for both compounds are summarized in Table I. The orientation matrix and unit cell parameters were determined with 25 machine-centered reflections having $15 \leq 2\theta \leq 20^\circ$ (M = Nb) and $17 \leq 2\theta \leq 28^\circ$ (M = Ta). Both crystals displayed symmetrical ω scans in the range $0.35\text{--}0.45^\circ$. No significant decay of the intensities of 3 standard reflections recorded after every 60 reflections was observed. Data reduction and an empirical absorption correction were performed with the

Table II. Atom Coordinates ($\times 10^4$) for $[\text{M}_6\text{S}_{17}]^{4-}$ (M = Nb, Ta)

atom	x	y	z
Nb(1)	7402 (1)	3156 (1)	1456 (1)
Nb(2)	5174 (1)	1834 (1)	1403 (1)
Nb(3)	5869 (1)	2753 (1)	677 (1)
Nb(4)	8096 (1)	1872 (1)	713 (1)
Nb(5)	8790 (1)	622 (1)	1472 (1)
Nb(6)	6936 (1)	596 (1)	1897 (1)
S _i	7793 (2)	4810 (3)	1671 (1)
S _b	6887 (2)	1199 (3)	1187 (1)
S(1)	5742 (2)	3712 (3)	1225 (1)
S(2)	4684 (2)	1509 (3)	812 (1)
S(3)	7375 (2)	3727 (3)	833 (1)
S(4)	6715 (2)	1630 (3)	324 (1)
S(5)	8941 (2)	2591 (3)	1258 (1)
S(6)	8706 (2)	53 (3)	891 (1)
S(7)	8293 (2)	1899 (3)	1913 (1)
S(8)	7977 (2)	-809 (3)	1740 (1)
S(9)	6313 (2)	2550 (3)	1878 (1)
S(10)	5413 (2)	18 (3)	1667 (1)
S(11)	3868 (2)	2260 (4)	1568 (1)
S(12)	5099 (3)	3903 (4)	322 (1)
S(13)	9021 (3)	2292 (4)	349 (1)
S(14)	10193 (3)	191 (4)	1668 (1)
S(15)	6904 (3)	159 (5)	2415 (1)
Ta(1)	7398 (1)	3161 (1)	1454 (1)
Ta(2)	5174 (1)	1859 (1)	1403 (1)
Ta(3)	5875 (1)	2758 (1)	679 (1)
Ta(4)	8091 (1)	1894 (1)	710 (1)
Ta(5)	8768 (1)	637 (1)	1466 (1)
Ta(6)	6928 (1)	617 (1)	1890 (1)
S _i	7803 (3)	4806 (4)	1674 (2)
S _b	6891 (3)	1227 (3)	1187 (1)
S(1)	5751 (3)	3717 (3)	1223 (1)
S(2)	4701 (3)	1515 (4)	816 (1)
S(3)	7373 (3)	3731 (3)	834 (1)
S(4)	6714 (3)	1608 (4)	333 (1)
S(5)	8932 (3)	2583 (3)	1257 (1)
S(6)	8674 (3)	80 (4)	885 (1)
S(7)	8285 (3)	1902 (3)	1913 (1)
S(8)	7931 (3)	-796 (4)	1721 (1)
S(9)	6309 (3)	2565 (3)	1879 (1)
S(10)	5417 (3)	46 (3)	1662 (1)
S(11)	3867 (3)	2283 (4)	1566 (1)
S(12)	5103 (4)	3883 (4)	320 (2)
S(13)	9016 (4)	2306 (5)	345 (2)
S(14)	10163 (4)	174 (5)	1659 (2)
S(15)	6895 (4)	148 (5)	2414 (2)

programs XTAPE and XEMP, respectively, of the SHELXTL structure determination program package (Nicolet XRD Corp., Madison, WI). Both compounds, which are isostructural, crystallize in the monoclinic space group $P2_1/c$, uniquely determined by the systematic absences $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$). Crystal data are given in Table I.

Solution and Refinement of the Structure. The direct-methods program SOLV revealed the positions of the metal atoms in the Nb compound. These were used in the first step of the computations of the Ta compound. Positions of the remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Structures were refined by the blocked-cascade least-squares method. Atom scattering factors were taken from a standard source.²¹ Isotropic refinement of all non-hydrogen atoms converged at $R = 14.5$ (Nb) and 10.4% (Ta). In the final stages of refinement, hydrogen atoms were included in the cation and solvate molecules at 0.96 Å from, and with isotropic thermal parameters $1.2\times$ that of, the bonded carbon atom. All non-hydrogen atoms were refined with anisotropic thermal parameters. Unique data used in the refinements and final R values are given in Table I; atom coordinates of the anions are listed in Table II.²²

Other Physical Measurements. Absorption spectra were recorded on a Cary Model 219 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer Model 599B spectrophotometer. ⁹³Nb NMR spectra were measured at 73.46 MHz on a Bruker WM-300 spectrometer equipped with a deuterium lock. Chemical shifts are referenced to 0.01

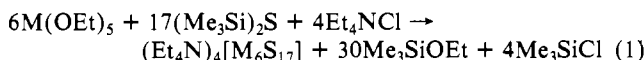
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(22) See paragraph at the end of this article concerning supplementary material available.

M (Et₄N)[NbCl₆]/CD₃CN external standard.

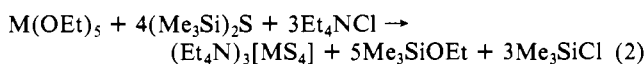
Results and Discussion

Synthesis. The usual method of preparation of the tetrathio-metalates [VS₄]²⁻, [MoS₄]²⁻, [WS₄]²⁻, and [ReS₄]⁻, by reaction of H₂S with aqueous ammoniacal solutions of [MO₄]²⁻,^{4,23} cannot be analogously applied to the M = Nb and Ta cases owing to the nonexistence of the ions [MO₄]³⁻ in aqueous solution.²⁴ The species present at pH > 7 are [H_xM₆O₁₉]^{(8-x)-}. Treatment of aqueous concentrated KOH or 30% NH₃ solutions prepared from K₇[HNNb₆O₁₉] or K₈[Ta₆O₁₉]²⁵ gave yellow colors and copious white precipitates. The use of other niobates²⁶ also did not afford any indication of the formation of soluble sulfides. Heterogeneous mixtures of these compounds, NaOMe, and Et₄NCl in Me₂SO gave similar indications, as did a refluxed mixture of NbCl₅ and Li₂S in acetonitrile. No appreciable reaction was found for a 1:4 mole ratio of Nb(OEt)₅ and (*n*-Bu₄N)(HS) in acetonitrile at 65 °C (24 h) in the presence or absence of methanolic (*n*-Bu₄N)(OH). All reactions were carried out under anaerobic conditions.

