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Electrochemical Synthesis of $[NEt_4]_2[enH]_2[Ge_2Se_6]$ and $[NEt_4]_4[Sn_4Se_{10}]$

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$[NEt_4]_2[enH]_2[Ge_2Se_6]$ and $[NEt_4]_4[Sn_4Se_{10}]$ have been synthesized electrochemically by the reduction of metal chalcogen alloys in an electrolyte solution of NEt_4Br in ethylenediamine. The structures of both compounds have been determined by single-crystal X-ray methods. $[NEt_4]_2[enH]_2[Ge_2Se_6]$ crystallizes in the triclinic space group $C_i^1-P\bar{1}$ with one formula unit in a cell of dimensions $a = 7.805(4)$ Å, $b = 10.747(6)$ Å, $c = 11.445(6)$ Å, $\alpha = 110.33(2)°$, $\beta = 97.19(3)°$, $\gamma = 92.62(2)°$, and $V = 889.0(8)$ Å^3 ($T = 115$ K). Final agreement indices for $[NEt_4]_2[enH]_2[Ge_2Se_6]$ are 0.116 for $R_w(F_o^2)$ for all the 2982 data and 0.055 for R_1 for the 1958 reflections with $F_o^2 \geq 2\sigma(F_o^2)$ (158 variables). $[NEt_4]_4[Sn_4Se_{10}]$ crystallizes in the cubic space group $T_d^4-P\bar{4}3n$ with eight formula units in a cell of dimensions $a = 22.170(7)$ and $V = 10897(6)$ Å^3 ($T = 115$ K). Final agreement indices for $[NEt_4]_4[Sn_4Se_{10}]$ are 0.123 for $R_w(F_o^2)$ for all the 1490 data and 0.057 for R_1 for the 1138 data with $F_o^2 \geq 2\sigma(F_o^2)$ (90 variables). The $[Ge_2Se_6]^{4-}$ anion is composed of a pair of edge-sharing tetrahedra. Each of the two independent $[Sn_4Se_{10}]^{4-}$ anions has the adamantane-type structure consisting of four Sn tetrahedra, each of which shares three edges with three similar tetrahedra; the symmetry of one anion is $\bar{4}$ (S_4) while that of the other is 23 (T). Although both the $[Ge_2Se_6]^{4-}$ and $[Sn_4Se_{10}]^{4-}$ anions are new, each has group 14 structural analogues.

Introduction

Metal chalcogenides and polychalcogenides made by solid-state and solution methods form an intriguing class of compounds. The unique behavior of tellurium with respect to its lighter congeners is apparent in these compounds. For example, among the chalcogenometalates there are no known sulfide or selenide analogues of the $[AuTe_7]^{3-}$,[1] $[AgTe_7]^{3-}$,[2] $[HgTe_7]^{2-}$,[2] and $[Pt_4Te_4(Te_3)_6]^{4-}$ [3] anions. In the solid state there is usually a clear delineation of bonding and ionic interchalcogen distances in sulfides and selenides, but tellurides may be fraught with Te−Te distances intermediate between a single bond and a van der Waals interaction.[4,5] Although there has been a concerted effort to understand solid-state and soluble chalcogenides, chiefly through exploratory synthesis, the interface between the solution state and solid state remains nebulous. One strategy to rectify this is to seek new routes to the dissolution of solid-state compounds. Historically, Joannis[6,7] and then Kraus[8] were the first to investigate the action of alkali metals dissolved in liquid ammonia on metals and semimetals, observing the formation of intensely colored solutions. Zintl and co-workers advanced this work by analyzing the stoichiometries of these solutions through the use of potentiometric titrations.[9,10] However, it was not until 1970 that Kummer and Diehl isolated the first crystalline compound, $[Na_4(en)_7][Sn_9]$,[11] from such solutions. Corbett and co-workers showed the utility of encapsulating agents in stabilizing these complexes;[12,13] many "Zintl anion" clusters have been subsequently synthesized and characterized.[14]

