Table III. Atomic Parameters Used in the Calculations

atom	orbital	H_{ii}, eV	ζ_1^a	ζ_2^a	c_1	c_2
Ta	6s	−10.1	2.28			
	6p	−6.86	2.24			
	5d	−12.12	4.76	1.94	0.6815	0.6815
Fe	4s	−8.40	1.90			
	4p	−5.00	1.90			
	3d	−12.2	5.35	2.00	0.5505	0.6815
Te	5s	−20.8	2.51			
	5p	−13.2	2.16			
Si	3s	−17.3	1.38			
	3p	−9.20	1.38			

[a] Exponent in the double ζ function for d orbitals.

in the Ta_4Te_4Si chain and is, by our calculations, to be attributed mostly to the Ta 5d orbitals. The Ta-Si bonding states are localized to a small energy interval. It is this bonding that greatly stabilizes the chain structure. The compound is expected to be metallic, with the conduction bands being largely made up of Ta 5d states. The staggered or antiprismatic form is more stable than the eclipsed one. While pairing of the interstitial atoms is in principle possible, it depends on the valence electron count. For a system with 96 electrons, as in Ta_4Te_4Si, the pairing distortion is not favored. An overlap population analysis indicates that replacing Si by Fe is quite feasible. The Fe compound thus obtained should again be conducting; the states around the Fermi level are now largely Fe 3d. Oxidation is more likely to take place than reduction, more so with the Fe compound than the Si compound.

Acknowledgment. We are grateful to the National Science Foundation for its generous support through Grant CHE 8912070. We thank Jane Jorgensen and Elisabeth Field for the drawings.

Appendix

The extended Hückel tight-binding method[8-9] is used throughout the paper. A summary of the atomic parameters is given in Table III. Atomic distances used in both structures, Ta_4Te_4M (M = Si, Fe), are 3.26 and 2.98 Å for the intra- and intersquare Ta-Ta bonds, 2.40 and 2.60 Å for the M-M and Ta-M bonds, and 2.85 Å (intrasquare) and 2.92 Å (intersquare) for the Ta-Te bonds. The *k*-point sets employed in the average property calculations are generated according to the Ramirez and Böhm method.[22]

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Synthesis and Structure of Ta_4SiTe_4, a New Low-Dimensional Material

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The new infinite chain compound Ta_4SiTe_4 has been prepared by reaction of the elements at high temperature. The structure was refined in the orthorhombic space group *Pbam* with $Z = 4$ and lattice constants $a = 10.536$ (3), $b = 18.275$ (5), and $c = 4.799$ (1) Å to a final $R = 6.1\%$, $R_W = 8.2\%$. Ta_4SiTe_4 is a new structure type and represents a new class of compounds, Ta_4ZTe_4, with Z = Cr, Fe, Co, Ni, Al, or Si. The structure consists of Si-centered chains of antiprismatically stacked Ta squares that are edge bridged by Te.

Introduction

In the last few years, an abundant zirconium halide cluster chemistry has been discovered.[1-4] Many of the new zirconium phases are isoelectronic with and have structures related to well-known niobium halide cluster phases; the key difference is that they contain a heteroatom in the center of the zirconium octahedron. The heteroatom provides electrons necessary for the formation of a cluster phase in an otherwise electron-deficient system. A great variety of elements (Be, B, C, N, K, Al, Si, Ge, P, and 3d transition metals)[1-4] have been found to act as stabilizing heteroatoms in the zirconium halide system.

We considered whether, by analogy to the zirconium-niobium halides, new tantalum chalcogenides similiar to the remarkable Chevrel phases[5] of molybdenum could be synthesized by the addition of an appropriate stabilizing heteroatom. Initially, we focused on synthesizing carbon-centered tantalum chalogenide cluster phases using, for example, Ta_2S_2C as a precursor.[6] To date, we have been unable to synthesize such carbon-centered cluster phases. Subsequently, we investigated other Ta-Z-X systems (Z = stabilizing heteroatom; X = chalcogenide).