With the failure of conventional sulfide reagents, attention was directed to the homogeneous system M(OEt)₅ + (Me₃Si)₂S in acetonitrile. Use of this sulfide reagent was predicated on its ability to replace bridging and terminal oxo ligands in other compounds.^{3,27,28} Such reactions derive a favorable enthalpy component from the ~35 kcal/mol larger homolytic bond energy of Si-O vs. that of Si-S.²⁹ Reaction systems with the mole ratio (Me₃Si)₂S:Et₄NCl:M(OEt)₅ = 4:1.4:1 afforded the hexanuclear salts (Et₄N)₄[M₆S₁₇]·3MeCN as black (M = Nb, 55%) and dark brown (M = Ta, 33%) crystalline solids in the indicated purified yields. The limiting stoichiometry of reaction 1 is plausible. This



process is evidently favored compared to reaction 2, which con-



forms to the experimental (Me₃Si)₂S:M(OEt)₅ mole ratio. Use of sufficient Et₄NCl to satisfy the stoichiometry of reaction 2 or larger excesses of the sulfide reagent gave (Et₄N)₄[M₆S₁₇] as the only isolable product. The Nb compound was also isolated from the system (Et₄N)₂[NbOCl₅]:Et₄NCl:5(Me₃Si)₂S in acetonitrile, but this method offers no advantage over that of reaction 1.

Description of the Structures. The compounds (Et₄N)₄[M₆S₁₇]·3CH₃CN (M = Nb, Ta) form isomorphous crystals in the monoclinic system with space group *P*2₁/*c* (Table I). The crystal structures consist of well-separated cations, anions, and solvate molecules. These structures are, therefore, unrelated to those of the stoichiometrically analogous oxo compounds M⁴Nb₆O₁₇·0.3H₂O,³⁰ which do not contain discrete anions. The structure of [M₆S₁₇]⁴⁻ is illustrated in two perspectives in Figure 1. Stereoviews are provided in Figure 2. Selected interatomic distances and angles are compiled in Table III. The structures of [Nb₆S₁₇]⁴⁻ and [Ta₆S₁₇]⁴⁻ are topologically identical and virtually isometric. The following are the leading structural features of these anions.

(i) The anion topology is that of an open cage built by the convex fusion of 10 nonplanar M₂S₂ rhombs to form a M₆S₁₀

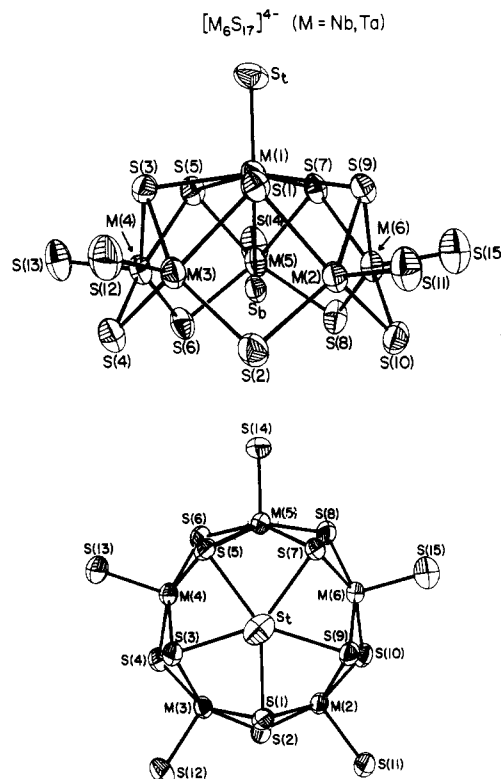


Figure 1. Two views of the structure of [M₆S₁₇]⁴⁻, with the atom-numbering scheme: (upper) side-on view with 50% probability ellipsoids; (lower) projection view down the fivefold axis with 50% probability ellipsoids, with the M(1) and S_b atoms lying directly beneath S_t.

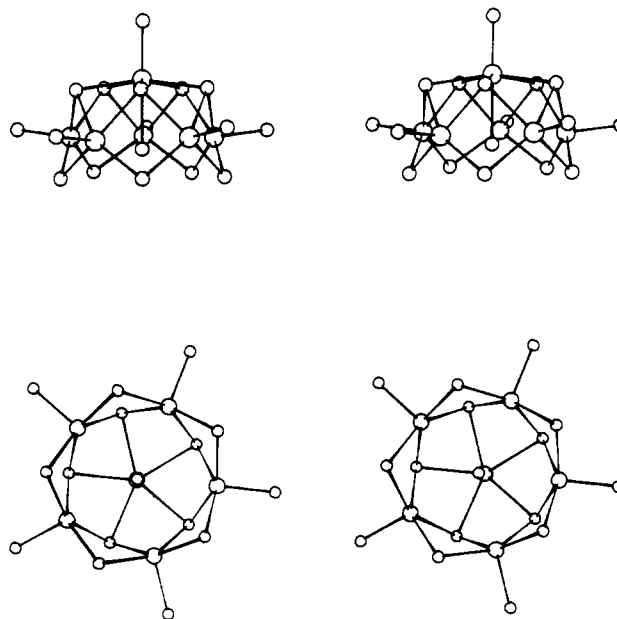


Figure 2. Two stereoviews of the structure of [M₆S₁₇]⁴⁻.

framework. The structure contains four types of sulfur atoms, all present as sulfide: six terminal S (S_t, S(11–15)) at the six M(V) sites, five μ-S(2,4,6,8,10) and five μ₃-S(1,3,5,7,9) in the framework, and one S (S_b) inside the cage.

