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Syntheses and Structures of the Infinite Chain Compounds $Cs_4Ti_3Se_{13}$, $Rb_4Ti_3S_{14}$, $Cs_4Ti_3S_{14}$, $Rb_4Hf_3S_{14}$, $Rb_4Zr_3Se_{14}$, $Cs_4Zr_3Se_{14}$, and $Cs_4Hf_3Se_{14}$

Fu Qiang Huang and James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

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The alkali metal/group 4 metal/polychalcogenides $Cs_4Ti_3Se_{13}$, $Rb_4Ti_3S_{14}$, $Cs_4Ti_3S_{14}$, $Rb_4Hf_3S_{14}$, $Rb_4Zr_3Se_{14}$, $Cs_4Zr_3Se_{14}$, and $Cs_4Hf_3Se_{14}$ have been synthesized by means of the reactive flux method at 823 or 873 K. $Cs_4Ti_3Se_{13}$ crystallizes in a new structure type in space group C_2^2-$P2_1$ with eight formula units in a monoclinic cell at $T =$ 153 K of dimensions $a = 10.2524(6)$ Å, $b = 32.468(2)$ Å, $c = 14.6747(8)$ Å, $\beta = 100.008(1)°$. $Cs_4Ti_3Se_{13}$ is composed of four independent one-dimensional $^{1}_{\infty}[Ti_3Se_{13}{}^{4-}]$ chains separated by Cs^+ cations. These chains adopt hexagonal closest packing along the [100] direction. The $^{1}_{\infty}[Ti_3Se_{13}{}^{4-}]$ chains are built from the face- and edge-sharing of pentagonal pyramids and pentagonal bipyramids. Formal oxidation states cannot be assigned in $Cs_4Ti_3Se_{13}$. The compounds $Rb_4Ti_3S_{14}$, $Cs_4Ti_3S_{14}$, $Rb_4Hf_3S_{14}$, $Rb_4Zr_3Se_{14}$, $Cs_4Zr_3Se_{14}$, and $Cs_4Hf_3Se_{14}$ crystallize in the $K_4Ti_3S_{14}$ structure type with four formula units in space group C_{2h}^6-$C2/c$ of the monoclinic system at $T = 153$ K in cells of dimensions $a = 21.085(1)$ Å, $b = 8.1169(5)$ Å, $c = 13.1992(8)$ Å, $\beta = 112.835(1)°$ for $Rb_4Ti_3S_{14}$; $a = 21.329(3)$ Å, $b = 8.415(1)$ Å, $c = 13.678(2)$ Å, $\beta = 113.801(2)°$ for $Cs_4Ti_3S_{14}$; $a = 21.643(2)$ Å, $b = 8.1848(8)$ Å, $c = 13.331(1)$ Å, $\beta = 111.762(2)°$ for $Rb_4Hf_3S_{14}$; $a = 22.605(7)$ Å, $b = 8.552(3)$ Å, $c = 13.880(4)$ Å, $\beta = 110.919(9)°$ for $Rb_4Zr_3Se_{14}$; $a = 22.826(5)$ Å, $b = 8.841(2)$ Å, $c = 14.278(3)$ Å, $\beta = 111.456(4)°$ for $Cs_4Zr_3Se_{14}$; and $a = 22.758(5)$ Å, $b = 8.844(2)$ Å, $c = 14.276(3)$ Å, $\beta = 111.88(3)°$ for $Cs_4Hf_3Se_{14}$. These $A_4M_3Q_{14}$ compounds (A = alkali metal; M = group 4 metal; Q = chalcogen) contain hexagonally closest-packed $^{1}_{\infty}[M_3Q_{14}{}^{4-}]$ chains that run in the [101] direction and are separated by A^+ cations. Each $^{1}_{\infty}[M_3Q_{14}{}^{4-}]$ chain is built from a $[M_3Q_{14}]$ unit that consists of two MQ_7 pentagonal bipyramids or one distorted MQ_8 bicapped octahedron bonded together by edge- or face-sharing. Each $[M_3Q_{14}]$ unit contains six $Q_2{}^{2-}$ dimers, with Q−Q distances in the normal single-bond range 2.0616(9)−2.095(2) Å for S−S and 2.367(1)−2.391(2) Å for Se−Se. The $A_4M_3Q_{14}$ compounds can be formulated as $(A^+)_4(M^{4+})_3(Q_2{}^{2-})_6(Q^{2-})_2$.

Introduction

Low-dimensional solids exhibit various interesting physical phenomena such as high T_c superconductivity, the formation of charge density waves, and low-dimensional magnetism. These solids are built from the stacking of two-dimensional slabs or from a juxtaposition (edge- or face-sharing) of fibers. Each slab or fiber is held together by ionic, covalent, or metallic interactions but is separated from similar units by weak interactions, such as van der Waals interactions, or by other species, such as alkali metal or alkaline-earth metal cations. Examples of two-dimensional structures are those of the stoichiometric MQ_2 (M = transition metal; Q = S, Se, Te) dichalcogenides.[1−5] In particular, the group 4 to group 7 metal dichalcogenides are two-dimensional layer structures with a rich intercalation chemistry.[6−9]