Numerous chalcogenometalates have been prepared by means of a solvent extraction technique that involves the fusion at high temperatures of an alkali metal with the desired elements, followed by extraction with a polar solvent such as ethylenediamine.[15−18] Recently, we have synthesized a variety of novel chalcogenometalates of the main-group metals by reduction of metal−chalcogen alloys by solvated alkali metal electrons.[19,20] Although this method has produced some fascinating new compounds, the process is limited by the invariant reduction potential of the alkali metal, and hence it does not lend itself well to subtleties in experimental procedure. Warren, Bocarsly, Haushalter, and co-workers have recently developed an elegant technique for crystallizing chalcogenometalates by electrochemical reduction of metal−chalcogen alloys in ethylenediamine.[21−25] This method is based on the constant discharge of chalcogenometalate anions into the cathodic cell from the metal chalcogenide alloy by application of potential at room temperature. Once sufficient concentration has been achieved,

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crystallization may occur in the reduction chamber. A benefit of electrochemical reduction is that both current and potential can easily be varied. A critical but often neglected degree of freedom in the crystallization of an ionic species is the variability of the counterion. Extraction of main-group metal−chalcogenide alloys relies on the reduction potential of an alkali metal or alkaline earth metal. Although there are different sizes of metals to choose from, each has a unique and fixed reduction potential; size and reduction potential cannot be varied simultaneously. This dilemma is not insurmountable; encapsulating agents, such as crown ethers or cryptands, serve not only to impede electron back-donation but also to present a crude means of altering the cation size. However, the cathodic dissolution experiment may be carried out with a host of cations (usually tetraalkylammonium or tetraarylphosphonium ions from their halide salts) present in the electrochemical cell dually functioning as supporting electrolyte. Thus this electrochemical technique is appealing as it provides a systematic means of studying the reduction chemistry and dissolution of metal−chalcogen alloys that abut the solution and solid states.

Table 1. Crystal Data and Structure Refinement for $[NEt_4]_2[enH]_2[Ge_2Se_6]$ and $[NEt_4]_4[Sn_4Se_{10}]$

compound	$[NEt_4]_2[C_2H_9N_2]_2[Ge_2Se_6]$	$[NEt_4]_4[Sn_4Se_{10}]$
chemical formula	$C_{20}H_{58}Ge_2N_6Se_6$	$C_{32}H_{80}N_4Se_{10}Sn_4$
formula weight	1001.66	1785.37
a (Å)	7.805(4)	22.170(7)[a]
b (Å)	10.747(6)	22.170(7)
c (Å)	11.445(6)	22.170(7)
α (deg)	110.33(2)	90
β (deg)	97.19(3)	90
γ (deg)	92.62(2)	90
V (Å^3)	889.0(8)	10897(6)
ρ_{calcd} (g cm^{-3})	1.871	2.093
space group	$C_i^1-P\bar{1}$ (No. 2)	$T_d^4-P\bar{4}3n$ (No. 218)
Z	1	8
μ (cm^{-1})	79	85
T data collection (K)[b]	115	115
$R_w(F^2)$[c] (all data)	0.116	0.123
$R_1(F)$[c] ($F_o^2 \geq 2\sigma(F_o^2)$)	0.055	0.057
transmission factors[d]	0.381−0.521	0.294−0.349

[a] The cell parameters were obtained from a refinement constrained so that $a = b = c$, $\alpha = \beta = \gamma = 90°$. [b] The low-temperature system is based on a design by Huffman.[65] The diffractometer was operated with the Indiana University PCPS system.[66] [c] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$; $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [d] The analytical method as performed in the Northwestern University absorption program AGNOST was used for the absorption correction.[27]

Table 2. Positional Parameters and Equivalent Isotropic Displacement Parameters for $[NEt_4]_2[enH]_2[Ge_2Se_6]$