(ii) The anions closely approach C_{5v} symmetry, with the C₅ axis containing the unique atoms S_t, M(1), and S_b. The distances and angles in Table III are organized according to this symmetry, under which there are 7 independent distances and 20 independent angles involving bonded atoms. The small variations in "symmetry-related" sets of metric values and in dihedral angles²² containing the pseudo-C₅ axis (range 71–73°), and certain other structural features considered below, substantiate description of

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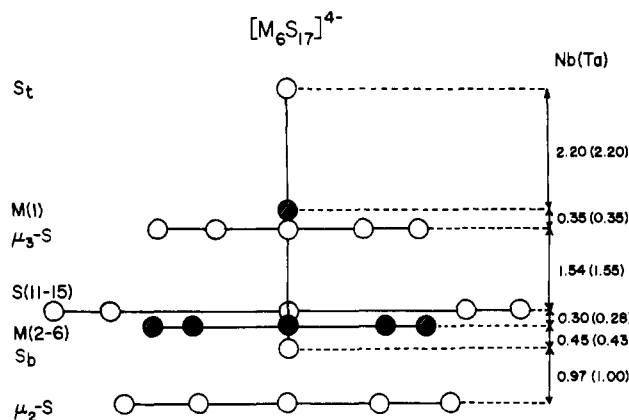


Figure 3. Illustration of the layer structure of $[M_6S_{17}]^{4-}$ showing distances between atoms and least-squares planes.

these species in terms of effective C_{5v} symmetry. This description is adopted, and hereafter metric features are considered in terms of mean values averaged under C_{5v} symmetry.

(iii) Below the $M(1)-S_t$ group the five μ_3-S , five terminal S, five M, and five $\mu-S$ atoms are arranged in that order in virtually parallel planes.²² The largest range of atom deviations from unweighted least-squares planes is found with the terminal S-(11-15) planes: Nb, 0.03–0.15 Å; Ta, 0.02–0.13 Å (absolute values). For planes containing framework atoms the largest range occurs with the $(\mu-S)_5$ planes (Nb, 0.01–0.08 Å; Ta, 0.01–0.05 Å) and the smallest range with the $(\mu_3-S)_5$ planes (<0.01 Å for Nb and Ta), which are nearly perfect. Dihedral angles between any two framework planes perpendicular to the C_5 axis are $\leq 0.5^\circ$. A side-on view of $[M_6S_{17}]^{4-}$, illustrating the layer structure and giving distances between atoms and planes, is presented in Figure 3. The perspective shown corresponds to that in Figure 1 (upper).

(iv) Because differences between (mean) values of corresponding distances and angles do not exceed 0.02 Å ($M-S_b$) and 1.5° ($\mu-S-M-\mu-S$), and are usually much less, $[Nb_6S_{17}]^{4-}$ and $[Ta_6S_{17}]^{4-}$ are, for all purposes, isometric. This property follows from the identical Shannon radii (0.78 Å³¹) for six-coordinate Nb(V) and Ta(V).

(v) The anions contain the coordination units $M(1)S_t(\mu_3-S)_5$ and five $MS(\mu-S)_2(\mu_3-S)_2$, of pentagonal and distorted-square-pyramidal geometries, respectively. The unique unit is nearly regular, but the second is significantly distorted owing to the presence of two types of bridging atoms and attendant differences in angles and distances in the $M(\mu-S)_2(\mu_3-S)_2$ basal fragment. Bond distances fall in the order $M-S(\text{terminal}) < M-\mu-S < M-\mu_3-S$. The terminal $M-S$ bond lengths (Nb, 2.196 (4), 2.177 (18) Å; Ta, 2.204 (4), 2.182 (4) Å) and the 0.28–0.35-Å displacement of M atoms from their basal planes toward terminal sulfur atoms (Figure 1) demonstrate the presence of multiply bonded $M=S$ units, for which very few distances have been previously determined. The $Nb=S$ distances are substantially longer than other values (2.09–2.13 Å³²) whereas the $Ta=S$ distances are in good agreement with previous measures (2.18–2.20 Å³³). These values may be dependent on the presence or absence of a ligand trans to the sulfur atom, but insufficient data are available to investigate this point. Other than the observation that $M-S$ distances to bridging ligands are near or in the ~ 2.4 – 2.5 -Å range found in several discrete Nb sulfide complexes^{32b,34} and in

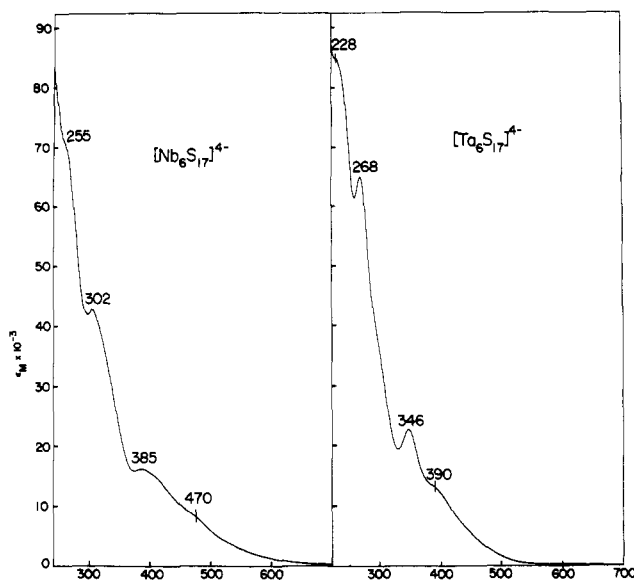


Figure 4. Absorption spectra of $[M_6S_{17}]^{4-}$ ($M = Nb, Ta$) in acetonitrile solution. Molar extinction coefficients are plotted, and band maxima are indicated.

Nb and Ta sulfides,^{35,36} further comparisons are unprofitable owing to differences in stereochemistry and oxidation state.

(vi) The atom S_b is located *inside* the cage at a position closer to $M(1) = Nb$ (2.636 (4) Å) and Ta (2.615 (4) Å) than to the atoms in the Nb_5 (2.94 (5) Å) and Ta_5 (2.92 (4) Å) planes. It is roughly equidistant from the five M atoms and is situated 0.45 (0.43) Å below the Nb_5 (Ta_5) plane and 0.97 (1.00) Å above the $(\mu-S)_5$ plane, which defines the bottom of the cage. The radial position of S_b along the C_5 axis is particularly evident in Figure 3. The situation of this atom within the cage is consistent with its description as μ_6-S .

The $[M_6S_{17}]^{4-}$ species display several remarkable structural aspects. They are among the very rare cases of molecular fivefold symmetry. Other examples include $(C_5H_5)NiNO$ ³⁷ (C_{5v}), $[(C_5Me_5)Sn]^+_{38}$ (C_{5v}), $[Cu_5I_7]^{2-}$ ³⁹ (D_{5h}), and the skeletal portion of $[B_{11}H_{13}]^{2-}$ ⁴⁰. Idealized symmetries are indicated. Like the last anion, the M_6S_{10} cage is an icosahedral fragment, but not of the usual 12-vertex polyhedron. As described previously,² this cage is half of the hypothetical *closo*- $M_{12}S_{20}$, a stellated icosahedron of I_h symmetry⁴¹ consisting of a M_{12} icosahedron with a sulfur atom capping each of the 20 faces. The $S_b = \mu_6-S$ atom is unprecedented in metal-sulfide systems, but this bridge multiplicity, while most uncommon, is not unknown. It has been found in certain oxometalates,⁴² among them $[M_6O_{19}]^{8-}$ ($M = Nb, Ta$) and $[Mo_6O_{19}]^{2-}$, which contain a μ_6-O atom in the center of their M_6O_{12} cages.⁴³ Neither $[M_6S_{17}]^{4-}$ in its entirety nor the M_6S_{10}

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(41) This polyhedron is illustrated in ref 2.