One-dimensional transition-metal polychalcogenides were virtually unknown until the discovery of the reactive flux method.[10,11] The use of this method has led to a variety of one-dimensional A/M/Q polychalcogenides (A = Na, K, Rb, Cs; M = Ti, Zr, Hf, Nb, Ta; Q = S, Se, Te).[10−30] In particular, the group 4 metal compounds contain infinite one-dimensional

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Table 1. Crystal Data and Structure Refinements for $Cs_4Ti_3Se_{13}$, $Rb_4Ti_3S_{14}$, $Cs_4Ti_3S_{14}$, $Rb_4Hf_3S_{14}$, $Rb_4Zr_3Se_{14}$, $Cs_4Zr_3Se_{14}$, and $Cs_4Hf_3Se_{14}$[a]

	$Cs_4Ti_3Se_{13}$	$Rb_4Ti_3S_{14}$	$Cs_4Ti_3S_{14}$	$Rb_4Hf_3S_{14}$	$Rb_4Zr_3Se_{14}$	$Cs_4Zr_3Se_{14}$	$Cs_4Hf_3Se_{14}$
fw	1701.81	934.42	1124.18	1326.19	1720.98	1910.74	2172.55
a (Å)	10.2524(6)	21.085(1)	21.329(3)	21.643(2)	22.605(7)	22.826(5)	22.758(5)
b (Å)	32.468(2)	8.1169(5)	8.415(1)	8.1848(8)	8.552(3)	8.841(2)	8.844(2)
c (Å)	14.6747(8)	13.1992(8)	13.678(2)	13.331(1)	13.880(4)	14.278(3)	14.276(3)
β (deg)	100.008(1)	112.835(1)	113.801(2)	111.762(2)	110.919(9)	111.456(4)	111.88(3)
V (Å^3)	4810.5(5)	2081.9(2)	2246.1(5)	2193.1(4)	2506(1)	2681(1)	2666.5(9)
ρ_c (g/cm^3)	4.700	2.981	3.324	4.017	4.561	4.732	5.412
μ (cm^{-1})	265.97	118.02	289.9	243.03	292.63	254.86	361.31
R1[b]	0.0431	0.021	0.022	0.047	0.041	0.042	0.047
wR2[c]	0.0949	0.052	0.056	0.084	0.090	0.090	0.113

[a] $T = 153(2)$ K, $\lambda = 0.710\,73$ Å. $Z = 4$ and space group $C2/c$ for $A_4M_3Q_{14}$; $Z = 8$ and space group $P2_1$ for $Cs_4Ti_3Se_{13}$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 > 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

chains that are linear rigid fibers. The one-dimensional chains in such compounds, for example, in $K_4Ti_3S_{14}$,[10,11] $Na_2Ti_2Se_8$,[12] $A_3Ti_3Te_{11}$ (A = Rb, Cs),[15,16] $A_4Zr_3Te_{16}$ (A = Rb, Cs)[14,31] $K_4M_3Te_{17}$ (M = Zr, Hf),[13] $Cs_5Hf_5Te_{26}$,[15] and $Cs_2Ti_2S_9$,[17] have varied and interesting formulations and structures. Here we describe the syntheses and structures of seven additional alkali metal/group 4 metal/polychalcogenides, namely, $Cs_4Ti_3Se_{13}$, $Rb_4Ti_3S_{14}$, $Cs_4Ti_3S_{14}$, $Rb_4Hf_3S_{14}$, $Rb_4Zr_3Se_{14}$, $Cs_4Zr_3Se_{14}$, and $Cs_4Hf_3Se_{14}$. In addition, we offer some simple connections among the seemingly varied formulations of the alkali metal/group 4 metal/polychalcogenides.

Experimental Section

Syntheses. The following reagents were used as obtained: Rb (Aldrich, 98+%), Cs (Aldrich, 99.5%), Ti (Aldrich, 99.7%), Zr (Aldrich, 99.9+%), Hf (Alfa, 99.8%), S (Alfa, 99.5%), Se (Aldrich, 99.5%). The isostructural compounds $Rb_4Ti_3S_{14}$, $Cs_4Ti_3S_{14}$, $Rb_4Hf_3S_{14}$, $Rb_4Zr_3Se_{14}$, $Cs_4Zr_3Se_{14}$, and $Cs_4Hf_3Se_{14}$ were systematically prepared by the reactions of M (M = Ti, Zr, Hf) with Q (Q = S, Se) and the reactive flux A_2Q_3 (A = Rb, Cs) in the molar ratio 1:1:3. The reactive fluxes[10] employed in the syntheses were prepared by stoichiometric reactions of the elements in liquid NH_3. The mixtures were loaded into fused-silica tubes under an argon atmosphere in a glovebox. These tubes were sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The samples were heated to 873 K at 60 K/h, kept at 873 K for 4 days, cooled at 3 K/h to 373 K, and then cooled to room temperature. These $A_4M_3Q_{14}$ phases appear to be very stable because these same phases could be synthesized under varied initial compositions and reaction conditions.

The compound $Cs_4Ti_3Se_{13}$ was prepared by the reaction of 0.5 mmol of Cs_2Se_3, 0.5 mmol of Ti, and 3.0 mmol of Se. The sample was heated to 823 K at 60 K/h, kept at 823 K for 3 days, cooled at 4 K/h to 373 K, and then cooled to room temperature. Attempts to synthesize $Cs_4Ti_3S_{13}$ in an analogous manner were unsuccessful.

