Inorg. Chem. **2001,** *40,* 4823−4829

Articles

Syntheses, Vibrational Spectra, and Theoretical Studies of the Adamantanoid $Sn_4Ch_{10}^{4-}$ (Ch = Se, Te) Anions: X-ray Crystal Structures of $[18\text{-Crown-6-K}]_4[Sn_4Se_{10}]\cdot 5en$ and $[18\text{-Crown-6-K}]_4[Sn_4Te_{10}]\cdot 3en\cdot 2THF$

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Received March 5, 2001

The salts $[18\text{-crown-6-K}]_4[Sn_4Se_{10}]\cdot 5en$ and $[18\text{-crown-6-K}]_4[Sn_4Te_{10}]\cdot 3en\cdot 2THF$ were isolated upon addition of THF to the ethylenediamine (en) extracts of the alloys $KSn_{0.90}Se_{1.93}$ and $K_4Sn_4Te_{10}$ that had been extracted in the presence of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane). The $Sn_4Te_{10}^{4-}$ anion has been structurally characterized for the first time by a single-crystal X-ray diffraction study of $[18\text{-crown-6-K}]_4[Sn_4Te_{10}]\cdot 3en\cdot 2THF$: $P2_1/n$, $a = 22.420(5)$ Å, $b = 19.570(4)$ Å, $c = 24.680(5)$ Å, $\beta = 96.90(3)°$, $Z = 4$, and $R_1 = 0.0468$ at −183 °C. In addition to $Si_4Te_{10}^{4-}$ and $Ge_4Te_{10}^{4-}$, the $Sn_4Te_{10}^{4-}$ anion represents the only other known group 14 adamantanoid telluride. The X-ray crystal structure determination of the related $[18\text{-crown-6-K}]_4[Sn_4Se_{10}]\cdot 5en$ salt has also been determined: $P2_1/n$, $a = 22.003(2)$ Å, $b = 18.966(2)$ Å, $c = 24.393(2)$ Å, $\beta = 97.548(8)°$, $Z = 4$, and $R_1 = 0.0843$ at −123 °C. The anion geometries are of the adamantanoid type where the Sn^{IV} atoms occupy the bridgehead positions and the chalcogen atoms occupy the bridging and terminal sites. The energy minimized geometries of $Sn_4Ch_{10}^{4-}$ have also been determined using density functional theory (DFT). Mayer bond order analyses, Mayer valencies, and empirical bond valencies indicate that the terminal Sn−Ch bonds have significant multiple bond character, with the terminal Sn−Se bond having more multiple bond character than the terminal Sn−Te bond. The vibrational frequencies of the $Sn_4Se_{10}^{4-}$ and $Sn_4Te_{10}^{4-}$ anions have been calculated using DFT methods, allowing the Raman spectrum of $Sn_4Se_{10}^{4-}$ to be fully assigned.

Introduction

We have recently synthesized and structurally characterized the classically bonded tin(IV) chalcogenide anions, $Sn_2Ch_6^{4-}$, $Sn_2Ch_7^{4-}$ (Ch = Se, Te),[1] and $Sn_4Se_{10}^{4-}$ [2] as their 2,2,2-crypt-K^+ salts. All anions were characterized in solution by multinuclear NMR spectroscopy, and $Sn_2Ch_6^{4-}$ and $Sn_4Se_{10}^{4-}$ were also characterized in the solid state by X-ray crystallography and Raman spectroscopy. Following these studies, the $(C_2H_5)_4N^+$ salt of $Sn_4Se_{10}^{4-}$ was characterized by X-ray crystallography,[3] and other adamantanoid chalcogenide anions of the group 13 ($B_4S_{10}^{8-}$,[4] $Ga_4S_{10}^{8-}$,[5,6] $Ga_4Se_{10}^{8-}$,[7] $In_4S_{10}^{8-}$,[6] $In_4Se_{10}^{8-}$ [6]) and group 14 ($Si_4S_{10}^{4-}$,[8] $Si_4Se_{10}^{4-}$,[9] $Ge_4S_{10}^{4-}$,[8,10−17] $Ge_4Se_{10}^{4-}$ [9,18−21]) elements have been recently reviewed.[22] Only two group 14 telluride analogues are known, namely $Si_4Te_{10}^{4-}$ [23] and

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10.1021/ic010242f CCC: $20.00

Ge$_4$Te$_{10}^{4-}$,[24] and to our knowledge, no group 13 telluride examples are presently known.

The present paper reports the syntheses and the structural characterization, by X-ray crystallography, of the novel Sn$_4$Te$_{10}^{4-}$ anion, which is the second example of an adamantanoid cage containing only tin and a chalcogen and the first example containing tellurium. The crystal structure of the new Sn$_4$Se$_{10}^{4-}$ salt, [18-crown-6-K]$_4$[Sn$_4$Se$_{10}$]·5en, is also reported. The vibrational frequencies of both Sn$_4$Ch$_{10}^{4-}$ anions have been calculated by density functional theory (DFT) and have been used to reassign the experimental spectrum of Sn$_4$Se$_{10}^{4-}$.