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Table III. Selected Interatomic Distances (Å) and Angles (deg) in $[M_6S_{17}]^{4-}$

	Distances					
	M = Nb	M = Ta	M = Nb	M = Ta	M = Nb	M = Ta
M=S						
M(1)-S _i	2.196 (4)	2.204 (4)				
M(2)-S(11)	2.186 (4)	2.183 (5)	M(4)-S(13)	2.188 (5)	2.188 (5)	M(6)-S(15)
M(3)-S(12)	2.184 (4)	2.179 (5)	M(5)-S(14)	2.180 (4)	2.179 (5)	mean
						2.145 (5)
						2.177 (18) ^a
						2.179 (7)
						2.182 (4)
M-μ ₃ -S						
M(1)-S(1)	2.592 (4)	2.579 (4)	M(1)-S(5)	2.599 (4)	2.593 (5)	M(1)-S(9)
M(1)-S(3)	2.583 (4)	2.573 (5)	M(1)-S(7)	2.584 (4)	2.593 (4)	mean
						2.590 (4)
						2.590 (7)
						2.593 (5)
M(2)-S(1)	2.524 (4)	2.518 (4)	M(4)-S(5)	2.514 (4)	2.513 (5)	M(6)-S(9)
M(3)-S(1)	2.503 (4)	2.491 (5)	M(5)-S(5)	2.516 (4)	2.497 (4)	mean
M(3)-S(3)	2.515 (4)	2.508 (4)	M(5)-S(7)	2.514 (4)	2.517 (5)	2.501 (4)
M(4)-S(3)	2.526 (4)	2.516 (4)	M(6)-S(7)	2.531 (4)	2.520 (4)	M(2)-S(9)
						2.516 (4)
						2.510 (10)
M-μ-S						
M(2)-S(2)	2.406 (4)	2.397 (5)	M(4)-S(6)	2.418 (4)	2.404 (4)	M(6)-S(10)
M(3)-S(2)	2.412 (4)	2.404 (5)	M(5)-S(6)	2.408 (4)	2.409 (5)	M(2)-S(10)
M(3)-S(4)	2.415 (4)	2.410 (5)	M(5)-S(8)	2.420 (4)	2.417 (5)	mean
M(4)-S(4)	2.415 (4)	2.397 (5)	M(6)-S(8)	2.414 (4)	2.404 (5)	2.417 (4)
						2.413 (4)
						2.414 (4)
						2.400 (4)
						2.411 (4)
						2.405 (6)
M-S _b						
M(1)-S _b	2.636 (4)	2.615 (4)				
M(2)-S _b	2.887 (4)	2.890 (4)	M(4)-S _b	2.890 (4)	2.888 (5)	M(6)-S _b
M(3)-S _b	3.006 (4)	2.992 (4)	M(5)-S _b	2.972 (4)	2.939 (4)	mean
						2.923 (4)
						2.94 (5)
						2.904 (5)
						2.92 (4)
M-M						
M(1)···M(2)	3.635 (3)	3.622 (1)	M(1)···M(4)	3.613 (3)	3.611 (1)	M(1)···M(6)
M(1)···M(3)	3.633 (3)	3.623 (1)	M(1)···M(5)	3.646 (3)	3.630 (1)	mean
						3.636 (3)
						3.633 (12)
						3.619 (1)
						3.621 (7)
M(2)···M(3)	3.390 (3)	3.381 (1)	M(4)···M(5)	3.414 (3)	3.412 (1)	M(6)···M(2)
M(3)···M(4)	3.442 (3)	3.424 (1)	M(5)···M(6)	3.418 (3)	3.394 (1)	mean
						3.392 (3)
						3.411 (21)
						3.380 (1)
						3.398 (19)
Angles						
	M = Nb	M = Ta		M = Nb	M = Ta	
S _i -M(1)-S _b	178.2 (1)	178.9 (2)				
S _i -M(1)-S(1)	95.6 (1)	96.2 (1)	S _i -M(1)-S(7)	99.2 (1)	98.6 (2)	
S _i -M(1)-S(3)	96.5 (1)	96.7 (2)	S _i -M(1)-S(9)	98.5 (1)	98.2 (2)	
S _i -M(1)-S(5)	99.0 (1)	99.0 (2)	mean	97.8 ^a	97.7	
S _b -M(1)-S(1)	82.7 (1)	82.8 (1)	S _b -M(1)-S(7)	82.4 (1)	82.4 (1)	
S _b -M(1)-S(3)	82.6 (1)	82.6 (1)	S _b -M(1)-S(9)	81.3 (1)	81.7 (1)	
S _b -M(1)-S(5)	82.1 (1)	81.7 (1)	mean	82.2 ^b	82.2	
S(1)-M(1)-S(3)	72.4 (1)	72.0 (1)	S(7)-M(1)-S(9)	71.3 (1)	71.1 (1)	
S(3)-M(1)-S(5)	71.0 (1)	71.2 (1)	S(9)-M(1)-S(1)	70.2 (1)	70.5 (1)	
S(5)-M(1)-S(7)	71.4 (1)	71.4 (1)	mean	71.3	71.2	
M(1)-S(1)-M(2)	90.5 (1)	90.6 (1)	M(1)-S(7)-M(5)	91.3 (1)	90.5 (2)	
M(1)-S(1)-M(3)	91.0 (1)	91.2 (1)	M(1)-S(7)-M(6)	90.6 (1)	90.1 (1)	
M(1)-S(3)-M(3)	90.9 (1)	91.0 (1)	M(1)-S(9)-M(6)	91.1 (1)	90.5 (1)	
M(1)-S(3)-M(4)	90.0 (1)	90.4 (1)	M(1)-S(9)-M(2)	90.7 (1)	90.3 (2)	
M(1)-S(5)-M(4)	89.9 (1)	90.0 (1)	mean	90.7	90.9	
M(1)-S(5)-M(5)	90.9 (1)	91.0 (2)				
M(2)-S(1)-M(3)	84.8 (1)	84.9 (1)	M(5)-S(7)-M(6)	85.3 (1)	84.7 (1)	
M(3)-S(3)-M(4)	86.1 (1)	85.9 (1)	M(6)-S(9)-M(2)	85.1 (1)	84.7 (1)	
M(4)-S(5)-M(5)	85.5 (1)	85.9 (1)	mean	85.4	85.2	
M(2)-S(2)-M(3)	89.4 (1)	89.5 (1)	M(5)-S(8)-M(6)	90.0 (1)	89.5 (1)	
M(3)-S(4)-M(4)	90.9 (1)	90.9 (2)	M(6)-S(10)-M(2)	89.2 (1)	89.3 (1)	
M(4)-S(6)-M(5)	90.0 (1)	90.3 (2)	mean	89.9	89.9	
S(9)-M(2)-S(1)	72.4 (1)	72.8 (1)	S(5)-M(5)-S(7)	73.9 (1)	74.2 (2)	
S(1)-M(3)-S(3)	75.0 (1)	74.6 (1)	S(7)-M(6)-S(9)	73.6 (1)	73.8 (1)	
S(3)-M(4)-S(5)	73.3 (1)	73.4 (1)	mean	73.6	73.8	
S(10)-M(2)-S(2)	107.1 (1)	106.1 (2)	S(6)-M(5)-S(8)	105.4 (1)	104.2 (2)	
S(2)-M(3)-S(4)	104.0 (1)	102.8 (2)	S(8)-M(6)-S(10)	107.4 (1)	105.8 (2)	
S(4)-M(4)-S(6)	109.5 (1)	107.3 (2)	mean	106.7	105.2	
S(1)-M(2)-S(2)	86.2 (1)	86.4 (2)	S(7)-M(5)-S(8)	84.5 (1)	85.1 (2)	
S(1)-M(3)-S(2)	86.6 (1)	86.9 (2)	S(7)-M(6)-S(8)	84.2 (1)	85.4 (1)	
S(3)-M(3)-S(4)	83.6 (1)	84.4 (1)	S(9)-M(6)-S(10)	86.1 (1)	86.4 (1)	
S(3)-M(4)-S(4)	83.4 (1)	84.4 (1)	S(9)-M(2)-S(10)	85.9 (1)	85.8 (1)	
S(5)-M(4)-S(6)	85.8 (1)	85.7 (2)	mean	85.2	85.6	
S(5)-M(5)-S(6)	86.0 (1)	85.9 (2)				
S(11)-M(2)-S(9)	102.8 (1)	102.9 (2)	S(14)-M(5)-S(5)	102.6 (2)	103.0 (2)	
S(11)-M(2)-S(1)	102.8 (1)	103.2 (2)	S(14)-M(5)-S(7)	104.2 (2)	104.2 (2)	
S(12)-M(3)-S(1)	101.0 (1)	101.6 (2)	S(15)-M(6)-S(7)	104.2 (2)	104.0 (2)	
S(12)-M(3)-S(3)	103.9 (1)	104.3 (2)	S(15)-M(6)-S(9)	101.5 (2)	101.7 (2)	
S(13)-M(4)-S(3)	104.1 (1)	104.7 (2)	mean	103.0	103.3	
S(13)-M(4)-S(5)	102.5 (1)	103.1 (2)				