Here we report on the synthesis and structure of a new phase in the Ta-Si-Te system, Ta_4SiTe_4. This compound has a very unusual, low-dimensional structure based on Si-centered square-antiprismatic Ta_4Te_4 infinite chains. Weak Te-Te van der Waals interactions bond the chains together.

Synthesis

The title compound was first synthesized from a 1-g mixture of the elements with the molar ratio Ta:Si:Te = 2:1:2 in an evacuated quartz tube. $TeCl_4$ (10 mg) was included as a transport agent. The sample was heated in a furnace at 600 °C for 1 day and removed and placed in another furnace at 1150 °C for 4 days, followed by rapid quenching to room temperature. Large needlelike crystals with a metallic luster were formed. Microprobe analysis of the crystals indicated the presence of only tantalum, silicon, and tellurium. It was difficult to find a crystal of the appropriate size for single-crystal diffractometry as most crystals tended to grow very long (>1 mm) or very thin (<0.01 mm). Repeated attempts at growing single crystals have been most successful when both excess Te and small amounts of Cl are present. Plates of $TaTe_2$ are observed in the presence of excess Te. The crystal used in the structure determination below was taken from a reaction containing a 1-g mixture of the elements in the molar ratio Ta:Si:Te = 4:1:5 with 10 mg of $TeCl_4$; the previously mentioned heating schedule was used. After the structure was determined, a powder sample of Ta_4SiTe_4 was obtained quantitatively by heating a stoichiometric mixture of Ta (3N6), Si (5N), and Te (5N) in an evacuated quartz ampule to 1050 °C for 2 days. The powder diffraction pattern of this material matched the calculated pattern of Ta_4SiTe_4.

The crystals are very fragile and moderately air-sensitive; they decompose on sitting in air after a few days. Finely divided powders, on the other hand, often ignite on air exposure.

Structure Determination

Weissenberg photographs of a crystal mounted along the needle axis yielded approximate lattice constants and an orthorhombic unit cell symmetry. After many attempts, a 0.36 × 0.05 × 0.03 mm^3 crystal of adequate quality for single-crystal diffraction was found. Data were collected on a Syntex $P2_1$ diffractometer using Mo Kα radiation and a graphite monochromator. The crystal was enveloped in a stream of room-temperature nitrogen gas to prevent slow decomposition of the crystal in air. The history of three check reflections, taken every 50

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Table I. Data Collection and Refinement Parameters for Ta_4SiTe_4

X-ray radiation, monochromator	Mo Kα, graphite
2θ range, deg; scan type	0–55; ω–2θ
octants measd	±h,k,l
no. of reflcns measd	2388
no. of indep reflcns	1196
no. of reflcns obsd^a	1154
no. of params	54
abs coeff (μ), cm^{-1}	589.6
approx cryst size, mm^3	0.3 × 0.05 × 0.36
R,^{b} %; R_w,^{c} %	6.1; 8.2
space group; Z	*Pbam*, 4
a, b, c, Å	10.536 (3), 18.275 (5), 4.799 (1)
V, Å^3	924.1

$^a F_o^2 > 3\sigma(F_o^2)$. $^b R = \sum(|F_o| - |F_c|)/\sum(|F_o|)$. $^c R_w = [\sum(w(|F_o| - |F_c|)^2)/\sum(w|F_o|^2)]^{1/2}$, $w = \sigma(F_o)^{-2}$.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

atom	site	x	y	z	U_{eq}
Ta1	4h	0.0655 (1)	0.1195 (1)	0.5	25 (1)
Ta2	4h	0.2086 (1)	−0.0369 (1)	0.5	25 (1)
Ta3	4g	0.1935 (1)	0.0587 (1)	0	24 (1)
Ta4	4g	−0.1012 (1)	0.1108 (1)	0	25 (1)
Te1	4g	0.3578 (2)	−0.0650 (2)	0	28 (1)
Te2	4h	−0.1725 (3)	0.1906 (2)	0.5	29 (1)
Te3	4h	0.3345 (2)	0.1004 (2)	0.5	28 (1)
Te4	4g	0.1105 (2)	0.2064 (2)	0	29 (1)
Si	4e	0	0	0.2451 (19)	22 (2)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