atom	x	y	z	U(eq)[a] (Å^2)
Ge(1)	0.11829(13)	0.12961(9)	0.11219(9)	0.0070(2)
Se(1)	0.3564(2)	0.23296(11)	0.06546(11)	0.0232(3)
Se(2)	0.0494(2)	0.21080(10)	0.31584(11)	0.0223(3)
Se(3)	0.1386(2)	0.88778(10)	0.04228(10)	0.0196(3)
N(1)	0.9140(12)	0.5964(8)	0.2677(8)	0.023(2)
N(2)	0.5578(12)	0.8698(10)	0.5255(9)	0.032(2)
N(3)	0.3551(12)	0.9448(9)	0.8223(9)	0.027(2)
C(1)	0.243(2)	0.5882(11)	0.3035(11)	0.031(3)
C(2)	0.7587(14)	0.6067(10)	0.3381(10)	0.021(3)
C(3)	0.724(2)	0.4681(11)	0.0557(10)	0.028(3)
C(4)	0.937(2)	0.7188(10)	0.2312(11)	0.028(3)
C(5)	0.701(2)	0.4811(11)	0.3597(11)	0.030(3)
C(6)	0.987(2)	0.8485(10)	0.3439(11)	0.029(3)
C(7)	0.884(2)	0.4741(10)	0.1475(10)	0.023(3)
C(8)	0.0733(14)	0.5836(10)	0.3520(10)	0.022(3)
C(9)	0.457(2)	0.8428(10)	0.6131(10)	0.021(3)
C(10)	0.4456(14)	0.9713(10)	0.7224(10)	0.023(3)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Experimental Section

Syntheses and NMR Measurements. Alloys of nominal composition Ge_2Se_3 and Sn_2Se_3 were fashioned into cathodes by fusing stoichiometric amounts of the powders of the constituent elements (sources: Ge, Johnson Matthey, 99.999%; Sn, Johnson Matthey, 99.5%; Se, Aldrich, 99.8%) in fused silica tubes in a H_2/O_2 flame under an argon atmosphere. The tubing was then shattered. Having conformed to the shape of the tube, the cylindrically shaped alloys (4 g) were soldered to copper wires with silver solder, inserted into fused silica sleeves, and fastened with epoxy. Nickel wire was used as the sacrificial anode. A saturated solution of NEt_4Br in ethylenediamine (distilled over CaH_2) was prepared and transferred to the cell with the use of standard Schlenk techniques. A constant current of 300 μA was applied to the electrochemical cells; the applied voltage was allowed to vary up to a maximum of 5 V.

For $[NEt_4]_4[Sn_4Se_{10}]$ a faint yellow stream from the cathode was observed upon application of the current. Yellow needle-like and tetrahedral-shaped crystals appeared in the cathodic chamber after 2 d. The reaction was interrupted after 5 d, and the crystals were separated by filtration. The crystals were washed with ether and mounted for diffraction studies under degassed Paratone N oil. $[NEt_4]_4[Sn_4Se_{10}]$ was also obtained upon substitution of the Sn_2Se_3 alloy with a Sn_2Se_5 (Sn_4Se_{10}) alloy.

No crystals of $[NEt_4]_2[enH]_2[Ge_2Se_6]$ formed in the electrochemical cell after 1 week, although the solution was yellow. The experiment was interrupted, and the electrolyte solution was layered with ether. Highly air- and moisture-sensitive pale yellow crystals formed after several days. No product could be isolated upon the reduction of a $GeSe_3$ (Ge_2Se_6) alloy under similar conditions.

The electrochemical dissolution of a Pb_2Se_3 alloy produced a purple solution from which no crystalline material could be isolated.

The ^{77}Se NMR spectrum of $[NEt_4]_4[Sn_4Se_{10}]$ dissolved in ethylenediamine was recorded on a Varian 400 MHz Unity Plus spectrometer equipped with a 10 mm tunable broad-band probe and a deuterium lock. Chemical shifts were referenced to the secondary external standard Ph_2Se_2 at $\delta = 460$ ppm. The chemical shift scale was based on $(CH_3)_2Se$ at $\delta = 0$ ppm. ^{77}Se NMR data: $\delta_t = 72$ ppm, $\delta_b = 36$ ppm ($J_{Sn-Se} = 1490$ Hz) (t = terminal, b = bridge).