Table III (Continued)

	Angles				
	M = Nb	M = Ta	M = Nb	M = Ta	
S(11)-M(2)-S(10)	99.1 (2)	99.6 (2)	S(14)-M(5)-S(6)	101.8 (2)	101.7 (2)
S(11)-M(2)-S(2)	99.9 (1)	100.3 (2)	S(14)-M(5)-S(8)	100.4 (2)	100.7 (2)
S(12)-M(3)-S(2)	101.5 (1)	101.6 (2)	S(15)-M(6)-S(8)	100.5 (2)	100.6 (2)
S(12)-M(3)-S(4)	103.4 (2)	103.7 (2)	S(15)-M(6)-S(10)	99.1 (2)	98.9 (2)
S(13)-M(4)-S(4)	98.5 (1)	99.5 (2)	mean	100.3	100.6
S(13)-M(4)-S(6)	99.1 (2)	99.5 (2)			
S(1)-M(2)-S(10)	152.0 (1)	151.6 (1)	S(5)-M(5)-S(8)	151.6 (1)	151.7 (2)
S(2)-M(2)-S(9)	151.6 (1)	151.7 (2)	S(6)-M(5)-S(7)	150.0 (1)	150.2 (1)
S(1)-M(3)-S(4)	150.7 (1)	150.3 (1)	S(7)-M(6)-S(10)	151.6 (1)	152.2 (2)
S(2)-M(3)-S(3)	151.0 (1)	150.6 (2)	S(8)-M(6)-S(9)	152.0 (1)	152.5 (2)
S(3)-M(4)-S(6)	151.5 (1)	150.9 (2)	mean	151.4	151.3
S(4)-M(4)-S(5)	151.7 (1)	151.6 (2)			
S(1)-M(1)-S(5)	141.7 (1)	141.5 (2)	S(7)-M(1)-S(1)	140.3 (1)	140.4 (1)
S(3)-M(1)-S(7)	141.0 (1)	141.2 (1)	S(9)-M(1)-S(3)	140.7 (1)	140.8 (1)
S(5)-M(1)-S(9)	140.8 (1)	140.6 (1)	mean	140.9	140.9
S(1)-M(2)-S _b	79.0 (1)	78.5 (1)	S(7)-M(5)-S _b	77.2 (1)	77.5 (1)
S(1)-M(3)-S _b	77.0 (1)	76.9 (1)	S(7)-M(6)-S _b	77.8 (1)	78.1 (1)
S(3)-M(3)-S _b	76.7 (1)	76.5 (1)	S(9)-M(6)-S _b	77.3 (1)	77.8 (1)
S(3)-M(4)-S _b	78.7 (1)	78.3 (1)	S(9)-M(2)-S _b	77.8 (1)	77.8 (1)
S(5)-M(4)-S _b	78.7 (1)	77.9 (1)	mean	77.7	77.7
S(5)-M(5)-S _b	77.1 (1)	77.2 (1)			
S(2)-M(2)-S _b	80.0 (1)	79.5 (1)	S(8)-M(5)-S _b	80.3 (1)	79.6 (1)
S(2)-M(3)-S _b	77.5 (1)	77.3 (1)	S(8)-M(6)-S _b	81.4 (1)	80.6 (1)
S(4)-M(3)-S _b	78.8 (1)	78.0 (1)	S(10)-M(6)-S _b	78.4 (1)	78.8 (1)
S(4)-M(4)-S _b	81.2 (1)	80.4 (1)	S(10)-M(2)-S _b	79.2 (1)	78.9 (1)
S(6)-M(4)-S _b	78.3 (1)	77.7 (1)	mean	79.2	78.7
S(6)-M(5)-S _b	76.8 (1)	76.6 (1)			
M(1)-S _b -M(2)	82.2 (1)	82.1 (1)	M(1)-S _b -M(5)	80.8 (1)	81.4 (1)
M(1)-S _b -M(3)	79.9 (1)	80.2 (1)	M(1)-S _b -M(6)	81.5 (1)	81.8 (1)
M(1)-S _b -M(4)	81.5 (1)	81.9 (1)	mean	81.2	81.5
M(2)-S _b -M(3)	70.2 (1)	70.1 (1)	M(5)-S _b -M(6)	70.9 (1)	71.0 (1)
M(3)-S _b -M(4)	71.4 (1)	71.2 (1)	M(6)-S _b -M(2)	71.4 (1)	71.4 (1)
M(4)-S _b -M(5)	71.2 (1)	71.7 (1)	mean	71.0	71.1
M(2)-S _b -M(4)	140.3 (1)	140.1 (1)	M(5)-S _b -M(2)	140.4 (1)	140.6 (2)
M(3)-S _b -M(5)	139.9 (1)	140.4 (2)	M(6)-S _b -M(3)	139.1 (1)	139.2 (2)
M(4)-S _b -M(6)	140.4 (1)	141.0 (1)	mean	140.0	140.3
S _b -M(2)-S(11)	178.2 (1)	178.2 (1)	S _b -M(5)-S(14)	178.5 (2)	178.3 (2)
S _b -M(3)-S(12)	177.8 (1)	178.1 (2)	S _b -M(6)-S(15)	177.3 (2)	177.6 (2)
S _b -M(4)-S(13)	177.1 (2)	177.0 (2)	mean	177.8	177.8
M(2)-M(3)-M(4)	105.4 (1)	105.9 (1)	M(5)-M(6)-M(2)	108.1 (1)	108.2 (1)
M(3)-M(4)-M(5)	110.0 (1)	109.4 (1)	M(6)-M(2)-M(3)	110.0 (1)	109.7 (1)
M(4)-M(5)-M(6)	106.3 (1)	106.7 (1)	mean	108.0	108.0