reflections, indicated no crystal decomposition during the 2-day data collection procedure. Systematic extinctions narrowed the possible space groups down to *Pba*2 or *Pbam*. The structure could be solved by using direct methods in either space group, but the atomic positions and refined R factors in *Pba*2 were not significantly different from those in *Pbam*. Two octants of data were collected and later merged to improve the data set. The four Ta and four Te atoms in the asymmetric unit were easily identified in the Fourier map; the Si atom was found as the only large peak in a difference Fourier map. The maximum peak in the final difference Fourier map was 6.7 electrons located 1.03 Å from a Ta atom. Two strong reflections, (002) and (004), were omitted from the final refinement on the basis of significant secondary extinction. An empirical absorption correction using the ψ-scan method was employed. The structure solution and refinement was carried out by using SHELXTL Plus software from Nicolet running on a Microvax computer. A summary of crystal and data collection parameters may be found in Table I. Atom positions are listed in Table II.

Results and Discussion

The structure of Ta_4SiTe_4 is based on a square Ta_4 monomer stacked antiprismatically to form an "infinite", one-dimensional metal atom network. A Si atom sits in the center of each Ta square antiprism, forming an infinite Si chain inside the Ta chain. Te atoms bridge each edge of the Ta square leading to the formula Ta_4SiTe_4. Individual Ta_4SiTe_4 chains are held together by weak Te–Te van der Waals interactions and pack in an orthorhombic unit cell (Figure 1).

A side view, which clearly illustrates the 10-fold coordination (eight Ta and two Si) of Si and the 4-fold coordination of Te, is displayed in Figure 2. Pertinent bond lengths are listed in Table III. The "intersquare" Ta–Ta distance (average 2.98 Å) is the shortest metal–metal distance and is close to the nearest-neighbor distance in elemental Ta (2.86 Å). The "intrasquare" Ta–Ta distance (average 3.25 Å) is significantly longer, indicating weaker bonding. The Ta–Te distances range from 2.827 to 2.856 Å for intrasquare Ta–Te bonds and from 2.915 to 2.979 Å for intersquare Ta–Te bonds. These distances are similar to the range of distances found in $TaTe_4$, which range from 2.807 (2) to 2.966 (2) Å.[7] The Ta–Si distances range from 2.576 to 2.606 Å, which are typical of tantalum silicides; the nearest-neighbor Ta–Si distance in Ta_3Si_5, for example, is 2.58 Å.[8] The Si–Si distances

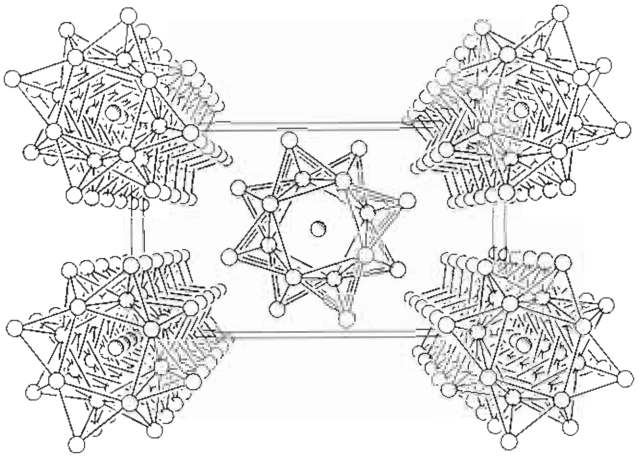

Figure 1. View of the Ta_4SiTe_4 structure parallel to the orthorhombic c axis. The Si atoms are partially hatched circles, Ta atoms are dotted circles, and Te atoms are open circles.

