description of the ground state is more important in the LT phase. Such a subtle effect explains the abrupt break in the magnetic susceptibility curve around 208 K upon cooling down.

The most thoroughly studied phase transitions in molecular inorganic chemistry are certainly those concerning the spin-crossover complexes.[13-15] In that case, however, the transition is driven by the intraionic electron transfer, which modifies the occupancy of the metal orbitals, and hence the electronic content of the metal-ligand bonds. When a single electron is involved in this intraionic transfer [Co(II)], the average variation of metal-ligand bond lengths is around 0.1 Å and when two electrons are involved, this variation is in the range 0.12-0.15 Å for Fe(III) and 0.14-0.24 Å for Fe(II).[13,15,31] In the present case, the phase transition is not related to an electronic instability, and on average, there is no variation of the metal-ligand bond lengths. However, the enthalpy and entropy variations associated with the transition are rather important; they are of the same order of magnitude as those in spin-crossover compounds.[13,32] Concerning the entropy variation ΔS, it is usual to write

$$\Delta S = \Delta S_{\mathrm{el}} + \Delta S_{\mathrm{vib,intra}} + \Delta S_{\mathrm{vib,inter}} \tag{2}$$

In the present case, it is clear that ΔS_{el} is almost negligible since the only electronic effect of the transition is to increase the S-T energy gap in absolute value from 207 to 215 cm^{-1}. $\Delta S_{\mathrm{vib,intra}}$ may also be expected to be rather small since the intramolecular geometry is weakly modified. It follows that the lattice term $\Delta S_{\mathrm{vib,inter}}$ would be predominant.

Registry No. $[(Cu(petdien))_2(CO_3)](ClO_4)_2$, 111959-29-6.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table SI) and coordinates of hydrogen atoms (Table SII) in HT (a) and LT (b) forms and a drawing of the crystal packing as projected down the screw axis in HT (A) and LT (B) forms (Figure S1) (6 pages); tables of calculated and observed structure factors (27 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of $Na_2Ti_2Se_8$, a New One-Dimensional Solid-State Polyselenide

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The compound $Na_2Ti_2Se_8$ has been prepared through the reaction of Ti metal with a Na_2Se/Se flux at 345 °C. The compound crystallizes with four formula units in space group C_{2h}^5-$P2_1/c$ of the monoclinic system in a cell of dimensions a = 12.841 (7) Å, b = 7.146 (4) Å, c = 12.994 (8) Å, β = 106.18 (2)° at -160 °C. The structure contains infinite, one-dimensional Ti/Se chains that run parallel to the c axis. In these chains the Ti centers are seven-coordinate. These chains are isolated from one another by Na$^+$ ions. When the Se-Se bonds are taken into account, the composition of the chain is $^1_\infty[Ti_2(Se_2)_3(Se)_2^{2-}]$ and the compound contains Ti^{4+}.

Introduction

Molten alkali-metal polysulfides have been used intermittently as fluxes in the crystal growth of solid-state sulfides.[1] Previous reports have involved syntheses at high temperatures (>800 °C) and appear not to have yielded solid-state polysulfides.[1-3] Recently,[4] we found that the addition of transition metals to alkali-metal polysulfides at low temperatures (300-400 °C) affords new solid-state polysulfides, typified by $K_4Ti_3S_{14}$, in which there occur chains of $^1_\infty[Ti_3(S_2)_6(S)_2^{4-}]$, that is, infinite one-dimensional chains composed of Ti^{4+} centers bonded to S_2^{2-} and S^{2-} species. This compound is the first member of an entirely new series of one-dimensional solid-state polysulfides.

Because low-dimensional materials are of wide interest,[5] we are engaged in extending this type of synthesis to other metals and other chalcogens. Here we present the synthesis and characterization of $Na_2Ti_2Se_8$, the first member of related series of one-dimensional polyselenides.

Experimental Section

$Na_2Ti_2Se_8$. A 0.048-g (0.38-mmol) sample of anhydrous Na_2Se (Alfa, 95%), 0.0090 g (0.19 mmol) of Ti metal powder (Aesar, 99.9%), and 0.152 g (1.9 mmol) of Se powder (Atomergic, 99.999%) were combined in a silica tube that was subsequently evacuated to $\sim 10^{-5}$ Torr. The mixture was heated to 345 °C and kept there for 100 h before being cooled to room temperature at 3 °C/h. The resultant material was washed with water to remove excess sodium polyselenides. The yield of purple-brown, slightly air-sensitive crystals of $Na_2Ti_2Se_8$ was approximately 18% based on the initial titanium present. The presence of Ti and Se was established by microprobe analysis (EDAX) of single crystals. The composition of the material was established from an X-ray structure determination.