^a The standard deviation of the mean was estimated from $\sigma \approx s = [\sum(x_i - \bar{x})^2/(n - 1)]^{1/2}$. No value is given for any angular quantity, as the variations usually exceed those expected from a sample taken from the same population. ^b Misstated as 80.2° in ref 2.

age is a fragment of any known Nb or Ta sulfide structure.^{35,36} These compounds usually contain M(IV) in octahedral or trigonal-prismatic S₆ sites.^{35,36} Other than M¹₃MS₄^{14,15} and Ba₆-Nb₄O₃S₁₃¹⁶ [M₆S₁₇]⁴⁻ is the only stable sulfide species of Nb(V) and Ta(V). Lastly, the structure of these anions bears no relation to that of [Cu₆S₁₇]²⁻,⁴⁴ which is actually [Cu₆(S₄)₃(S₃)²⁻.

Properties. The absorption spectra of [M₆S₁₇]⁴⁻ in acetonitrile solution, shown in Figure 4, consist of analogous patterns of four bands arising from LMCT transitions, with energies for M = Ta > Nb. These spectra provide particularly clear examples of blue-shifted charge-transfer spectra of isostructural and isoelectronic molecules as the atomic number of the metal increases and its optical electronegativity decreases.⁴⁵ Similar behavior is found in the solution spectra of [MS₄]²⁻ (M = Mo, W^{4,23}) and the poorly

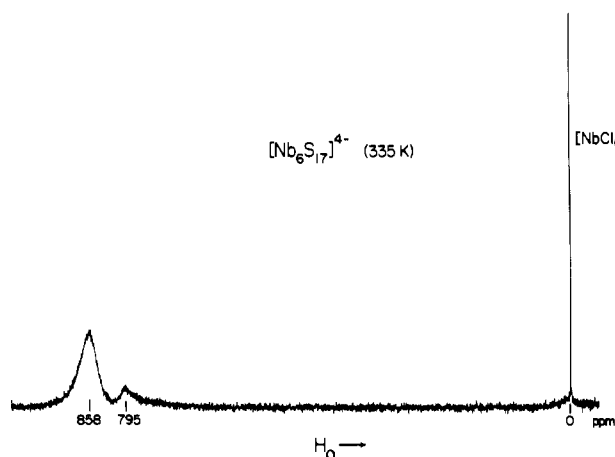


Figure 5. ⁹³Nb NMR spectrum of [Nb₆S₁₇]⁴⁻ in 3 mM acetonitrile solution at 335 K.

resolved solid-state spectra of Tl₃MS₄ (M = V, Nb, Ta⁴⁶), which are otherwise dissimilar to the spectra of Figure 4. In the infrared

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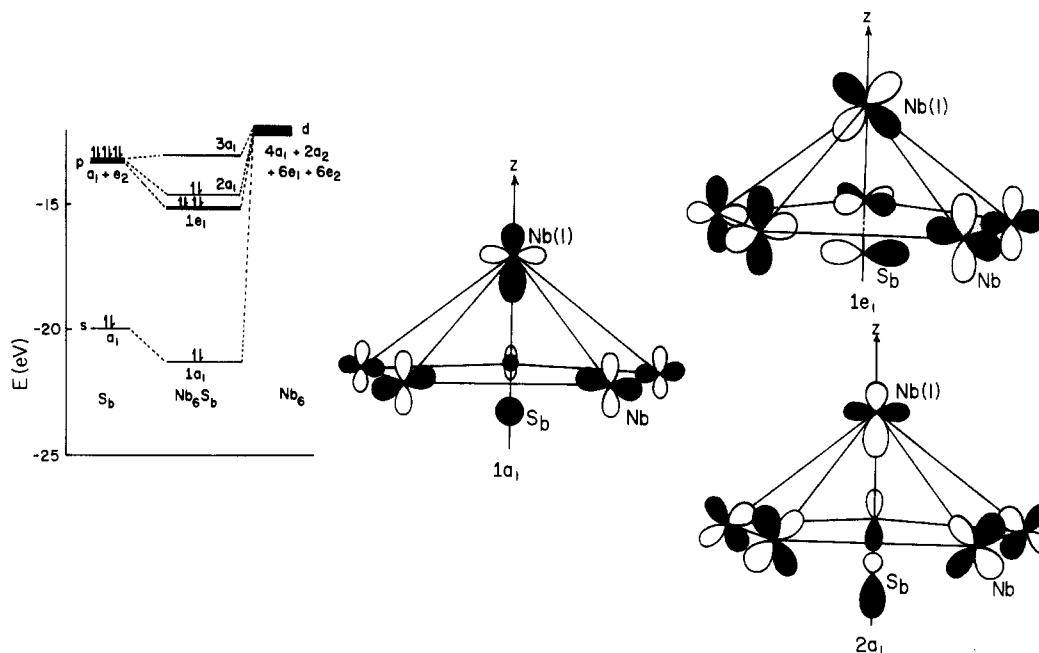