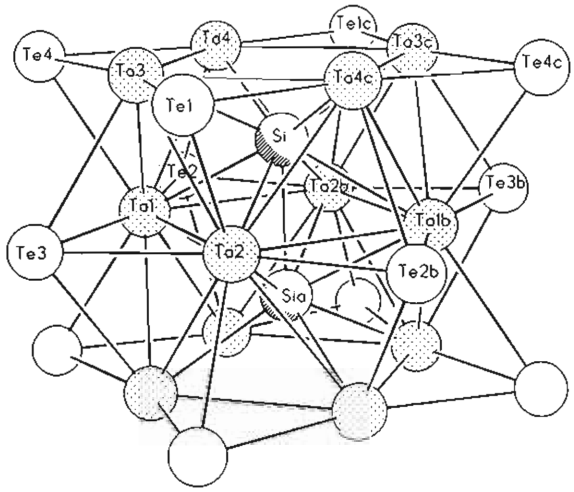

Figure 2. Side view of one repeat unit in the Ta_4SiTe_4 chain showing the labels used to identify the atoms in Table III. The point symmetry is C_{2h}.

Table III. Important Distances (Å) and Angles (deg)

Distances			
Ta1–Ta2	3.238 (3)	Ta1–Te2	2.827 (3)
Ta1–Ta2b	3.261 (2)	Ta1–Te3	2.856 (3)
Ta1–Ta3	2.970 (2)	Ta1–Te4	2.919 (2)
Ta1–Ta4	2.979 (2)	Ta2–Te1	2.915 (2)
Ta2–Ta3	2.976 (2)	Ta2–Te3	2.845 (3)
Ta2–Ta4c	2.979 (2)	Ta2–Te2b	2.841 (3)
Ta3–Ta4	3.249 (2)	Ta3–Te1	2.853 (2)
Ta3–Ta4c	3.253 (3)	Ta3–Te3	2.925 (2)
		Ta3–Te4	2.844 (3)
Ta1–Si	2.601 (5)	Ta4–Te2	2.910 (2)
Ta2–Si	2.606 (5)	Ta4–Te4	2.837 (3)
Ta3–Si	2.588 (4)	Ta4–Te2	2.910 (2)
Ta4–Si	2.577 (5)	Ta4–Te1c	2.832 (3)
Si–Sia	2.448 (19)	Te1–Te3	3.875 (3)
Si–Sib	2.353 (19)	Te1–Te2b	3.856 (3)
		Te2–Te4	3.840 (3)
		Te2–Te1c	3.856 (3)
		Te3–Te4	3.886 (3)
Nearest-Neighbor Te–Te Interchain Distances			
Te1	3.830 (5)	Te3	3.829 (4)
Te2	3.815 (3)	Te4	3.815 (3)
Angles			
Ta2–Ta1–Ta2b	90.1 (1)	Ta4–Ta3–Ta4c	89.7 (1)
Ta1–Ta2–Ta1b	89.9 (1)	Ta3–Ta4–Ta3c	90.3 (1)

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of 2.45 Å and 2.35 Å are very close to the nearest-neighbor distance in elemental Si (2.34 Å). The intrachain Te–Te distances range from 3.840 (3) to 3.886 (3) Å; these are much longer than the nearest-neighbor Te–Te distance in the element (2.86 Å). The nearest-neighbor Te–Te interchain distances range from 3.815 (3) to 3.830 (5) Å, which are typical for Te–Te van der Waals bonding; interlayer Te–Te distances in the layered compound $TaTe_2$, for example, range from 3.527 (8) to 3.999 (10) Å.[9]

The silicon-centered square-antiprismatic tantalum chain found in Ta_4SiTe_4 is similar to that found in one type of Ta_5Si_3[10] that adopts the W_5Si_3 structure.[11] In this structure, the metal squares stack in a nearly antiprismatic Si-centered chain with additional W and Si atoms bonding between the chains. In comparison, Ta_4SiTe_4 is novel in that the tantalum silicon chains are surrounded by tellurium and are relatively isolated from one another.

It would be interesting to compare this structure with those of other ternary tantalum tellurides. However, the ternary tantalum tellurides have not been extensively investigated—only five have been reported in the literature—Cu_3TaTe_4,[12] Ag_2TaTe_3,[13] Mo_2TaTe_4,[14] $Ta_3Pd_3Te_{14}$,[15] and $TaNiTe_5$.[15] The Ta_4SiTe_4 structure is very different from any of these phases.