The reaction mixtures were washed free of alkali-metal chalcogenides with dimethylformamide and then dried with acetone. In each reaction the major product consisted of orange-red needles of $A_4M_3Q_{14}$ or black needles of $Cs_4Ti_3Se_{13}$. Analysis of these crystals with an energy dispersive X-ray (EDX) equipped Hitachi S-4500 scanning electron microscope showed only the presence of A, M, and Q approximately in the ratio of 1:1:4. These compounds are stable in air for at least a month.

Structure Determinations. Single-crystal X-ray diffraction data were obtained with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer.[32] The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606, 606, 606, and 606 frames at ϕ settings of 0°, 90°, 180°, and 270° for $Cs_4Ti_3Se_{13}$ and $Cs_4Ti_3S_{14}$, in groups of 606, 435, and 230 frames at ϕ settings of 0°, 90°, and 180° for $Rb_4Zr_3Se_{14}$, and in groups of 606, 606, and 606 frames at ϕ settings of 0°, 120°, and 240° for the others. The exposure times were 15 s/frame. Intensity data were collected with the program SMART.[32] Cell refinement and data reduction were carried out with the use of the program SAINT,[32] face-indexed absorption corrections were made with the program XPREP,[33] and the redundancies in the data were used in the program SADABS[32] to make other corrections, such as for frame variations.

Systematic absences and Laue symmetry led to the monoclinic space groups $P2_1$ *or* $P2_1/m$ for $Cs_4Ti_3Se_{13}$ and to Cc or $C2/c$ for the $A_4M_3Q_{14}$ compounds. For $Cs_4Ti_3Se_{13}$ a solution could only be found in the noncentrosymmetric space group $P2_1$ with the use of the direct methods program SHELXS.[33] The structure was refined by full-matrix least-squares methods with the program SHELXL in the SHELXTL-97 suite.[33] In this refinement the Flack parameter was near 0.6, consistent either with a racemic twin or with $P2_1/m$ being the correct space group. Examination of the atomic coordinates with the program ADDSYM in the PLATON program suite[34−36] did not suggest the presence of an inversion center. The structures of the $A_4M_3Q_{14}$ compounds were solved and refined in space group $C2/c$ in a similar manner. Each final refinement included anisotropic displacement parameters. Additional experimental details are shown in Table 1. Tables 2−4 present selected bond distances for $Cs_4Ti_3Se_{13}$, $Rb_4Ti_3S_{14}$, $Cs_4Ti_3S_{14}$, $Rb_4Hf_3S_{14}$, $Rb_4Zr_3Se_{14}$, $Cs_4Zr_3Se_{14}$, and $Cs_4Hf_3Se_{14}$.

Results

Structures. The structure of the $A_4M_3Q_{14}$ compounds, as viewed down [010], is shown in Figure 1. These compounds are isostructural with $K_4Ti_3S_{14}$.[10,11] The structure of $Cs_4Ti_3Se_{13}$ viewed down [100] is shown in Figure 2. This is a new structure type. The infinite chains in these compounds are illustrated in Figure 3. The unique ${}^{1}_{\infty}[M_3Q_{14}{}^{4-}]$ chain of $A_4M_3Q_{14}$, which runs along [101], is shown in Figure 3a. Among the four independent ${}^{1}_{\infty}[Ti_3Se_{13}{}^{4-}]$ chains of $Cs_4Ti_3Se_{13}$, which run

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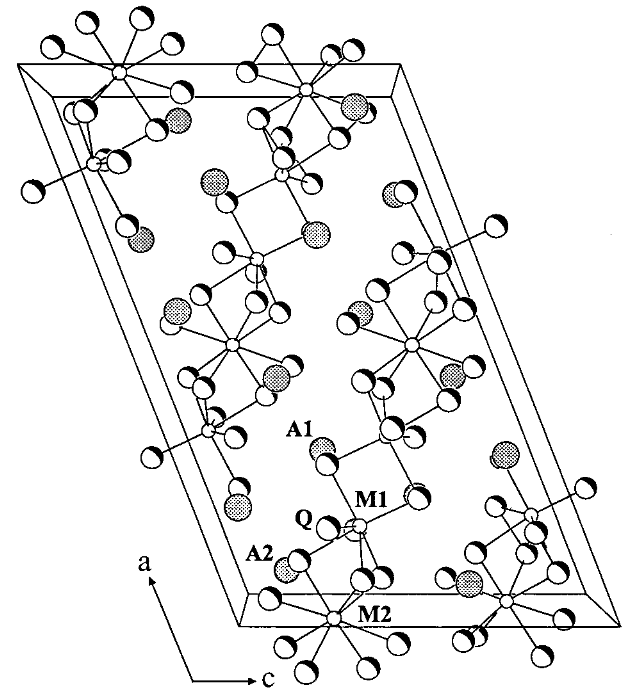

Figure 1. Unit cell of $A_4M_3Q_{14}$ viewed down [010]. The dotted, open, and shaded circles represent A, M, and Q, respectively.