X-ray Structure Analysis. A suitable crystal was mounted directly in the cold stream of an Enraf Nonius CAD4 diffractometer. Crystal data and experimental details are given in Table I. The six standards from diverse regions of reciprocal space that were monitored every 3 h during data collection remained constant within counting statistics.

The structure was solved through a combination of Patterson and direct methods. A successful trial structure was difficult to find owing to a lack of knowledge of the composition of the material and reluctance to accept what turned out to be the correct solution for the Se positions. The structure was refined in a straightforward manner. The model was restricted to isotropic motion because the thermal parameters are very small for this low-temperature data set and because we felt that the magnitude of the absorption correction would render any anisotropic thermal parameters suspect. The final refinement was carried out on F_o^2, use being made of all unique data including those for which $F_o^2 \leq 0$. The peaks on a final difference electron density synthesis ranged from +3.5 to -3.8 e/Å^3; these heights may be compared with that of about 24 e/Å^3 for a Na atom in the structure. An analysis of $\sum w(F_o^2 - F_c^2)^2$ as a function of F_o^2, Miller indices, and setting angles displayed no unexpected trends. There is no evidence of nonstoichiometry or of oxygen contamination. Table II presents the final positional and isotropic thermal parameters while Table SI[6] presents a list of $10|F_o|$, $10|F_c|$, and $\sigma(F_o^2)$.

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(1) Scheel, H. J. *J. Cryst. Growth* **1974**, *24*, 669-673 and references therein.

(2) Bronger, W.; Günther, O. *J. Less-*Common *Met.* **1972**, *27*, 73-79.

(3) Huster, J.; Bronger, W. *Z. Naturforsch., Anorg. Chem., Org. Chem.* **1974**, *29B*, 594-595.

(4) Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202-6204.

(5) As an example, see: *Electron Properties of Inorganic Quasi-One-Dimensional Compounds*; Monceau, P., E.; Reidel: Dordrecht, The Netherlands, 1985.

(6) Supplementary material.

Table I. Data Collection and Refinement Details for $Na_2Ti_2Se_8$[a]

formula	$Na_2Ti_2Se_8$
fw	773.46
space group	C^5_{2h}-$P2_1/c$
a, Å	12.841 (7)
b, Å	7.146 (4)
c, Å	12.994 (8)
β, deg	106.18 (2)[b]
vol, Å^3	1145
Z	4
temp of data collcn	−160 °C[c]
d(calcd, −160 °C), g/cm^3	4.485
cryst dimens, mm	0.2 × 0.3 × 0.5
bounding planes	{010}, {110}, $(\bar{1}02)$, $(10\bar{2})$, {001}
cryst vol, mm^3	0.025
radiation	graphite-monochromated Mo $K\alpha_1$ (λ = 0.7093 Å)
linear abs coeff, cm^{-1}	266
transmission factors	0.006–0.048[d]
takeoff angle, deg	3.0
receiving aperture	3 mm × 3 mm, 17.3 cm from crystal
scan type	ω
scan range	±1.5° in ω
bkg counts	extension of $^1/_4$ scan range on each side; reflcns with $I < 3\sigma(I)$ rescanned for a max of 100 s
2θ limits, deg	$4.0 \leq 2\theta \leq 52.0$
data collcd	$\pm h,+k,+l$
no. of unique data	2223
no. of unique data ($F_o^2 > 2\sigma(F_o^2)$)	1722
p factor	0.05
final no. of variables	49
$R(F^2)$	0.13
$R_w(F^2)$	0.15
$R(F)$ for $F_o^2 > 3\sigma(F_o^2)$	0.067
error in observn of unit wt	1.69

[a] Techniques and programs used are standard in this laboratory. See: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277. [b] In the cell refinement α and γ were constrained to 90°. [c] The low-temperature system for the Enraf-Nonius CAD4 diffractometer is based on a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. T. de Vic, 31320 Castanet-Tolosan, France. [d] The analytical method as employed in the Northwestern absorption program AGNOST was used for the absorption correction (de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014).