Results and Discussion

Syntheses and Structural Charaterization by X-ray Crystallography of the Sn$_4$Ch$_{10}^{4-}$ (Ch = Se, Te) Anions. Single crystals of [18-crown-6-K]$_4$[Sn$_4$Se$_{10}$]·5en were isolated upon addition of THF to an en extract of the alloy KSn$_{0.90}$Se$_{1.93}$ in the presence of a nonstoichiometric amount of 18-crown-6 with respect to K$^+$, where K$^+$/18-crown-6 = 1.00/0.71. Because no conclusive NMR evidence was found for the Sn$_4$Te$_{10}^{4-}$ anion in the liquid NH$_3$ extracts of KSn$_{0.63}$Te$_{1.70}$ and NaSn$_{0.43}$Te in the presence or absence of 2,2,2-crypt, attempts were made to prepare solutions of Sn$_4$Te$_{10}^{4-}$ by extraction of K$_4$Sn$_4$Te$_{10}$ into liquid NH$_3$ in the absence of 2,2,2-crypt. The known SnTe$_3^{2-}$,[1,25] Sn$_2$Te$_6^{4-}$,[1] and Sn$_2$Te$_7^{4-}$ [1] anions were identified by ^{119}Sn and ^{125}Te NMR spectroscopy (−70 °C) in the resulting red solution. One new ^{119}Sn (−1267.5 ppm) resonance and two new ^{125}Te (−15.1 and 177.3 ppm) resonances having relative peak areas of 6.8/4.2 were also observed. These signals, however, could not be assigned with certainty to the Sn$_4$Te$_{10}^{4-}$ anion, because the low signal-to-noise ratio prevented observation of the complete ^{117}Sn and ^{125}Te satellite patterns expected for this anion. Each ^{125}Te resonance displayed satellites arising from $^1J(^{125}\mathrm{Te}-^{117,119}\mathrm{Sn}) = 3200$ Hz (−15.1 ppm) and 3800 Hz (177.3 ppm). The ^{119}Sn NMR resonance was flanked by only one set of ^{125}Te satellites ($^1J(^{119}\mathrm{Sn}-^{125}\mathrm{Te}) = 3200$ Hz). Crystals of [18-crown-6-K]$_4$[Sn$_4$Te$_{10}$]·3en·2THF were, however, isolated upon addition of THF to an en extract of K$_4$Sn$_4$Te$_{10}$ in the presence of a nonstoichiometric amount of 18-crown-6 with respect to K$^+$, where K$^+$/18-crown-6 = 1.00/0.18. An attempt was subsequently made to prepare a solution of Sn$_4$Te$_{10}^{4-}$ by dissolving crystalline [18-crown-6-K]$_4$[Sn$_4$Te$_{10}$]·3en·2THF in liquid ammonia; however, the resulting red solution was shown by ^{119}Sn NMR spectroscopy to contain only SnTe$_3^{2-}$ ($\delta(^{119}\mathrm{Sn}) = -1181.7$ ppm; $^1J(^{119}\mathrm{Sn}-^{125}\mathrm{Te}) = 3378$ Hz).[1,25]

A summary of the crystal data and refinement results are given in Table 1. The most significant bond distances and angles in the Sn$_4$Ch$_{10}^{4-}$ anions are given in Table 2. In both structures, the anions and crown ether cation chelates are well separated from one another and show no intermolecular contacts; the closest K···Ch distances, K(1)···Te(1) = 4.290 Å and K(4)···Se(5) = 4.312 Å, are well above the sum of the ionic radius of K$^+$ (1.52 Å)[26] and the van der Waals radii of Te (2.10[26] or 2.20[27] Å) and Se (1.90[26] or 2.00[27] Å).

The most interesting aspects of the structures are the adamantanoid geometries of the anions (~T_d point symmetry) in which the tin atoms occupy the bridgehead positions and the chalcogen atoms occupy the bridging and terminal sites (Figures 1 and 2). The Ch−Sn−Ch bond angles range from 105.64(2) to 113.98(2)° [107.48(2) to 111.91(2)°] in the Te [Se] anion (note that the bracket notation distinguishing the chalcogens is applicable throughout the Introduction and Results and Discussion sections), so that the Sn$_4$Ch$_{10}^{4-}$ anions can be described as composed of four nearly tetrahedral Sn^{IV} centers to which are bonded four Ch$_t$ (t, terminal) atoms and six Ch$_b$ (b, bridging) atoms. The Ch$_b$−Sn−Ch$_b$ bond angles within the central Sn$_4$Ch$_6$ core are 108.44(2)−113.98(2)° [107.74(2)−111.91(2)°] and are comparable to the Ch$_t$−Sn−Ch$_b$ bond angles 105.64(2)−112.06(3)° [107.48(3)−110.77(3)°], a trend that is also observed in the Si$_4$Te$_{10}^{4-}$ [23] and Ge$_4$Te$_{10}^{4-}$ [24] anions. The Ch$_t$-Sn−Ch$_b$ angles are close to the ideal tetrahedral angles observed in SnCh$_4^{4-}$,[28,29] and the Ch$_b$−Sn−Ch$_b$ angles are similar to those observed in other systems containing Sn$_4$Ch$_6$ cores: that is, [Cp(CO)$_3$Mo]$_4$Sn$_4$Te$_6$, 108.0(1)−114.4(1)°;[30] (CH$_3$)$_4$Sn$_4$Se$_6$, 110.13(4)−115.19(4)°;[31] and [Cp(CO)$_2$Fe]$_4$Sn$_4$Se$_6$, 108.8(1)−111.8(1)°.[32] The average Sn−Ch$_b$−Sn bond angles, 108.3(3)° [106.8(8)°], are comparable to those observed in [Cp(CO)$_3$Mo]$_4$Sn$_4$Te$_6$ (104.4(1)−108.1(1)°), (CH$_3$)$_4$Sn$_4$Se$_6$ (102.13(4)−103.75(4)°), and [Cp(CO)$_2$Fe]$_4$Sn$_4$Se$_6$ (107.3(1)−109.0(1)°).

Table 1. Summary of Crystal Data and Refinement Results for [18-crown-6-K]$_4$[Sn$_4$Se$_{10}$]·5en and [18-crown-6-K]$_4$[Sn$_4$Te$_{10}$]·3en·2THF

	Sn$_4$Se$_{10}^{4-}$	Sn$_4$Te$_{10}^{4-}$
formula	C$_{58}$H$_{136}$N$_{10}$O$_{24}$K$_4$Sn$_4$Se$_{10}$	C$_{62}$H$_{136}$N$_6$O$_{26}$K$_4$Sn$_4$Te$_{10}$
fw	2778.53	3288.93
space group (no.)	$P2_1/n$ (14)	$P2_1/n$ (14)
a, Å	22.003(2)	22.420(5)
b, Å	18.966(2)	19.570(4)
c, Å	24.393(2)	24.680(5)
β, deg	97.548(8)	96.90(3)
V, Å^{-3}	10 091.0(17)	10 750.2(37)
Z	4	4
T (°C)	−123	−183
ρ_{calcd}, g cm^{-3}	1.829	2.032
μ, mm^{-1}	4.815	3.80
R$_1$,[a] wR$_2$[b]	0.0843, 0.1859	0.0468, 0.1741

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $I > 2\sigma(I)$. [b] $wR_2 = \sum|(|F_o| - |F_c|)w^{1/2}|/\sum(|F_o|w)$ for $I > 2\sigma(I)$.