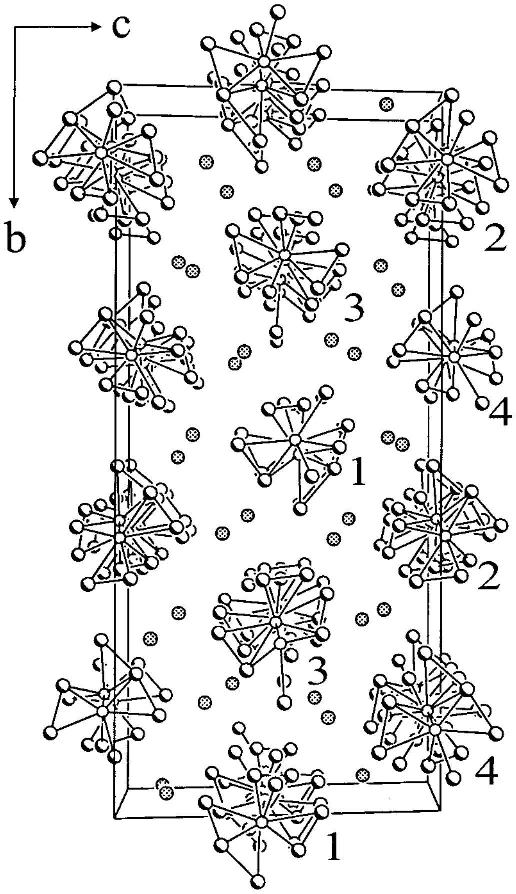

Figure 2. Unit cell of $Cs_4Ti_3Se_{13}$ viewed along [100]. The dotted, open, and shaded circles represent A, M, and Q, respectively.

along [100], there are two different kinds. These are shown in Figure 3b and 3c. This is the first compound in the alkali metal/group 4 metal/polychalcogenide family to exhibit different chains in the same unit cell. If all chains in these ternary compounds are considered as cylinders, each cylinder is surrounded by six nearest-neighboring cylinders and the A^+ cations are located in the triangular gaps of three neighboring cylinders. The structures adopt hexagonal closest packing along the chain direction.

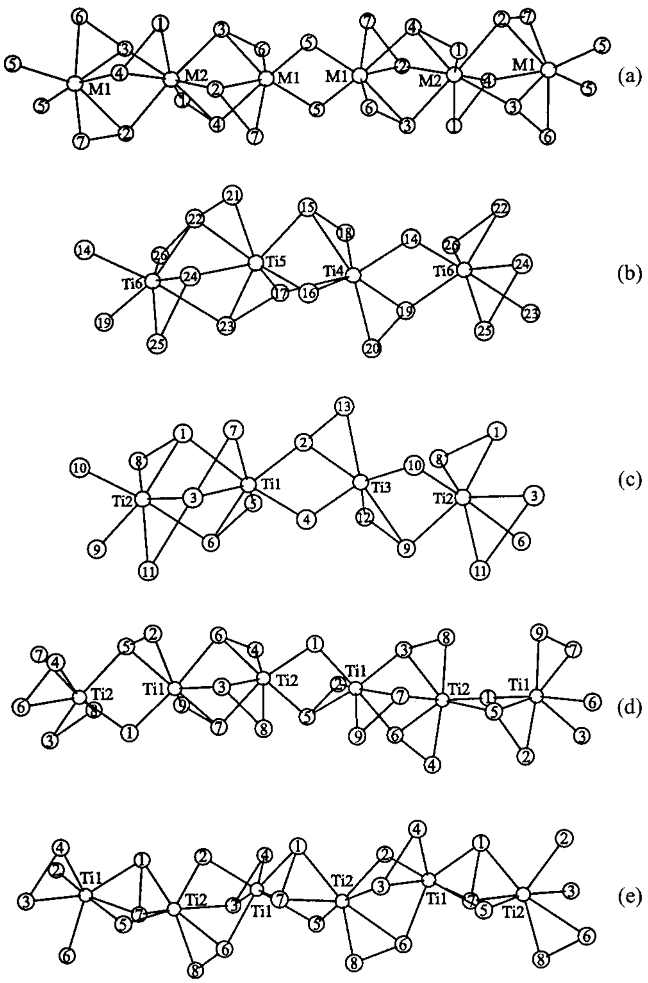

Figure 3. (a) $^1_\infty[M_3Q_{14}{}^{4-}]$ chain in $A_4M_3Q_{14}$, (b) first type of $^1_\infty[Ti_3Se_{13}{}^{4-}]$ chain in $Cs_4Ti_3Se_{13}$, (c) second type of $^1_\infty[Ti_3Se_{13}{}^{4-}]$ chain in $Cs_4Ti_3Se_{13}$, (d) $^1_\infty[Ti_2S_9{}^{2-}]$ chain in $Cs_2Ti_2S_9$, and (e) $^1_\infty[Ti_2Se_8{}^{2-}]$ chain in $Na_2Ti_2Se_8$.