Table II. Positional and Isotropic Thermal Parameters for $Na_2Ti_2Se_8$

atom	x	y	z	B,[a] Å^2
Se(1)	0.103 67 (12)	0.134 96 (25)	−0.048 94 (12)	0.56 (3)
Se(2)	0.122 45 (12)	0.121 69 (26)	0.229 59 (12)	0.61 (3)
Se(3)	0.248 45 (12)	0.585 51 (25)	0.245 72 (12)	0.56 (3)
Se(4)	0.090 34 (12)	0.578 11 (26)	0.100 48 (12)	0.69 (3)
Se(5)	0.322 94 (12)	0.013 89 (25)	0.501 11 (12)	0.61 (3)
Se(6)	0.400 55 (12)	0.185 65 (25)	0.257 75 (12)	0.58 (3)
Se(7)	0.269 35 (12)	−0.010 67 (25)	0.035 20 (12)	0.57 (3)
Se(8)	0.456 36 (12)	0.091 84 (25)	−0.104 89 (12)	0.59 (3)
Ti(1)	0.218 75 (21)	0.296 55 (46)	0.124 87 (22)	0.55 (5)
Ti(2)	0.269 53 (20)	0.224 94 (45)	−0.115 78 (21)	0.48 (5)
Na(1)	−0.460 84 (52)	0.169 5 (11)	−0.382 65 (53)	1.3 (1)
Na(2)	−0.096 76 (53)	0.190 2 (12)	−0.370 49 (55)	1.4 (1)

[a] $B = 8\pi^2\langle u^2\rangle$, where $\langle u^2\rangle$ is the mean-square displacement.

A negative entry for F_o indicates that $F_o^2 < 0$.

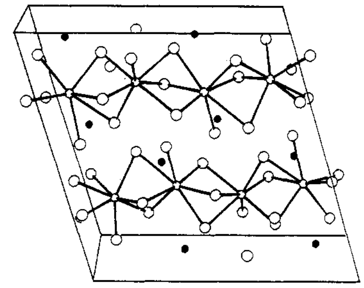

Figure 1. Unit cell of $Na_2Ti_2Se_8$. The c axis is along the horizontal from left to right; the a axis is along the vertical from bottom to top. The small black circles are Na^+ ions; the small white circles are Ti^{4+} ions; the large white circles are Se sites.

Table III. Selected Distances (Å) and Angles (deg) in $Na_2Ti_2Se_8$

Ti(1)–Se(2)	2.425 (3)	Se(6)–Se(8)	2.348 (3)
Ti(1)–Se(3)	2.558 (4)	Na(1)–Se(5)	2.956 (7)
Ti(1)–Se(4)	2.565 (4)	Na(1)–Se(5)	2.982 (7)
Ti(1)–Se(1)	2.600 (3)	Na(1)–Se(6)	2.996 (8)
Ti(1)–Se(6)	2.610 (3)	Na(1)–Se(8)	3.024 (9)
Ti(1)–Se(7)	2.650 (4)	Na(1)–Se(6)	3.062 (7)
Ti(1)–Se(5)	2.722 (3)	Na(1)–Se(8)	3.266 (7)
Ti(2)–Se(5)	2.383 (4)	Na(1)–Se(3)	3.311 (7)
Ti(2)–Se(8)	2.548 (3)	Na(2)–Se(2)	2.961 (8)
Ti(2)–Se(7)	2.586 (4)	Na(2)–Se(2)	3.063 (7)
Ti(2)–Se(2)	2.587 (3)	Na(2)–Se(4)	3.117 (7)
Ti(2)–Se(1)	2.595 (3)	Na(2)–Se(4)	3.178 (8)
Ti(2)–Se(6)	2.735 (3)	Na(2)–Se(5)	3.271 (7)
Ti(2)–Se(3)	2.822 (4)	Na(2)–Se(3)	3.279 (7)
Se(1)–Se(7)	2.347 (2)	Na(2)–Se(1)	3.339 (8)
Se(3)–Se(4)	2.356 (2)	Na(2)–Se(7)	3.379 (8)
Se(1)–Ti(1)–Se(2)	90.2 (1)	Se(1)–Ti(2)–Se(2)	82.8 (1)
Se(1)–Ti(1)–Se(3)	147.5 (1)	Se(1)–Ti(2)–Se(3)	94.4 (1)
Se(1)–Ti(1)–Se(4)	92.9 (1)	Se(1)–Ti(2)–Se(5)	95.6 (1)
Se(1)–Ti(1)–Se(5)	87.8 (1)	Se(1)–Ti(2)–Se(6)	163.5 (1)
Se(1)–Ti(1)–Se(6)	128.8 (1)	Se(1)–Ti(2)–Se(8)	137.5 (1)
Se(2)–Ti(1)–Se(3)	94.8 (1)	Se(2)–Ti(2)–Se(3)	85.3 (1)
Se(2)–Ti(1)–Se(4)	93.6 (1)	Se(2)–Ti(2)–Se(5)	100.5 (1)
Se(2)–Ti(1)–Se(5)	178.0 (1)	Se(2)–Ti(2)–Se(6)	82.7 (1)
Se(2)–Ti(1)–Se(6)	88.5 (1)	Se(2)–Ti(2)–Se(7)	135.3 (1)
Se(2)–Ti(1)–Se(7)	92.6 (1)	Se(2)–Ti(2)–Se(8)	132.4 (1)
Se(3)–Ti(1)–Se(5)	87.0 (1)	Se(3)–Ti(2)–Se(5)	169.0 (1)
Se(3)–Ti(1)–Se(6)	83.5 (1)	Se(3)–Ti(2)–Se(6)	76.5 (1)
Se(3)–Ti(1)–Se(7)	157.8 (1)	Se(3)–Ti(2)–Se(7)	87.2 (1)
Se(4)–Ti(1)–Se(5)	86.6 (1)	Se(3)–Ti(2)–Se(8)	70.3 (1)
Se(4)–Ti(1)–Se(6)	138.2 (1)	Se(5)–Ti(2)–Se(6)	94.8 (1)
Se(4)–Ti(1)–Se(7)	145.5 (1)	Se(5)–Ti(2)–Se(7)	95.0 (1)
Se(5)–Ti(1)–Se(6)	92.6 (1)	Se(5)–Ti(2)–Se(8)	99.1 (1)
Se(5)–Ti(1)–Se(7)	86.1 (1)	Se(6)–Ti(2)–Se(7)	137.6 (1)
Se(6)–Ti(1)–Se(7)	75.9 (1)	Se(7)–Ti(2)–Se(8)	85.1 (1)