As observed in other adamantanoid structures involving group 14 atoms, that is, Si$_4$Ch$_{10}^{4-}$ [8,9,23] and Ge$_4$Ch$_{10}^{4-}$ [8−21,24] (Ch = S, Se, Te), the terminal Sn−Ch bond lengths in Sn$_4$Ch$_{10}^{4-}$, which are 2.6337(8)−2.6506(8) Å [2.4187(7) −2.4310(7) Å], are significantly shorter than the bridging Sn−Ch bond lengths, 2.7405(8)−2.7705(7) Å [2.5438(7)−2.5600(6) Å]. This trend has also been observed in the related Sn$_2$Ch$_6^{4-}$ (Ch = S,[33] Se,[1,34] Te[1]) and Sn$_2$Te$_7^{4-}$ [35] anions and in the adamantanoid structures of group 13, that is, B$_4$S$_{10}^{8-}$,[4] Ga$_4$Ch$_{10}^{8-}$,[5−7] and In$_4$Ch$_{10}^{8-}$ [6] (Ch = S, Se). The differences between E−Ch$_t$ and E−Ch$_b$ are, however, greater in the Sn$_4$Ch$_{10}^{4-}$ anions and are a consequence of stronger terminal tin−chalcogen bonds. Longer and more polar E−Ch$_t$ bonds have been observed in the group 13

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for [18-crown-6-K]$_4$[Sn$_4$Se$_{10}$]·5en and [18-crown-6-K]$_4$[Sn$_4$Te$_{10}$]·3en·2THF

[18-crown-6-K]$_4$[Sn$_4$Se$_{10}$]·5en

Bond Lengths (Å)

Sn(1)−Se(1)	2.5507(7)	Sn(3)−Se(1)	2.5461(7)
Sn(1)−Se(2)	2.5446(7)	Sn(3)−Se(5)	2.5472(6)
Sn(1)−Se(3)	2.5566(8)	Sn(3)−Se(6)	2.5572(7)
Sn(1)−Se(10)	2.4217(8)	Sn(3)−Se(8)	2.4310(7)
Sn(2)−Se(2)	2.5489(7)	Sn(4)−Se(3)	2.5439(8)
Sn(2)−Se(4)	2.5526(7)	Sn(4)−Se(4)	2.5438(7)
Sn(2)−Se(5)	2.5600(6)	Sn(4)−Se(6)	2.5493(7)
Sn(2)−Se(7)	2.4187(7)	Sn(4)−Se(9)	2.4302(8)

Bond Angles (deg)

Se(1)−Sn(1)−Se(2)	109.98(2)	Se(5)−Sn(3)−Se(6)	111.45(2)
Se(1)−Sn(1)−Se(3)	110.84(2)	Se(5)−Sn(3)−Se(8)	107.48(3)
Se(1)−Sn(1)−Se(10)	108.56(3)	Se(6)−Sn(3)−Se(8)	107.50(2)
Se(2)−Sn(1)−Se(3)	109.85(2)	Se(3)−Sn(4)−Se(4)	107.74(2)
Se(2)−Sn(1)−Se(10)	109.72(3)	Se(3)−Sn(4)−Se(6)	110.64(2)
Se(3)−Sn(1)−Se(10)	107.84(3)	Se(3)−Sn(4)−Se(9)	109.43(3)
Se(2)−Sn(2)−Se(4)	111.83(3)	Se(4)−Sn(4)−Se(6)	111.91(2)
Se(2)−Sn(2)−Se(5)	108.01(2)	Se(4)−Sn(4)−Se(9)	107.53(3)
Se(2)−Sn(2)−Se(7)	108.34(2)	Se(6)−Sn(4)−Se(9)	109.52(3)
Se(4)−Sn(2)−Se(5)	108.25(2)	Sn(3)−Se(1)−Sn(1)	107.52(2)
Se(4)−Sn(2)−Se(7)	109.93(2)	Sn(1)−Se(2)−Sn(2)	108.45(2)
Se(5)−Sn(2)−Se(7)	110.46(2)	Sn(4)−Se(3)−Sn(1)	108.37(3)
Se(1)−Sn(3)−Se(5)	111.36(2)	Sn(4)−Se(4)−Sn(2)	109.26(2)
Se(1)−Sn(3)−Se(6)	108.22(2)	Sn(3)−Se(5)−Sn(2)	109.07(2)
Se(1)−Sn(3)−Se(8)	110.77(3)	Sn(4)−Se(6)−Sn(3)	107.28(2)

[18-crown-6-K]$_4$[Sn$_4$Te$_{10}$]·3en·2THF

Bond Lengths (Å)

Sn(1)−Te(1)	2.7519(7)	Sn(3)−Te(1)	2.7705(7)
Sn(1)−Te(2)	2.7582(9)	Sn(3)−Te(5)	2.7590(9)
Sn(1)−Te(3)	2.7502(8)	Sn(3)−Te(6)	2.7480(8)
Sn(1)−Te(10)	2.6506(8)	Sn(3)−Te(8)	2.6337(8)
Sn(2)−Te(2)	2.7566(8)	Sn(4)−Te(3)	2.7618(8)
Sn(2)−Te(4)	2.7416(9)	Sn(4)−Te(4)	2.7497(9)
Sn(2)−Te(5)	2.7536(8)	Sn(4)−Te(6)	2.7405(8)
Sn(2)−Te(7)	2.6413(9)	Sn(4)−Te(9)	2.6325(9)

Bond Angles (deg)

Te(1)−Sn(1)−Te(2)	113.98(2)	Te(5)−Sn(3)−Te(6)	112.36(3)
Te(1)−Sn(1)−Te(3)	109.74(2)	Te(5)−Sn(3)−Te(8)	109.94(2)
Te(1)−Sn(1)−Te(10)	106.14(3)	Te(6)−Sn(3)−Te(8)	107.04(3)
Te(2)−Sn(1)−Te(3)	109.24(3)	Te(3)−Sn(4)−Te(4)	110.75(2)
Te(2)−Sn(1)−Te(10)	105.64(2)	Te(3)−Sn(4)−Te(6)	112.00(3)
Te(3)−Sn(1)−Te(10)	112.06(3)	Te(3)−Sn(4)−Te(9)	107.99(3)
Te(2)−Sn(2)−Te(4)	113.77(3)	Te(4)−Sn(4)−Te(6)	111.39(2)
Te(2)−Sn(2)−Te(5)	110.07(3)	Te(4)−Sn(4)−Te(9)	106.10(4)
Te(2)−Sn(2)−Te(7)	108.99(2)	Te(6)−Sn(4)−Te(9)	108.35(3)
Te(4)−Sn(2)−Te(5)	108.64(2)	Sn(3)−Te(1)−Sn(1)	107.79(3)
Te(4)−Sn(2)−Te(7)	106.51(4)	Sn(1)−Te(2)−Sn(2)	105.16(2)
Te(5)−Sn(2)−Te(7)	108.70(3)	Sn(4)−Te(3)−Sn(1)	106.51(2)
Te(1)−Sn(3)−Te(5)	108.65(2)	Sn(4)−Te(4)−Sn(2)	106.11(4)
Te(1)−Sn(3)−Te(6)	108.44(2)	Sn(3)−Te(5)−Sn(2)	109.03(2)
Te(1)−Sn(3)−Te(8)	110.40(3)	Sn(4)−Te(6)−Sn(3)	106.08(2)