Figure 6. Results of the interaction of orbitals of the Nb_6 and S_6^{2-} portions of the Nb_6S_6 fragment of $[\text{Nb}_6\text{S}_{17}]^{4-}$. Shown in the fragment orbitals are the principal contributing atomic orbitals (in hybridized forms where appropriate). One of the $1e_1$ orbitals is not depicted, and higher energy, empty orbitals are omitted from the energy level diagram.

spectrum, intense $\nu_{\text{M}=\text{S}}$ bands occur at 483 (Nb) and 471 (Ta) cm^{-1} for solid samples. The frequency order $\nu_{\text{Nb}=\text{S}} > \nu_{\text{Ta}=\text{S}}$ in analogous molecules is usual, but the frequencies are among the lowest reported for these groups.^{27,32a,c,33a,47,48}

In order to examine cage structural integrity in solution, the NMR spectrum of the quadrupolar nucleus ^{93}Nb ($I = 9/2$, $Q \approx -0.2 \times 10^{-24} \text{ cm}^2$, 100% abundance) in $[\text{Nb}_6\text{S}_{17}]^{4-}$ was investigated. In acetonitrile at ambient temperature a broad asymmetric signal ($\Delta H_{1/2} \approx 3300 \text{ Hz}$) at $\sim 860 \text{ ppm}$ with a shoulder at $\sim 800 \text{ ppm}$ was observed. Resolution is improved at higher temperatures, presumably due to the diminished effect of correlation broadening. The spectrum at 335 K, shown in Figure 5, contains two resolved but partially overlapping signals at 858 and 795 ppm with $\Delta H_{1/2} \approx 2400$ and 2600 Hz, respectively. The apparent 4.3:1 intensity ratio leads to assignment of the more and less intense signals to Nb(2-6) and Nb(1) atoms, respectively. This ratio is sufficiently close to 5:1 to indicate retention of the solid-state structure in acetonitrile solution. An inverse dependence of metal deshielding on the electronegativity of ligands in M(V) complexes of group 5 elements is well documented.⁴⁹ With niobium, examples include halides, $[\text{NbYX}_4]^{-48}$ ($Y = \text{O}, \text{S}, \text{Se}, \text{Te}; X = \text{F}, \text{Cl}, \text{Br}$), and M_3NbY_4 ⁵⁰ ($Y = \text{S}, \text{Se}, \text{Te}$; solid state). Qualitative theoretical interpretations of these trends, in terms of varying contributions of the dominant paramagnetic shielding term, have been presented.⁴⁸⁻⁵¹ The chemical shifts of both environments in $[\text{Nb}_6\text{S}_{17}]^{4-}$ vs. that of, e.g., $[\text{NbSBr}_4]^{-48}$ (725 ppm), all relative to $[\text{NbCl}_6]^{-}$ external standard, are consistent with the smaller electronegativity of S compared to that of Br. The relative shifts of $[\text{Nb}_6\text{S}_{17}]^{4-}$ imply the intuitively reasonable electronegativity order $\mu_3\text{-S} > \mu\text{-S}$ at the sites $\text{NbS}(\mu_3\text{-S})_5$ and $\text{NbS}(\mu_3\text{-S})_2(\mu\text{-S})_2$. It has also

Table IV. Overlap Populations and Orbital Symmetries for $[\text{Nb}_6\text{S}_{17}]^{4-}$

atoms	Orbital Symmetry		
	orbitals	symmetries	
Nb(1), S_1 , S_6	s, p	$a_1, a_1 + e_1$	
Nb(1)	d	$a_1 + e_1 + e_2$	
Nb(2-6)	s, p_z, d_{z^2}	$a_1 + e_1 + e_2$	
$\text{S}(11-15)$	$(p_x, p_y)^a$	$a_1 + a_2 + 2e_1 + 2e_2$	
$\mu\text{-S}(2,4,6,8,10)$	$(d_{x^2-y^2}, d_{xy})$		
$\mu_3\text{-S}(1,3,5,7,9)$	(d_{xz}, d_{yz})		
Overlap Population ^b			
Nb(1)- S_1	0.58	Nb(1)- $\mu_3\text{-S}$	0.24
Nb(2-6)- $\text{S}(11-15)$	0.60	Nb(1)- S_6	0.23
Nb(2-6)- $\mu\text{-S}$	0.36	Nb(2-6)- S_6	0.11
Nb(2-6)- $\mu_3\text{-S}$	0.28		

^aSets of equivalent orbitals in parentheses. ^bAs defined by: Mulliken, R. S. *J. Chem. Phys.* **1955**, 23, 1833.

been argued that in d^0 molecules containing a doubly bonded ligand, the stronger the double bond the greater the paramagnetic deshielding.⁴⁸ This effect is considered to arise from larger contribution of metal d orbitals to the bond. MO calculations of $[\text{Nb}_6\text{S}_{17}]^{4-}$ (vide infra) yield the overlap population 0.60 for $\text{S}=\text{Nb}(2-6)$ bonds, slightly larger than the value of 0.58 for the $\text{S}=\text{Nb}(1)$ bond and consistent with the more deshielded nature of Nb(2-6).