Results and Discussion

Although some phase diagrams[7] are known for A_2Q/Q systems, where A = alkali metal and Q = S, Se, or Te, we proceeded in an empirical fashion in the synthesis of new alkali-metal–transition-metal chalcogenides. Generally, we added a transition metal M to various polychalcogenide compositions obtained through variation of the A_2Q/Q ratio. The materials were combined in silica tubes (satisfactory for A = Na, K, Rb, Cs), which were then evacuated, sealed, and heated in a tube furnace. After the mixtures were heated in the range 300–400 °C for 3–4 days, they were slowly cooled to room temperature. Excess polychalcogenide was removed by water washing. This process, of course, only yields materials that neither dissolve in nor react with water. Often the color of the product indicates that it is a new ternary compound. However, the difficulty of obtaining single crystals, a criterion for proper characterization, in some instances is great.

For example, we initially prepared material of approximate composition $NaNbS_6$[8] by heating a mixture of $Na_2S + {}^1/_2Nb + 4S$ at 375 °C for 100 h, but no suitable crystals have yet been obtained. On the other hand, the fact that a new material had been prepared, as evidenced by color, EDAX analysis, and an X-ray powder pattern, led us to try other mixtures of $A_2Q + {}^1/_2M + nQ$, where $n \approx 4$. Crystals of $K_4Ti_3S_{14}$ were prepared in this way,[4] although better crystals are obtained through initial heating at 890 °C for 5 h followed by extended heating at 375 °C. In an attempt to make a new Na/Ti/Se compound and hence extend

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(7) For example, see: *Gmelins Handbuch der Anorganischen Chemie*, 8th ed.; Verlag Chemie: Weinheim/Bergstr., FRG, 1966; Sodium, Supplement Part 3, pp 1188–1191 and references therein.

(8) Sunshine, S. A.; Kang, D.; Ibers, J. A., unpublished work.

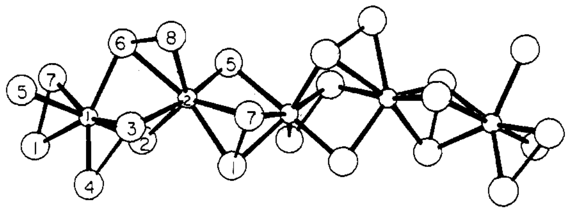

Figure 2. The ${}^{1}_{\infty}[Ti_2(Se_2)_3(Se)_2{}^{2-}]$ chain in $Na_2Ti_2Se_8$.

this type of synthesis to selenides, mixtures of $Na_2Se + {}^{1}/_{2}Ti + n$Se, where $n = 3$–7, were heated at 375 °C for 100 h. Reactions where $n = 3$ or 4 afforded no ternary product; reactions where $n \geq 5$ gave crystals of $Na_2Ti_2Se_8$ in very low yield. A reaction at 345 °C where $n = 5$ afforded the same product in about 18% yield. No attempt was made to optimize the yield.