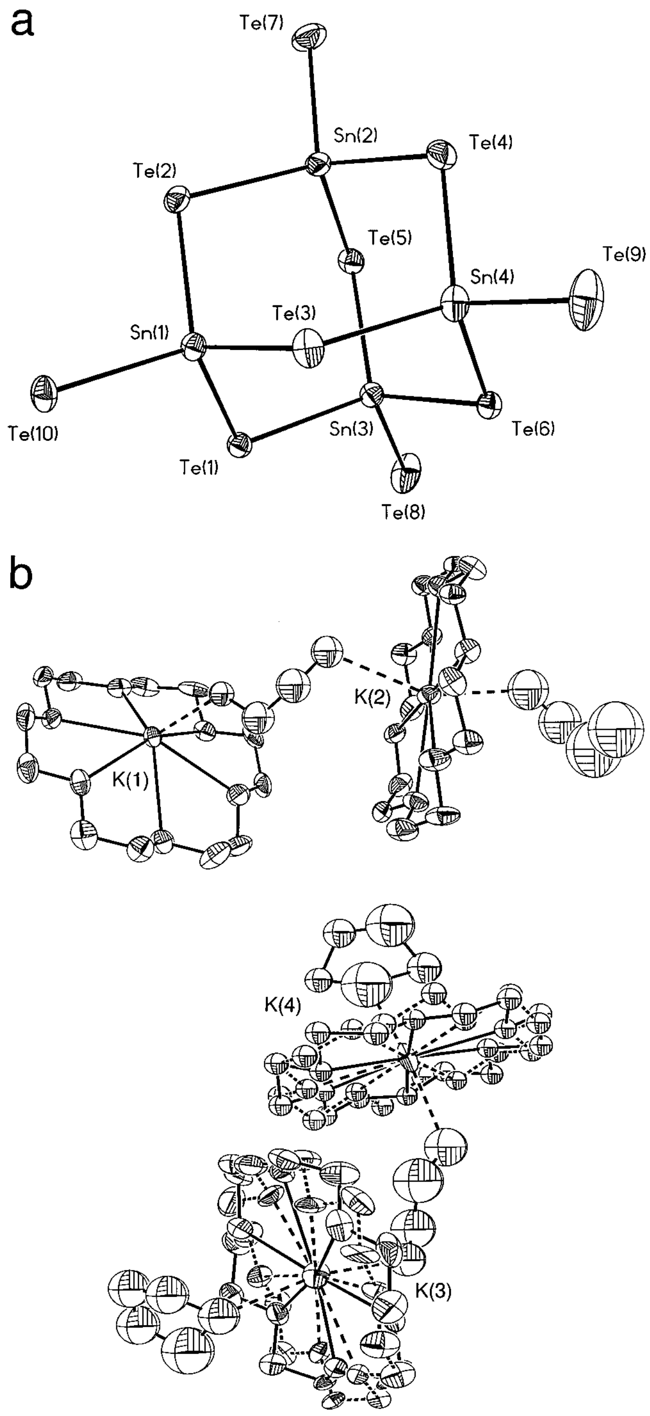

Figure 1. Views of (a) the $Sn_4Te_{10}^{4-}$ anion and (b) the solvated 18-crown-6-K$^+$ cations in [18-crown-6-K]$_4$[Sn$_4$Te$_{10}$]·3en·2THF with displacement ellipsoids drawn at the 70% probability level.

analogues, which may be attributed to higher charges on the terminal chalcogen atoms of these highly charged anions. The average Sn−Ch$_t$ bond lengths are shorter than those found in the tetrahedral $SnCh_4^{4-}$ anions [Na$_4$SnTe$_4$, 2.751(4) Å;[29] Na$_4$SnSe$_4$, 2.523(1) Å;[28] and K$_4$SnSe$_4$, 2.510(10) Å [28]], and the average Sn−Ch$_b$ bond lengths are comparable to those in [Cp(CO)$_3$Mo]$_4$Sn$_4$Te$_6$ (2.740(2)−2.774(2) Å),[30] (CH$_3$)$_4$Sn$_4$Se$_6$ (2.513(1)−2.541(1) Å),[31] and [Cp(CO)$_2$Fe]$_4$Sn$_4$Se$_6$ (2.524(5)−2.554(4) Å).[32] The Sn···Sn distances in $Sn_4Ch_{10}^{4-}$ range from 4.380(1) to 4.489(1) Å [4.111(1) to 4.160(1)Å] in the Te [Se] anion and are significantly longer than the corresponding distances in the $Sn_2Te_6^{4-}$ (3.865(3) Å)[1] and for $Sn_2Se_6^{4-}$ (3.4930(9) Å)[34] anions. The geometrical parameters of the $Sn_4Se_{10}^{4-}$ anion are in agreement with those previously reported for [2,2,2-crypt-K]$_4$[Sn$_4$Se$_{10}$] (Sn−Se$_b$, 2.533(2)−2.562(2) Å, and Sn−Se$_t$, 2.416(2)−2.433(2) Å; ∠Se$_b$−Sn−Se$_b$, 107.16(6)−113.06(6)°, and ∠Se$_t$−Sn−Se$_b$, 103.55(7)−12.96(6)°)[2] and for [(C$_2$H$_5$)$_4$N]$_4$ [Sn$_4$Se$_{10}$] (Sn−Se$_b$, 2.543(3)−2.558(3) Å, and Sn−Se$_t$, 2.429(7)−2.432(4) Å; ∠Se$_b$−Sn−Se$_b$, 109.22(9)−110.17(10)°, and ∠Se$_t$−Sn−Se$_b$, 106.50(12)−111.87(12)°).[3]

The C−O and C−C bond distances within the crown ether moieties are in good agreement with those reported previously[36] and are not discussed further. Each structural unit contains four 18-crown-6 molecules chelated to K$^+$ cations which complete their coordination by bridging to the nitrogen atoms of en and/