In the $A_4M_3Q_{14}$ structure there are two crystallographically independent A^+ sites coordinated to 10 Q atoms. There are 16 independent Cs^+ cations in $Cs_4Ti_3Se_{13}$, and these cations are coordinated to 9 or to 12 Se atoms. The A−Q and M−Q distances in these compounds are reasonable (Tables 2 and 3). For example, the Rb−S distances in $Rb_4Ti_3S_{14}$ range from 3.2326(7) to 3.8107(6) Å and the Rb−Se distances in $Rb_4Zr_3Se_{14}$ range from 3.377(2) to 3.961(2) Å. These are comparable with those in Rb_2S_5 (from 3.301(5) to 3.969(6) Å)[37] and Rb_2Se_5 (from 3.36(1) to 3.89(2) Å),[37] respectively. Ti−S distances range from 2.2773(7) to 2.6537(7) Å in $Rb_4Ti_3S_{14}$ and from 2.2749(8) to 2.6576(9) Å in $Cs_4Ti_3S_{14}$, compared with distances from 2.283(2) to 2.652(2) Å in $K_4Ti_3S_{14}$.[10,11] Ti−Se distances in $Cs_4Ti_3Se_{13}$ range from 2.422(3) to 3.017(3) Å, compared with those in $Na_2Ti_2Se_8$ (from 2.382(4) to 2.735(4) Å).[12] The similar bond distances between $Cs_4Zr_3Se_{14}$ and $Cs_4Hf_3Se_{14}$ result from very similar radii for Zr^{4+} and Hf^{4+} (0.92 and 0.90 Å).[38]

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Table 2. Selected Bond Lengths (Å) for $Rb_4Ti_3S_{14}$, $Cs_4Ti_3S_{14}$, $Rb_4Hf_3S_{14}$, $Rb_4Zr_3Se_{14}$, $Cs_4Zr_3Se_{14}$, and $Cs_4Hf_3Se_{14}$

	$Rb_4Ti_3S_{14}$	$Cs_4Ti_3S_{14}$	$Rb_4Hf_3S_{14}$	$Rb_4Zr_3Se_{14}$	$Cs_4Zr_3Se_{14}$	$Cs_4Hf_3Se_{14}$
A1−Q1	3.4339(6)	3.5193(8)	3.500(2)	3.618(2)	3.693(2)	3.686(1)
A1−Q3	3.5882(6)	3.7131(7)	3.636(2)	3.794(2)	3.922(1)	3.910(2)
A1−Q4	3.2604(6)	3.3998(7)	3.255(2)	3.416(1)	3.546(1)	3.541(1)
A1−Q5	3.2326(7)	3.3740(8)	3.254(2)	3.377(2)	3.527(2)	3.521(2)
A1−Q5	3.5589(6)	3.6982(8)	3.631(2)	3.783(2)	3.891(2)	3.899(2)
A1−Q6	3.4474(6)	3.5627(7)	3.486(2)	3.634(2)	3.728(1)	3.717(1)
A1−Q6	3.6526(7)	3.7680(8)	3.701(2)	3.743(2)	3.917(2)	3.922(1)
A1−Q6	3.6705(7)	3.8242(8)	3.748(2)	3.944(2)	4.001(2)	3.989(2)
A1−Q7	3.3766(6)	3.4514(8)	3.440(2)	3.553(2)	3.612(2)	3.616(1)
A1−Q7	3.4159(7)	3.5838(8)	3.468(2)	3.572(2)	3.710(2)	3.704(2)
A2−Q1	3.3628(6)	3.5024(8)	3.367(2)	3.504(2)	3.630(2)	3.627(2)
A2−Q1	3.4057(7)	3.5417(8)	3.419(2)	3.556(2)	3.691(2)	3.684(2)
A2−Q2	3.3129(6)	3.4798(8)	3.338(2)	3.448(2)	3.608(2)	3.609(1)
A2−Q2	3.6896(6)	3.7528(7)	3.705(2)	3.943(2)	3.980(2)	3.986(2)
A2−Q3	3.5908(7)	3.7487(8)	3.617(2)	3.687(2)	3.832(1)	3.823(1)
A2−Q3	3.8107(6)	3.8637(8)	3.874(2)	3.961(2)	3.979(2)	3.979(1)
A2−Q4	3.3679(6)	3.5297(8)	3.392(2)	3.488(2)	3.644(1)	3.649(2)
A2−Q5	3.5958(7)	3.7761(8)	3.631(2)	3.735(2)	3.905(2)	3.905(2)
A2−Q6	3.3290(6)	3.4948(7)	3.312(2)	3.433(2)	3.602(2)	3.594(2)
A2−Q7	3.4619(7)	3.6047(8)	3.448(2)	3.591(2)	3.718(2)	3.718(2)
M1−Q2	2.4930(7)	2.4623(8)	2.613(2)	2.771(1)	2.779(2)	2.777(1)
M1−Q3	2.4591(7)	2.4950(8)	2.574(2)	2.726(1)	2.745(2)	2.732(1)
M1−Q4	2.6537(7)	2.6576(9)	2.738(2)	2.871(2)	2.882(2)	2.842(1)
M1−Q5	2.2773(7)	2.2749(8)	2.426(2)	2.555(2)	2.548(2)	2.539(1)
M1−Q5	2.4919(7)	2.4982(9)	2.534(2)	2.709(1)	2.728(2)	2.706(1)
M1−Q6	2.3912(7)	2.3971(8)	2.501(2)	2.637(2)	2.654(2)	2.632(1)
M1−Q7	2.4679(7)	2.4727(9)	2.557(2)	2.721(2)	2.723(2)	2.706(1)
M2−Q1 ×2	2.4575(6)	2.4549(7)	2.545(2)	2.710(1)	2.708(1)	2.700(1)
M2−Q2 ×2	2.5729(7)	2.5840(8)	2.660(2)	2.794(1)	2.809(1)	2.785(1)
M2−Q3 ×2	2.5940(7)	2.5996(8)	2.683(2)	2.824(1)	2.834(2)	2.808(1)
M2−Q4 ×2	2.4283(6)	2.4268(7)	2.537(2)	2.694(1)	2.695(1)	2.688(1)
Q1−Q4	2.0624(8)	2.0616(9)	2.090(2)	2.384(1)	2.386(2)	2.391(2)
Q2−Q7	2.0709(8)	2.0702(9)	2.092(2)	2.372(1)	2.378(2)	2.378(2)
Q3−Q6	2.0699(8)	2.0683(9)	2.095(2)	2.367(1)	2.373(2)	2.374(2)