It is interesting to compare Ta_4SiTe_4 with other infinite chain structures, including $InMo_3Te_3$ and Ta_2S. The structure of $InMo_3Te_3$[16] consists of infinite chains of triangular Mo_3 monomer, edge-bridged by Te, which are stacked antiprismatically to form a one-dimensional metal atom network. Individual chains are separated by channels occupied by the ternary cation, In. The Ta_2S structure[17] contains infinite chains of a pentagonal Ta_5 monomer stacked antiprismatically. An additional Ta atom sits in the center of the pentagonal antiprism, similar to Si in the Ta_4SiTe_4 structure. The chains in Ta_2S are interconnected via sulfur atoms. The Ta_4SiTe_4 chain structure (antiprismatically stacked squares, Si centered) may be viewed as intermediate between $InMo_3Te_3$ (triangles) and Ta_2S (pentagons, Ta centered).

Since it was found that the new zirconium halide cluster phases could be synthesized with a wide variety of heteroatoms,[1–4] many of which adopt the same structure, we investigated whether other atoms could substitute for Si in the interstitial site. Results from X-ray powder diffraction indicate that Ta_4SiTe_4 is in fact just one member of a class of isostructural compounds with the general formula Ta_4ZTe_4, where Z = Cr, Fe, Co, Ni, Al, and Si. Furthermore, we have found,[18] by powder diffraction, that niobium forms an analogous class, Nb_4ZTe_4, with the same set of interstitial heteroatoms. A detailed study of these new phases will be the subject of a future publication.

In summary, we have synthesized a new material, Ta_4SiTe_4, which is one member of the new class of isostructural low-dimensional compounds, Ta_4ZTe_4. A comparative study of the properties of these phases, where only the stabilizing heteroatom is changing, should be interesting.

Acknowledgment. We wish to thank Greg VanDuyne of the Cornell Chemistry X-ray facility for aid with the structure determination. Valuable discussions with R. P. Ziebarth and J. Li are also greatly appreciated. The work was supported by the Department of Energy, Division of Basic Energy Sciences, Grant DE-FG02-87ER45298.

Supplementary Material Available: A table of refined anisotropic thermal parameters for Ta_4SiTe_4 (1 page); tables of observed and calculated structure factors for Ta_4SiTe_4 (5 pages). Ordering information is given on any current masthead page.

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An Open Structure for the Adduct of Fluoride Ion with Oxalyl Fluoride

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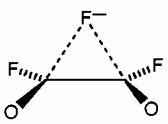
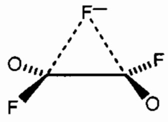
Stable, isolable tris(dimethylamino)sulfonium salts of the perfluoroalkoxides $FC(O)(CF_2)_nCF_2O^-$ (n = 0, 1, 3) and $^-OCF_2(CF_2)_nCF_2O^-$ (n = 1, 3) have been synthesized and characterized. The $C_2F_3O_2^-$ anion generated from oxalyl fluoride has an open ground-state structure $FC(O)CF_2O^-$ and not a bridged-fluoride structure as previously proposed. High-level ab initio calculations on the isomers of $C_2F_3O_2^-$, including vibrational spectra calculations, corroborate the open structure. The bridged structures for $C_2F_3O_2^-$ actually are transition states for intramolecular fluoride transfers.

Introduction

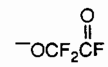
Ault has reported the synthesis of $C_2F_3O_2^-Cs^+$ by codeposition of CsF with oxalyl fluoride in an argon matrix.[1] On the basis of the analysis of the matrix infrared spectrum, the species produced were assigned the unusual symmetrically fluoride-bridged structures *cis*-**1** and *trans*-**1**, rather than the open structure **2**. These bridged anions were reported to rearrange to the trifluoroacetate anion, $CF_3CO_2^-$, upon warming the matrix to room temperature.



cis-1



trans-1



$$^-OCF_2\overset{\overset{O}{\|}}{C}F$$

2

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