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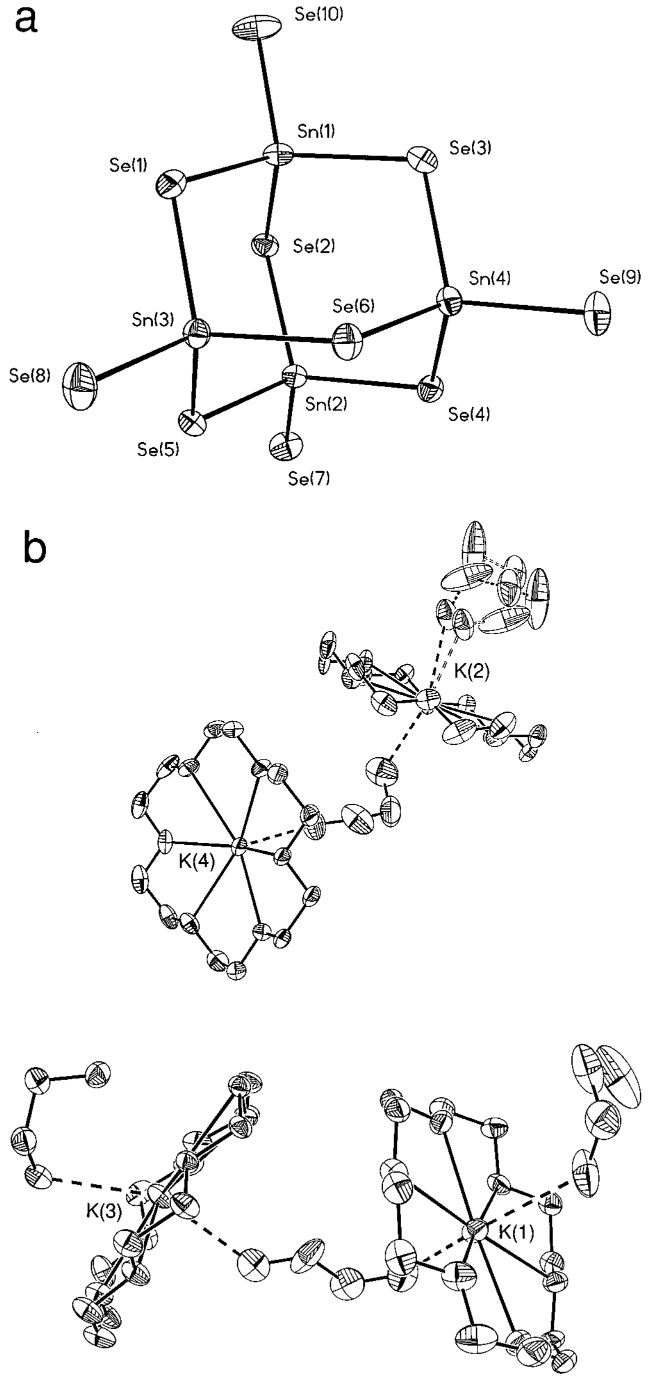

Figure 2. Views of (a) the $Sn_4Se_{10}^{4-}$ anion and (b) the solvated 18-crown-6-K$^+$ cations in [18-crown-6-K]$_4$[Sn_4Se_{10}]·5en with displacement ellipsoids drawn at the 70% probability level.

or the oxygen of a THF solvent molecule (Figures 1 and 2). In both $Sn_4Ch_{10}^{4-}$ salts, three K$^+$ ions are eight-coordinate and one is seven-coordinate. In all cases, the K$^+$ ions are coordinated to the six O atoms of the crown (K···O, 2.727(5)−2.967(5) [2.64(1)−2.99(1)] Å). The seven-coordinate K$^+$ ions are bonded to only one N atom of a bridging en molecule, which results in significant displacements of the K$^+$ ions from the O$_6$ least-squares planes, 0.734 [0.772] Å, and in the direction of the N atom of en. A similar displacement has been observed in (18-crown-6-K)$_2$Cu(S$_2$C$_2$O$_2$)$_2$·HCON(CH$_3$)$_2$ (0.9 Å).[37] The eight-coordinate K$^+$ ions are coordinated to one nitrogen of a bridging en molecule and to a nitrogen atom of a terminal en molecule (K(1), K(2), and K(3) in the $Sn_4Se_{10}^{4-}$ salt and K(2) in the $Sn_4Te_{10}^{4-}$ salt) and to the oxygen of THF (K(3) and K(4) in the $Sn_4Te_{10}^{4-}$ salt). The K$^+$ ions of the $Sn_4Te_{10}^{4-}$ salt are located well inside the cavity of the macrocycle; that is, their distance from the least-squares plane through the six O atoms of 18-crown-6 is −0.019 to 0.099 Å. In $Sn_4Se_{10}^{4-}$, two K$^+$ ions are located inside the cavity of the macrocycle (−0.112 to 0.082 Å from the O$_6$-plane), whereas one K$^+$ ion is slightly displaced from the O$_6$-plane (−0.278 Å), which likely results from a weak K(3)···N interaction at 3.273(7) Å. The K···N(en) contacts, 2.84(2)−2.99(1) [2.69(2)−3.046(8)] Å, are similar in both salts, and the K···O(THF) contacts [2.58(2)−2.79(1) Å] are comparable to other K···O contacts reported in the literature.[36] The (18-crown-6-K(3))$^+$ and (18-crown-6-K(4))$^+$ anions of the $Sn_4Te_{10}^{4-}$ salt are positionally disordered and occupy the same site in two equally populated orientations. In each case, the two orientations are related by a 30° rotation about an axis that passes through K(3) or K(4) and is perpendicular to the least-squares planes defined by the six crown oxygen atoms.

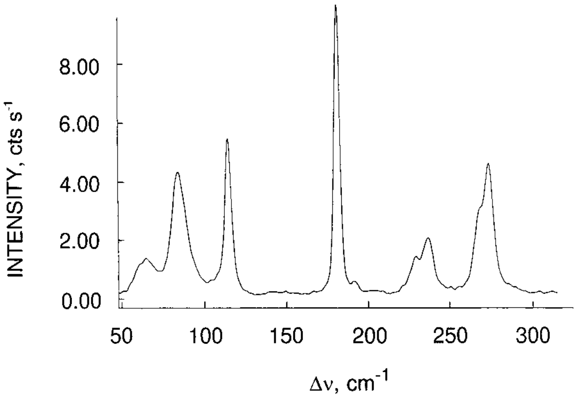

Figure 3. Raman spectrum of a randomly orientated [18-crown-6-K]$_4$[Sn_4Se_{10}]·5en crystal recorded at room temperature using 514.5-nm excitation.