In the alkali metal/group 4 metal/polychalcogenides the coordination environments of the group 4 metals are varied. This is illustrated in Figure 4 for M = Ti. The present $Cs_4Ti_3S_{13}$ compound provides a new Ti coordination environment. Group 4 metals in other chalcogenides are mostly coordinated to tetrahedra as in $Cs_2ZrAg_2Te_4$,[39] to octahedra as in $KZrCuS_3$,[18] or to bicapped trigonal prisms as in $ZrTe_3$.[40]

Formal Oxidation States. In known alkali metal/group 4 metal/polychalcogenides there are no M−M bonding interactions, and the formal oxidation state of the M atoms is +4. By way of illustration, the respective M1−M1 and M1−M2 distances in $A_4M_3Q_{14}$ are 3.3238(8) and 3.3568(4) Å in $Rb_4Ti_3S_{14}$ and 3.629(2) and 3.662(1) Å in $Rb_4Zr_3Se_{14}$. These are too long to be M−M bonding distances. In these structures the three Q atoms (Q2, Q3, and Q4) that bridge the M1 and M2 atoms are each a part of a Q_2^{2-} unit. These Q−Q distances range from 2.0616(9) to 2.095(2) Å for Q = S and from 2.367(1) to 2.391(2) Å for Q = Se and are single bonds. The Q atoms (Q5) that link M1−M1 do not form Q_2^{2-} pairs. So $A_4M_3Q_{14}$ can be described as $(A^+)_4(M^{4+})_3(Q_2^{2-})_6(Q^{2-})_2$. On the other hand, in $Cs_4Ti_3Se_{13}$ it is not possible to assign formal oxidation states because the Se−Se interactions vary widely. Only those interactions less than 3.0 Å in length are listed in Table 4. Inability to assign formal oxidation states is uncommon in the polyselenides but is the rule in the polytellurides.[13−16,30,31]

Interrelationships. In the $A_4M_3Q_{14}$ compounds, the $^{1}_{\infty}[M_3Q_{14}{}^{4-}]$ chain illustrated in Figure 3a has $[M_3Q_{14}]$ as the repeat unit. The chain contains two crystallographically unique M sites; M1 at the Wyckoff 8f site of space group *C*2/*c* is coordinated to a pentagonal bipyramid of seven Q atoms ($M1Q_7$), whereas M2 at the Wyckoff 4c site is coordinated to a distorted bicapped octahedron of eight Q atoms ($M2Q_8$). The arrangement of the M atoms along the chain is ..., [M1, M2, M1], [M1, M2, M1], ..., with each M2 atom sharing three Q atoms with two neighboring M1 atoms and each M1 atom sharing two Q atoms with one neighboring M1 atom. If the face-sharing and edge-sharing are expressed as "≡" and "=", respectively, the $[M_3Q_{14}]$ repeat unit can be written as [M1≡M2*≡M1=], where ∗ denotes an eight-coordinated metal atom. The chains in the compounds $Cs_4Zr_3Te_{16}$[14] and $K_4M_3Te_{17}$ (M = Zr, Hf)[13] are similar. There are three independent M atoms in these structures, and each M atom is coordinated to a distorted bicapped octahedron of eight Te atoms. The $[M_3Te_{16}]$ chain can be written [M1*≡M2*≡M3*=]. The $[M_3Te_{17}]$ chain has two Te atoms, not bonded to M atoms, and the chain becomes $[M_3Te_{15}]$ if these two unique Te atoms are excluded. This $[M_3Te_{15}]$ chain can be expressed as [M1*≡M2*≡M3*≡].

In $Cs_4Ti_3Se_{13}$, each $^{1}_{\infty}[Ti_3Se_{13}{}^{4-}]$ chain can be described by the $[Ti_3Se_{13}]$ repeat unit. Atoms Ti1 to Ti3 and Se1 to Se13 form the first chain (**1**), Ti4 to Ti6 and Se14 to Se26 form the second chain (**2**), Ti7 to Ti9 and Se27 to Se39 form the third chain (**3**), and Ti10 to Ti12 and Se40 to Se52 form the fourth chain (**4**). The locations of these chains in the unit cell are shown in Figure 2, where two equivalent ones in the cell are related by the 2_1 symmetry operation. Chains **2** and **3** belong to one type, and they are composed of three independent Ti atoms that are coordinated to pentagonal bipyramids of seven Se atoms to form a [Ti≡Ti≡Ti=] chain, as shown in Figure 3b. Chains **1** and **4** belong to another type and consist of three independent Ti atoms, as shown in Figure 3c. Ti1, Ti2, Ti10, and Ti12 are coordinated to pentagonal bipyramids of seven Se atoms, but

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(39) Pell, M. A.; Ibers, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 6284−6286.
(40) Brattås, L.; Kjekshus, A. *Acta Chem. Scand.* **1972**, *26*, 3441−3449.