A view of the unit cell of $Na_2Ti_2Se_8$ is shown in Figure 1. Selected distances and angles are given in Table III. The structure is composed of infinite one-dimensional Ti/Se chains that run parallel to *c*. These chains are isolated from one another by the Na^+ cations. These Na^+ ions show their expected high coordination numbers: in particular, there are seven Na(1)–Se and eight Na(2)–Se contacts less than 3.4 Å (Table III). Figure 2 shows part of one such chain and includes the numbering system as well as the Se–Se bonds within the $Se_2{}^{2-}$ pairs that are present. Because of such pairs, the composition of the chain is ${}^{1}_{\infty}[Ti_2(Se_2)_3(Se)_2{}^{2-}]$ and the compound contains Ti^{4+}.

The structure contains two crystallographically distinct Ti atoms. The Ti(1) and Ti(2) centers are bridged together in two different ways. In one instance, there is a three-atom bridge composed of atom Se(5) and the Se(1)–Se(7) pair; in the other instance, there is another three-atom bridge composed of Se(2), Se(6) of the Se(6)–Se(8) pair, and Se(3) of the Se(3)–Se(4) pair. Seven-coordination about atom Ti(1) is completed through a bond to Se(4) of the Se(3)–Se(4) pair, while seven-coordination about atom Ti(2) is completed by a bond to Se(8) of the Se(6)–Se(8) pair. As a result, atom Ti(1) bonds to all eight unique Se atoms except Se(8) and atom Ti(2) bonds to all except atom Se(4). The crystallographic *c*-glide plane generates the infinite structure of the chain. The Ti–Se bond distances are irregular, probably as a result of the steric demands of the three independent Se_2 pairs. Thus the Ti(1)–Se distances range from 2.425 (3) to 2.722 (3) Å, while the Ti(2)–Se distances range from 2.383 (4) to 2.822 (4) Å. For a comparison, in $TiSe_2$, where the Ti atom is six-coordinate, the Ti–Se distance is 2.554 (1) Å.[9] On the other hand, the Se–Se bonds in the Se_2 pairs are normal (2.347 (2)–2.356 (2) Å).

The interesting contrasts in the infinite Ti/Q chains in $K_4Ti_3S_{14}$[4] and $Na_2Ti_2Se_8$ are shown in Figure 3. Both structures contain two independent Ti atoms: those in the selenide are both seven-coordinate; in the sulfide, one is seven-coordinate and the other eight-coordinate. While these two Ti chains are the only ones in the literature that are roughly analogous, one-dimensional chains occur in other chalcogenides. In particular, one-dimensional behavior and Se–Se bonding occur in Nb_2Se_9.[10] But the prototype chalcogen (but not polychalcogen) chain compounds are SiS_2 and $SiSe_2$; these are composed of infinite chains of distorted, edge-sharing SiS_4 or $SiSe_4$ tetrahedra.[11]

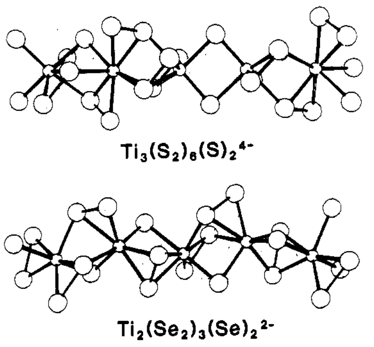

Figure 3. Comparison of the ${}^{1}_{\infty}[Ti_3(S_2)_6(S)_2{}^{4-}]$ chain in $K_4Ti_3S_{14}$ with the ${}^{1}_{\infty}[Ti_2(Se_2)_3(Se)_2{}^{2-}]$ chain in $Na_2Ti_2Se_8$.

$K_4Ti_3S_{14}$ is a semiconductor.[12] While the conductivity of $Na_2Ti_2Se_8$ has not been measured, we presume that it too is a semiconductor since both compounds are readily formulated as those of Ti^{4+}.

The material described here and its predecessor $K_4Ti_3S_{14}$ are the first in two series of new polychalcogenides. More interesting transport properties in these one-dimensional materials should occur if nonstoichiometry or partial oxidation can be introduced. Cation exchange of the present compound may bring about such effects.

Acknowledgment. This research was supported by the National Science Foundation—Solid-State Chemistry, Grant DMR-83-15554.

Registry No. $Na_2Ti_2Se_8$, 110354-76-2; Na_2Se, 1313-85-5; Ti, 7440-32-6; Se, 7782-49-2.

Supplementary Material Available: Table SI, structure amplitudes (9 pages). Ordering information is given on any current masthead page.

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