Raman Spectroscopy. The solid-state Raman spectrum of [18-crown-6-K]$_4$[Sn_4Se_{10}]·5en is shown in Figure 3. The observed and calculated frequencies and their assignments are summarized in Table 3. The fundamental modes of the $Sn_4Se_{10}^{4-}$ anion were assigned under T_d point symmetry and belong to the irreducible representations $3A_1 + 3E + 3T_1 + 6T_2$, where the A$_1$, E, and T$_2$ modes are Raman active, the T$_2$ modes are infrared active, and the T$_1$ modes are inactive.

The Raman spectrum of $Sn_4Se_{10}^{4-}$ anion has been reported previously for the 2,2,2-crypt-K$^+$ salt,[2] and the assignments were made by analogy with those of $Ge_4S_{10}^{4-}$ [38] and the Sn$_4$Se$_6$ moiety of (CH$_3$)$_4$Sn$_4$Se$_6$.[31] The Raman spectrum of $Sn_4Se_{10}^{4-}$ has now been reassigned by comparison with calculated frequencies derived from DFT calculations (see Computational Results). As a result, only the assignment of the $\nu_2(A_1)$ mode at 178 cm^{-1} remains unchanged (Table 3). Moreover, two modes that were previously assigned to site symmetry split T$_2$ bands have now been reassigned to four distinct vibrational modes.

Several attempts were made to record the Raman spectrum of $Sn_4Te_{10}^{4-}$ but were unsuccessful because of sample decomposition at the very low power levels used for laser excitation (514.5, 647.1, and 1064 nm).

Computational Results. We have previously shown that density functional theory[39−43] can be used to calculate the geometries and the vibrational frequencies of classically bonded

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Table 3. Experimental Vibrational Frequencies for the $Sn_4Se_{10}^{4-}$ Anion and Calculated Vibrational Frequencies and Assignments for the $Sn_4Ch_{10}^{4-}$ (Ch = Se, Te) Anions

frequency, cm^{-1}				
exptl[a]		DFT[d]		
$Sn_4Se_{10}^{4-}$ [b]	$Sn_4Se_{10}^{4-}$ [c]	$Sn_4Se_{10}^{4-}$	$Sn_4Te_{10}^{4-}$	assignment (T_d)
290, sh	290, sh			$\nu_1 + \nu_2$ combination
274(51)	275(48)	265	210	$\nu_3(A_1)$, $\nu_s(Sn{-}Se_t)$
268, sh	271, sh	259(313)	206(207)	$\nu_{15}(T_2)$, $\nu_{as}(Sn{-}Se_t)$
238(11)	237(20)	233(157)	192(84)	$\nu_{14}(T_2)$, $\nu_{as}(Sn{-}Se_b)$
227(4)	229(13)	226	191	$\nu_6(E)$, $\nu_{as}(Sn{-}Se_b)$
200(4)	202(2), br	213	176	$\nu_9(T_1)$, $\nu_{as}(Sn{-}Se_b)$
188(9)	190(5)	182(17)	131(14)	$\nu_{13}(T_2)$, $\nu_{as}(Sn{-}Se_b)$
178(100)	178(100)	176	128	$\nu_2(A_1)$, $\nu_s(Sn{-}Se_b)$
108(50)	109(55)	104	79	$\nu_1(A_1)$, $SnSe_3$ inversion
81, sh	81, sh	97(14)	70(8)	$\nu_{12}(T_2)$, ring bends
74(40)	75(44)	70	49	$\nu_8(T_1)$, bends
		69(0)	49(0)	$\nu_{11}(T_2)$, bends
59(12)	55(13)	61	45	$\nu_5(E)$, bends
	51, sh	48(10)	32(6)	$\nu_{10}(T_2)$, bends
		44	27	$\nu_4(E)$, bends
		40	29	$\nu_7(T_1)$, bends

[a] Values in parentheses denote relative Raman intensities, and abbreviations denote shoulder (sh) and broad (br). [b] Present work. [c] Reference 2. [d] Values in parentheses denote calculated infrared intensities, in km mol^{-1}; only the T_2 modes are infrared active.

Table 4. Calculated Geometric Parameters, Charges, Mayer Valencies, and Bond Orders for the $Sn_4Ch_{10}^{4-}$ (Ch = Se, Te) Anions

	$Sn_4Se_{10}^{4-}$	$Sn_4Te_{10}^{4-}$
Geometric Parameters and Bond Orders[a]		
$Sn{-}Ch_b$ (Å)	2.590 [0.98]	2.800 [1.00]
$Sn{-}Ch_t$ (Å)	2.480 [1.44]	2.705 [1.26]
Ch_b-$Sn{-}Ch_b$ (deg)	109.7	110.2
Ch_t-$Sn{-}Ch_b$ (deg)	109.1	108.7
$Sn{-}Ch_b{-}Sn$ (deg)	108.7	107.7
Charges and Valencies[a]		
Sn	0.15 [4.56]	0.15 [4.47]
Ch_b	−0.25 [2.20]	−0.22 [2.31]
Ch_t	−0.78 [1.66]	−0.82 [1.58]

[a] Bond orders and valencies are reported in square brackets.

anions of the heavy main group elements.[44,45] In the present study, DFT calculations provide fully optimized geometries and definitive vibrational assignments for the $Sn_4Ch_{10}^{4-}$ (Ch = Se, Te) anions.

The calculated geometries (Table 4) are in good agreement with the experimental ones (Table 2) and reproduce experimental trends, with the $Sn{-}Ch_t$ bonds ~0.1 Å shorter than the $Sn{-}Ch_b$ bonds. The calculated bond lengths are found to be slightly longer than the experimental values, and consequently, the calculated Sn−Ch stretching frequencies are, in general, found to be slightly lower than the experimental values. The vibrational frequencies follow the expected trends (Table 3), with the $Sn_4Se_{10}^{4-}$ modes appearing at higher frequency than the $Sn_4Te_{10}^{4-}$ modes because of the reduced mass effect, and with the terminal $Sn{-}Ch_t$ stretches appearing at higher frequency than the $Sn{-}Ch_b$ ring stretches. The asymmetric and symmetric $Sn{-}Se_t$ stretches are higher than the highest asymmetric ring stretch in both anions. The spread in the ring stretching frequencies is almost 60 cm^{-1} for both Sn−Se and Sn−Te. As a consequence of the similar masses of tin and tellurium, the vibrational modes of $Sn_4Te_{10}^{4-}$ are found to be more strongly coupled. A similar trend has been observed for the Raman spectrum of $Sn_2Te_6^{4-}$ when compared with that of $Sn_2Se_6^{4-}$.[1]