Table 3. Ti−Se Interactions (Å) in $Cs_4Ti_3Se_{13}$

Ti1−Se6	2.524(3)	Ti7−Se31	2.522(3)
Ti1−Se4	2.534(3)	Ti7−Se28	2.523(3)
Ti1−Se7	2.535(3)	Ti7−Se33	2.542(3)
Ti1−Se5	2.568(3)	Ti7−Se29	2.547(3)
Ti1−Se3	2.580(3)	Ti7−Se27	2.579(3)
Ti1−Se2	2.583(3)	Ti7−Se30	2.626(3)
Ti1−Se1	2.820(3)	Ti7−Se32	2.831(3)
Ti2−Se10	2.422(3)	Ti8−Se35	2.437(3)
Ti2−Se11	2.509(3)	Ti8−Se37	2.515(3)
Ti2−Se8	2.545(3)	Ti8−Se36	2.539(3)
Ti2−Se1	2.574(3)	Ti8−Se32	2.545(3)
Ti2−Se9	2.591(3)	Ti8−Se34	2.617(3)
Ti2−Se3	2.612(3)	Ti8−Se27	2.627(3)
Ti2−Se6	2.760(3)	Ti8−Se31	2.748(3)
Ti3−Se4	2.434(3)	Ti9−Se29	2.458(3)
Ti3−Se13	2.514(3)	Ti9−Se38	2.513(3)
Ti3−Se12	2.522(3)	Ti9−Se39	2.517(3)
Ti3−Se10	2.576(3)	Ti9−Se35	2.587(3)
Ti3−Se2	2.628(3)	Ti9−Se30	2.624(3)
Ti3−Se9	2.696(3)	Ti9−Se34	2.723(3)
Ti4−Se14	2.472(3)	Ti9−Se36	3.017(3)
Ti4−Se20	2.508(3)	Ti10−Se46	2.534(3)
Ti4−Se18	2.518(3)	Ti10−Se45	2.542(3)
Ti4−Se16	2.585(3)	Ti10−Se41	2.546(3)
Ti4−Se19	2.618(3)	Ti10−Se40	2.551(3)
Ti4−Se15	2.740(3)	Ti10−Se44	2.561(3)
Ti4−Se17	2.987(3)	Ti10−Se43	2.569(3)
Ti5−Se16	2.427(3)	Ti10−Se42	2.804(3)
Ti5−Se23	2.536(3)	Ti11−Se41	2.435(3)
Ti5−Se17	2.538(3)	Ti11−Se49	2.498(3)
Ti5−Se21	2.541(3)	Ti11−Se48	2.507(3)
Ti5−Se15	2.632(3)	Ti11−Se50	2.579(3)
Ti5−Se24	2.639(3)	Ti11−Se43	2.649(3)
Ti5−Se22	2.717(3)	Ti11−Se47	2.728(3)
Ti6−Se26	2.515(3)	Ti12−Se50	2.441(3)
Ti6−Se25	2.537(3)	Ti12−Se51	2.519(3)
Ti6−Se14	2.541(3)	Ti12−Se52	2.541(3)
Ti6−Se22	2.548(3)	Ti12−Se42	2.553(3)
Ti6−Se24	2.580(3)	Ti12−Se47	2.603(3)
Ti6−Se19	2.627(3)	Ti12−Se44	2.651(3)
Ti6−Se23	2.856(3)	Ti12−Se46	2.732(3)

Ti3 and Ti11 are coordinated to pentagonal pyramids of six Se atoms to form a [Ti≡Ti═Ti$^{\#}$═] chain, where # denotes a six-coordinated metal atom.

Although six-, seven-, and eight-coordinated M atoms are found in alkali metal/group 4 metal/polychalcogenides, seven- and eight-coordinated M atoms are most common. If a chain contains only seven- or eight-coordinated M atoms in the structure and all Q atoms are bonded to M atoms, the chain can be expressed systematically. If the [M/Q] chain contains only seven-coordinated M atoms there are four possibilities. The first is the [M≡] chain; each polyhedron shares one face (three Q atoms) with two neighbors, and the chain can be expressed as $[MQ_{7-3=4}]$. Such a chain exists in $Na_2Ti_2Se_8$[12] (Figure 3e). The second possibility is the [M═] chain; each polyhedron shares one edge (two Q atoms) with two neighbors, and the chain becomes $[MQ_{7-2=5}]$. This kind of chain is yet to be discovered. The third possibility is the [M≡M═] chain. The chain is $[M_2Q_{7+7-3-2=9}]$, which has been found in $Cs_2Ti_2S_9$ (Figure 3d).[17] The fourth possibility is the [···M···M···] chain. This chain contains *m* "═" and *n* "≡" and may be formulated as $[M_{m+n}Q_{7(m+n)-2m-3n}]$. If such a chain [···M*···M*···] contains only *m* "═" and *n* "≡" eight-coordinated M atoms, then it becomes $[M_{m+n}Q_{8(m+n)-2m-3n}]$. When $m = 0$, the face-sharing chain is $[MQ_5]$, which can be found in $K_4M_3Te_{17}$ (M = Zr, Hf)[13] and $Cs_5Hf_5Te_{26}$.[15] When $m = 1$ and $n = 2$, the chain becomes $[M_3Q_{16}]$, which is found in $A_4Zr_3Te_{16}$ (A = Rb, Cs).[14,31] Some compounds contain both seven- and eight-coordinated M atoms, such as $A_4M_3Q_{14}$. If seven- or eight-coordinated M atoms are expressed as M and M*, respectively, and the chain [···M···M*···] contains *i* M, *j* M*, *m* "═", and *n* "≡", where $i + j = m + n$, the chain is $[M_{i+j}Q_{7i+8j-2m-3n}]$. In $A_4M_3Q_{14}$, $i = 2$, $j = 1$, $m = 1$, $n = 2$.