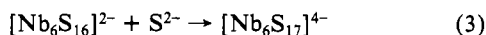
Bonding. The electronic structure of $[\text{Nb}_6\text{S}_{17}]^{4-}$ has been examined at the extended Hückel level of approximation.⁵² Atom coordinates were averaged to C_{5v} symmetry in a coordinate system with Nb(1) at the origin, the z axis being coincident with the Nb(1)-S₁ vector and the -y axis placed so as to project on the M(1)-S(1) vector. Orbital symmetries and overlap populations are contained in Table IV. The 68 filled MO's of the anion span 11 eV, are bonding or essentially nonbonding, and are dominantly sulfur in character. The LUMO-HOMO energy gap is 1.60 eV. The HOMO is composed primarily of p_x, p_y contributions from $\mu\text{-S}$ and $\mu_3\text{-S}$ atoms and has a_2 symmetry. The LUMO is mainly of Nb d-orbital character and is doubly degenerate with e_2 sym-

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metry. The MO results reduce to several approximate descriptions of framework bonding, facilitated in part by the nil interaction (essentially zero overlap population) between Nb atoms, no two of which are closer than 3.39 Å. Basal atoms Nb(2-6) can be viewed as being in square-pyramidal NbS₅ units⁵³ with a σ -bonding framework consisting of Nb(V) $d_{sp^3} + S^{2-}$ s/p hybrid orbital interactions. For the apical Nb(1)S₅ portion a fragment analysis was performed. The five μ_3 -S atoms can be considered to contribute one sp^3 -like orbital each, with the set transforming as $a_1 + e_1 + e_2$. These mix with metal orbitals of the same symmetry, affording 5 fragment orbitals filled with 10 electrons. The bonding interactions are similar to those in certain boranes and carboranes of fivefold symmetry.⁵⁴ Bonding is completed at Nb(1) by σ - and π -bond formation with the atom S₁ by use of a_1 and e_1 orbitals, respectively. Similar π bonding occurs at basal Nb atom sites. Overlap populations vary as Nb-S distances. Those involving terminal atoms are consistent with an effective double bond Nb=S, which has been detected in the infrared spectrum.

Other than its framework topology, the most intriguing feature of $[M_6S_{17}]^{4-}$ is the presence of atom S_b within the cage. Designation of this atom as, functionally, μ_6 -S on the basis of M-S_b distances is further supported by the overlap populations of 0.23 and 0.11 for the interactions with apical and basal Nb atoms, respectively. To derive a bonding description, a fragment analysis was performed with S_b²⁻ and $[Nb_6S_{16}]^{2-}$, which retains C_{3v} symmetry. In the hypothetical reaction (3) the product is stabilized



by 1.90 eV over the fragments. Further, the LUMO-HOMO separation increases from 1.11 eV in the fragment to 1.60 eV in the product. In both species the HOMO has a_2 symmetry and thus cannot interact with S_b (Table IV). The fragment LUMO is of a_1 symmetry. Its antibonding interaction with the S_b a_1 orbitals drives its energy above that of the e_2 orbital set next to

it, which becomes the LUMO of $[Nb_6S_{17}]^{4-}$. This ion has been further fragmented into Nb₆S₆ for the purpose of the bonding analysis.

Leading results of the interactions of the orbitals of the six Nb(V) atoms with the orbitals of S_b²⁻ are displayed in Figure 6. Four bonding orbitals are filled, affording the configuration $(1a_1)^2(1e_1)^4(2a_1)^2$. Simplified depictions of these orbitals, showing principal atomic contributions, are provided. The fragment orbitals are mixed with other sulfur orbitals in the complete anion. It is noteworthy that the overlap populations between S_b and the apical and basal Nb atoms, 0.23 and 0.11, respectively, are very close to the values for $[Nb_6S_{17}]^{4-}$ itself. Thus, in spite of its simplicity, the fragment analysis provides a reasonable first approach to a description of the bonding of the S_b atom to the cage framework. The apparent spontaneity of reaction 3 is now interpretable in terms of the formation of four additional filled bonding MO's upon insertion of S_b²⁻ in the precursor cage. The interior of this cage can be conceived of in terms of virtual metal orbitals directed toward its center or along its roof. Hence, the interior is acidic or electron deficient, a condition that is attenuated by the binding of a suitable ligand. This situation is quite prevalent in polyoxometalates,²⁴ where atoms with high bridging multiplicities enclosed within metal-oxo cages are often encountered. The previously cited ions $[M_6O_{19}]^{2-}$,⁸⁻ with μ_6 -O atoms in M₆O₁₂ cages,⁴³ are cases in point. With $[M_6S_{17}]^{4-}$ the cage is not closed, and it remains to be seen if an extensive chemistry of open cages with and without interior occupation can be developed. Such chemistry may be expected with complexes of the early transition elements, inasmuch as these metals furnish the required empty and relatively stable d orbitals.

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Registry No. (Et₄N)₄[Nb₆S₁₇]·3CH₃CN, 95979-72-9; (Et₄N)₄[Ta₆S₁₇]·3CH₃N, 95979-75-2; (Me₃Si)₂S, 3385-94-2.

Supplementary Material Available: Listings of atom coordinates and anisotropic temperature factors for cations and solvate molecules, anisotropic temperature factors for $[M_6S_{17}]^{4-}$, hydrogen atom coordinates and isotropic temperature factors, ranges of atom deviations from and dihedral angles between unweighted least-squares planes of $[M_6S_{17}]^{4-}$, and calculated and observed structure factors for (Et₄N)₄[M₆S₁₇]·3MeCN (M = Nb, Ta) (80 pages). Ordering information is given on any current masthead page.

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(55) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Notes

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Excited-State Spectroscopy of Tetrachloroplatinate(II)

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In this paper we report the transient absorption spectrum of the tetrachloroplatinate(II) anion in a matrix of ethylene glycol and water at 158 K. The spectrum could be identified as the excited-state absorption (ESA) of PtCl₄²⁻ in its lowest triplet state. This assignment is shown to be consistent with a detailed analysis of the doubly excited ligand field states in a d⁸ square-planar complex. The present work follows a methodology that is similar to an earlier treatment, reporting the ESA spectrum of the lowest

excited triplet in Co(CN)₆³⁻, and d⁶ octahedral complex.²

Transient Detection

A 10⁻² M solution of K₂PtCl₄ in a 2:1 mixture of ethylene glycol and water, containing an excess of KCl, was cooled down to 158 K and excited at 347 nm with a pulsed ruby laser source. The details of the measurement have been described elsewhere.² In emission one readily observes a broad-band luminescence peaking at about 12 150 cm⁻¹ (see Figure 1). Moreover, a well-structured transient absorption could be monitored from 16 500 to 33 000 cm⁻¹. Traces of transient absorption were also detectable at the low-energy side of the emission peak.

Since the parent compound is not transparent in the region above 17 000 cm⁻¹, the absorption observed immediately after excitation had to be corrected for the transient depletion of the ground state. In Figure 1 this corrected absorbance is plotted against wavenumber. Four main bands at 8400, 18 150, 25 600, and 30 000 cm⁻¹ have been labeled from I to IV. Assuming a unit

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