The Mayer valencies[46−49] at Sn are predicted to be 4.47 [4.56] (Table 4), somewhat higher than the value expected for four coordination. The bridging chalcogens have total Mayer valencies of 2.31 [2.20], consistent with two Sn atoms bonded to a chalcogen. The terminal chalcogens have Mayer valencies of 1.58 [1.66].[50] The $Sn{-}Ch_b$ bonds have Mayer bond orders of 1.00 [0.98], and the $Sn{-}Ch_t$ bonds have bond orders of 1.26 [1.44]. The Mayer bond orders are consistent with the valencies and the experimental and calculated bond length trends described above. The higher Mayer bond orders and valencies of the $Sn{-}Ch_t$ bonds relative to those of the $Sn{-}Ch_b$ bonds indicate considerable back-bonding from the terminal chalcogen to the tin. The $Sn{-}Te_t$ Mayer bond order and valence values are lower than those of $Sn{-}Se_t$ and are consistent with the reduced tendency of the heavy main-group elements to form multiple bonds.[51] The $Sn{-}Ch_t$ back-bonding also serves to diminish the formal charges on the terminal chalcogens. The Mulliken charges show that both cages have similar charge distributions, with the Sn atoms having a charge of 0.15 each. Most of the negative charge, −0.82 [−0.78], is localized on the terminal chalcogen atoms, when compared with the Ch_b charges (−0.22 [−0.25]).

Conclusion

The $Sn_4Ch_{10}^{4-}$ anions have been synthesized as their 18-crown-6-K^+ salts. The adamantanoid geometries (T_d point symmetry) of the anions were established in the solid state by X-ray crystallography and, in the case of the $Sn_4Se_{10}^{4-}$ anion, by Raman spectroscopy. The $Sn_4Te_{10}^{4-}$ anion has been characterized for the first time and, in addition to $Si_4Te_{10}^{4-}$ and $Ge_4Te_{10}^{4-}$, represents the only other known group 14 adamantanoid telluride. Density functional theory calculations have been used to calculate the vibrational spectra of both $Sn_4Ch_{10}^{4-}$ anions and to reassign the Raman spectrum of $Sn_4Se_{10}^{4-}$. The terminal Sn−Ch bonds are shown to have considerable multiple bond character with the terminal Sn−Se bonds exhibiting greater multiple bond character than the terminal Sn−Te bonds.

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(50) The empirically derived bond valence values of Brown (Brown, I. D. In *Structure and Bonding in Crystals*; O'Keeffe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. 2, pp 1−30.) have also been calculated (Brown, I. D. *J. Appl. Crystallogr.* **1996**, *29*, 479.) from the experimental bond distances but show trends opposite to those from the Mayer values, with total bridging Ch values of 2.04 [2.22] and terminal Ch values of 1.56 [1.39]. The bond valence parameters for tin that were used to calculate the empirical bond valence values for the terminal and bridging chalcogen atoms (O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226.) are general; i.e., they do not differentiate between formal oxidation numbers and therefore are not as reliable as the Mayer values. Moreover, the bond valencies of Brown are totally empirical and are not representative, in many cases, of the actual molecule; they represent an average, idealized picture and do not take into account changes in ionicity and electronic structure.

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Experimental Section

Apparatus and Materials. All compounds used and prepared during the course of this work were air and moisture sensitive. Consequently, all manipulations were carried out under rigorously anhydrous and oxygen-free conditions as previously described.[2]

Potassium metal (BDH Chemicals, >99%) was cut and cleaned as previously described.[2] Tin granules (Baker Analyzed Reagent, 99.9%), selenium shot (Alfa Inorganics, 99.9%), and tellurium powder (Alfa Inorganics, 99.9%) were used as received and vacuum-dried prior to use. Potassium monotelluride was prepared as previously described.[52] The ligand 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, Aldrich) was recrystallized twice from freshly distilled acetonitrile (Fisher Scientific Co.) and then distilled under vacuum (<0.1 Torr) at 115 °C. The ligand was then transferred to, and stored inside, the drybox.

The solvents, ethylenediamine (Fisher Scientific Co., 99%), tetrahydrofuran (Aldrich, 99.9%), and anhydrous ammonia (Matheson, 99.99%), were dried, stored, and transferred as previously described.[2]

The alloy, $KSnSe_2$, was prepared as previously described[25] by fusing the elements in the required molar ratios inside a thick-walled Pyrex glass tube (K, 0.5114 g, 13.080 mmol; Sn, 1.5183 g, 12.790 mmol; Se, 1.9976 g, 25.299 mmol). The resulting dark green alloy was ground and its stoichiometry corrected for the recovered tin lump (0.1174 g, 0.989 mmol) to $KSn_{0.90}Se_{1.93}$.

Because the formation of $K_4Sn_4Te_{10}$ required large quantities of the chalcogen and could therefore result in a potentially strongly exothermic reaction, the fusion was carried out in two steps inside a quartz vessel by gently heating to the fusion temperature and continuously mixing over a Meeker burner flame. Initially, K_2Te (2.903 g, 1.411 mmol) was heated with the required amount of tin metal (0.3344 g, 2.817 mmol) until a free-flowing, homogeneous melt was obtained. In a second step, the resulting ternary K/Sn/Te alloy was mixed with tellurium powder (0.7215 g, 5.654 mmol) and fused to give a homogeneous and free-flowing melt. Excessive heating of the molten alloy, which resulted in adhesion of the molten alloy to the walls of the quartz vessel at higher temperatures and led to cracking of the vessel upon cooling, was avoided. The resulting alloy, which was gray, brittle, and homogeneous, was ground to a powder inside a drybox.

Crystal Structure Determination of [18-crown-6-K]$_4$[Sn_4Se_{10}]·5en and [18-crown-6-K]$_4$[Sn_4Te_{10}]·3en·2THF. (a) Crystal Growing. The vapor phase diffusion of THF (1/2 v/v) over 1−2 weeks into the yellow-orange colored en solution obtained by extraction of the alloy $KSn_{0.90}Se_{1.93}$ (0.1178 g, 0.395 mmol) in the presence of a nearly stoichiometric amount of 18-crown-6 (0.1101 g, 0.417 mmol) with respect to K^+ led to the formation of two crystal morphologies. The first type, yellow plates, had cell parameters (a = 15.572(8) Å, b = 8.434(7) Å, c = 23.252(14) Å, β = 108.54(4)°, V = 2895.14(3.37) Å^3, 24 °C, Ag Kα radiation) which were identical to those of [K]$_2$[18-crown-6-K]$_2$[Sn_2Se_6]·4en[34] and were not further studied. The second type, orange parallelepipeds, gave rise to a new set of cell parameters; the crystals were shown by an X-ray crystal structure determination to be [18-crown-6-K]$_4$[Sn_4Se_{10}]·5en.