As discussed previously,[17] these compounds have closed valence bands near the Fermi surface and are expected to be semiconductors.

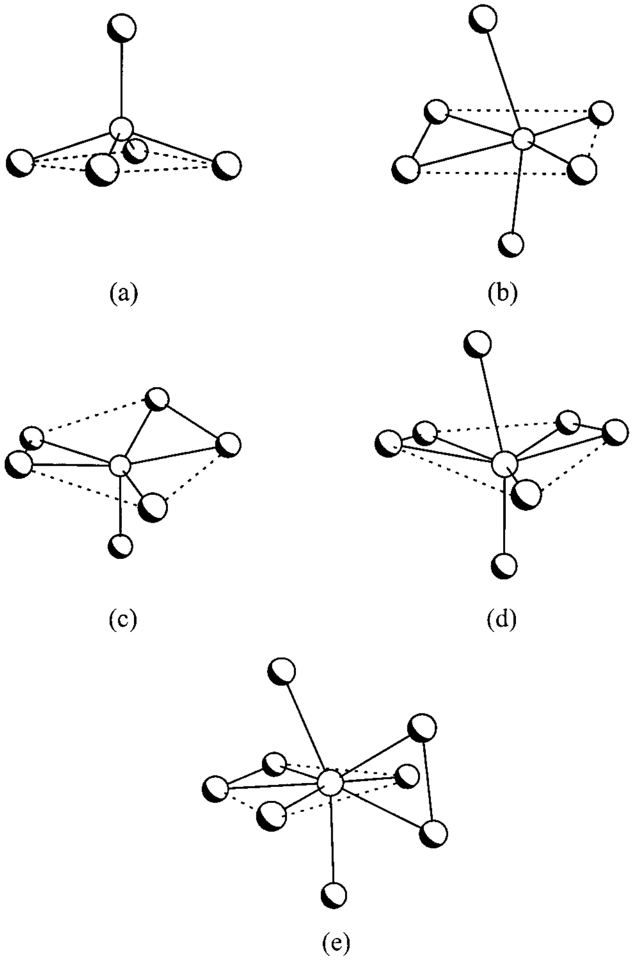

Figure 4. Coordination environments of Ti in some one-dimensional alkali metal/titanium/chalcogenides: (a) square pyramid in K_2TiS_3; (b) distorted octahedron in $Cs_3Ti_3Te_{11}$; (c) pentagonal pyramid in $Cs_4Ti_3Se_{13}$; (d) pentagonal bipyramid in $Cs_4Ti_3S_{14}$; (e) distorted bicapped octahedron in $Cs_4Ti_3S_{14}$. Here open circles represent Ti atoms and shaded circles are chalcogen atoms.

Table 4. Selected Se−Se Distances (Å) in $Cs_4Ti_3Se_{13}$

chain **1**		chain **3**	
Se1−Se8	2.415(2)	Se27−Se33	2.463(2)
Se1−Se7	2.984(2)	Se27−Se37	2.851(2)
Se2−Se13	2.352(2)	Se28−Se31	2.493(2)
Se3−Se7	2.446(2)	Se30−Se38	2.365(2)
Se3−Se11	2.834(2)	Se31−Se37	2.743(2)
Se5−Se6	2.427(2)	Se32−Se36	2.404(2)
Se6−Se11	2.875(2)	Se32−Se33	2.958(2)
Se9−Se12	2.402(2)	Se34−Se39	2.381(2)
Se9−Se11	2.989(2)		
chain **2**		chain **4**	
Se15−Se18	2.378(2)	Se40−Se44	2.401(2)
Se17−Se23	2.402(2)	Se42−Se51	2.387(2)
Se19−Se20	2.370(2)	Se43−Se49	2.373(2)
Se21−Se22	2.663(2)	Se44−Se52	2.973(2)
Se21−Se24	2.879(2)	Se45−Se46	2.513(2)
Se22−Se26	2.549(2)	Se46−Se52	2.716(2)
Se23−Se25	2.963(2)	Se47−Se48	2.410(2)
Se24−Se25	2.453(2)	Se47−Se52	2.951(2)

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Supporting Information Available: CIF format crystallographic files for $Cs_4Ti_3Se_{13}$, $Rb_4Ti_3S_{14}$, $Cs_4Ti_3S_{14}$, $Rb_4Hf_3S_{14}$, $Rb_4Zr_3Se_{14}$, $Cs_4Zr_3Se_{14}$, and $Cs_4Hf_3Se_{14}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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