Crystals of [18-crown-6-K]$_4$[Sn_4Te_{10}]·3en·2THF were obtained by the vapor phase diffusion of THF (1:2 v/v) over 3−4 weeks into the deep red en extract of $K_4Sn_4Te_{10}$ (0.300 g, 0.156 mmol) containing a molar deficit of 18-crown-6 (0.0437 g, 0.165 mmol) with respect to K^+. In all cases, the mother liquor was decanted back into the first arm of the Pyrex glass reaction vessel and was subsequently pipetted out of the vessel inside a glovebag which had been previously flushed for 24 h and filled with dry nitrogen gas. The crystals were then dried under dynamic vacuum for ∼2−3 min.

Crystals of both compounds were transferred to a drybox equipped with a stereomicroscope, and the reaction vessel was cut open. Single crystals of both compounds were heat sealed inside Lindemann glass capillaries (previously dried under vacuum at 250 °C for 24 h) and were stored at room temperature prior to mounting on the diffractometer. The crystals used in this study had the dimensions 0.16 × 0.32 × 0.28 ($Sn_4Se_{10}^{4-}$) and 0.19 × 0.45 × 0.38 ($Sn_4Te_{10}^{4-}$) mm^3.

(b) Collection and Reduction of X-ray Data. The diffraction data were collected on a Stoe image plate diffractometer system equipped with a one-circle goniometer and a graphite monochromator. Molybdenum radiation (λ = 0.710 73 Å) was used. Values for the $Sn_4Se_{10}^{4-}$ structures, when differing from those of $Sn_4Te_{10}^{4-}$, are given in square brackets. Data were collected in two stages: (a) 467 [420] exposures (3 [4] min per exposure) were obtained at 65 [55] mm with 0 [160]° $\leq \phi \leq$ 140 [286]° and with the crystal oscillated through 0.4 [0.3]° in ϕ; (b) 200 [150] exposures (2 min/exposure) were obtained at 120 [125] mm with 0 [150]° $\leq \phi \leq$ 150 [300]° and with the crystal oscillated through 1.0° in ϕ. In total, 59 396 [42 373] reflections were collected, and 16 747 [15 270] unique reflections remained after averaging of equivalent reflections. A total of 15 061 [10 398] reflections satisfying the condition $I \geq 2\sigma(I)$ were used for structure solution. During refinement, reflections were either omitted if $F^2 < 0$ or flagged for potential systematic errors. Corrections were made for Lorentz and polarization effects, and absorption corrections were applied for $Sn_4Te_{10}^{4-}$ using an empirical absorption correction based on redundant reflections. No absorption correction was applied for $Sn_4Se_{10}^{4-}$.

(c) Solution and Refinement of the Structures. The Siemens *SHELXTL-Plus* software package was used for structure determination, refinement, and molecular graphics.[53] The *XPREP* program[53] was used to confirm the unit-cell dimensions and the crystal lattices. Conventional direct methods located the general and/or special positions of the main-group and alkali-metal atoms. The full-matrix least-squares refinement of the positions and isotropic thermal parameters of the assigned atoms located the general and/or special positions of the C, N, and O atoms of the 18-crown-6-K$^+$ cations. Any disorder in the cations was modeled at this point in the refinement. Ethylenediamine or THF solvent molecules were assigned after the atoms of the anions and cations were refined with anisotropic thermal parameters, and any disorder was satisfactorily modeled. Crystallographically well-behaved solvent molecules were refined with anisotropic thermal parameters, whereas disordered solvent molecules were isotropically refined at 0.5 occupancy and by constraining the C−C, C−N, and C−O bond lengths and the nonadjacent C−N and C−O distances to values observed in ordered solvent molecules. Hydrogen atom positions were calculated (d(C−H) = 0.96 Å, d(O−H) = 0.82 Å, d(N−H) = 0.96 Å), and U(H) was fixed to −1.2 × U(C), U(O), or U(N). In the case of [18-crown-6-K]$_4$[Sn_4Te_{10}]·3en·2THF, the C and O atoms of the positionally disordered 18-crown-K$^+$ cations were refined with common C and O thermal parameters for each cation. During the final stages of the refinement, all reflections with $F^2 < -2\sigma(F^2)$ were suppressed, and weighting factors recommended by the refinement program were introduced. The maximum electron densities in the final difference maps were located around the anions.

Raman Spectroscopy. The Raman spectrum of a single crystal of [18-crown-6-K]$_4$[Sn_4Se_{10}]·5en was recorded as previously described using a microscope.[2,45] The 514.5-nm line of a Spectra Physics model 2016 Ar$^+$ ion laser was used for the excitation of the yellow sample. The Raman spectrometer frequencies were calibrated by the use of the 1018.3 cm^{-1} line of neat liquid indene. A laser power of 100 mW was used, and slit settings corresponding to a resolution of ± 2 cm^{-1} were employed. A total of 15 reads having 60 s integration times were summed. The Raman spectrum was recorded at room temperature on a randomly orientated single crystal sealed inside a previously vacuum-dried Pyrex melting-point capillary.

Calculations. The calculations were carried out at the density functional theory (DFT) level on SGI computers using the program DGauss.[54−56] A DZVP basis set[57] was used for Se, Te, and Sn. The

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calculations were done at the local level with the potential fit of Vosko, Wilk, and Nusair.[58] The geometries were optimized by using analytic gradient methods, and second derivatives were also calculated analytically.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for support in the form of a research grant and the Ontario Ministry of Education and Training for the award of a graduate scholarship to A.M.P. The density functional theory calculations were performed in the William R. Wiley Environmental Molecular Sciences Laboratory funded by the Office of Biological Environmental Research, U.S. Department of Energy, under Contract DE-AC06-76RLO 1830 with the Battelle Memorial Institute, which operates the Pacific Northwest National Laboratory, a multiprogram national laboratory for the Department of Energy. We gratefully acknowledge Prof. Arndt Simon, Max-Planck-Institut, Stuttgart, Germany, for making the Stoe image plate diffractometer system available.

Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of $[18\text{-crown-6-K}]_4[Sn_4Se_{10}]\cdot 5en$ and $[18\text{-crown-6-K}]_4[Sn_4Te_{10}]\cdot 3en\cdot 2THF$. This material is available free of charge via the Internet at http://pubs.acs.org.

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