Structure Determinations

The unit cell of $[NEt_4]_2[enH]_2[Ge_2Se_6]$ was determined from a least-squares analysis of the setting angles of 31 reflections automatically centered on a Picker diffractometer at 115 K. Six standard reflections monitored every 100 reflections showed no significant change during data collection. The data were processed[26] and corrected for absorption[27] by methods standard to this laboratory. There was good agreement among Friedel pairs, and the structure was solved in the centrosymmetric space group $C_1^1-P\bar{1}$ with the direct methods program XS in the SHELXTL package;[28] it was refined on F_o^2 with the use of the program SHELXL.[29] The resultant crystal structure contains one $[Ge_2Se_6]^{4-}$ anion that has a crystallographically imposed center of symmetry. It also contains a $[NEt_4]^+$ cation and an ethylenediamine, both in general positions. As a second unique tetraethylammonium cation needed for charge balance was not found, the ethylenediamine was assumed to be monoprotonated. The source of the proton is probably insufficiently dried NEt_4Br. Monoprotonated ethylenediamine has previously been observed in several chalcogenide compounds.[30,31] The positions of the hydrogen atoms were determined from geometrical

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Table 3. Positional Parameters and Equivalent Isotropic Displacement Parameters for $[NEt_4]_4[Sn_4Se_{10}]$

atom	Wyckoff site	*x*	*y*	*z*	U(eq) (Å^2)
Sn(1)	24i	0.07260(8)	0.55848(8)	−0.18346(9)	0.0273(7)
Sn(2)	8e	−0.56603(9)	−0.43397(9)	−0.43397(9)	0.0301(11)
Se(1)	12f	−$^1/_2$	−$^1/_2$	−0.3662(2)	0.0309(13)
Se(2)	24i	0.13171(13)	0.48583(12)	−0.25035(12)	0.0315(9)
Se(3)	12h	0	$^1/_2$	−0.1157(2)	0.0301(13)
Se(4)	24i	0.14327(13)	0.61878(13)	−0.12516(13)	0.0368(9)
Se(5)	8e	−0.6293(2)	−0.3707(2)	−0.3707(2)	0.044(2)
N(1)	24i	0.8408(10)	0.3602(10)	0.5855(10)	0.034(6)
N(2)	8e	0.6556(14)	0.3444(14)	0.3444(14)	0.08(2)
C(1)	24i	0.848(2)	0.367(2)	0.646(2)	0.17(2)
C(2)	24i	0.810(2)	0.309(2)	0.575(2)	0.12(2)
C(3)	24i	0.910(2)	0.363(2)	0.559(2)	0.18(2)
C(4)	24i	0.807(3)	0.413(2)	0.563(3)	0.21(3)
C(5)	24i	0.6659	0.3187	0.4085	0.26(3)
C(6)	8e	0.698(4)	0.302(4)	0.302(4)	0.42(9)
C(11)	24i	0.794(2)	0.371(2)	0.688(2)	0.13(2)
C(21)	24i	0.811(2)	0.2839(12)	0.5045(13)	0.064(10)
C(31)	24i	0.9489(14)	0.324(2)	0.569(2)	0.088(13)
C(41)	24i	0.831(2)	0.476(2)	0.568(2)	0.11(2)

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[NEt_4]_2[enH]_2[Ge_2Se_6]^a$

Ge(1)−Se(2)	2.329(2)
Ge(1)−Se(1)	2.334(2)
Ge(1)−Se(3)^1	2.456(2)
Ge(1)−Se(3)^2	2.459(2)
N(2)−C(9)	1.446(13)
N(3)−C(10)	1.516(13)
C(9)−C(10)	1.522(14)
average NEt_4^+ distances:	
N−C	1.521(6)
C−C	1.518(8)
Se(2)−Ge(1)−Se(1)	119.04(7)
Se(2)−Ge(1)−Se(3)^1	110.22(7)
Se(1)−Ge(1)−Se(3)^1	109.85(6)
Se(2)−Ge(1)−Se(3)^2	110.88(6)
Se(1)−Ge(1)−Se(3)^2	109.64(6)
Se(3)^1−Ge(1)−Se(3)^2	94.46(5)
Ge(1)^1−Se(3)−Ge(1)^3	85.54(5)

[a] Symmetry transformations used to generate equivalent atoms: (1) $-x, -y + 1, -z$; (2) $x, y - 1, z$; (3) $x, y + 1, z$.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[NEt_4]_4[Sn_4Se_{10}]$

Sn(1)−Se(4)	2.432(4)
Sn(1)−Se(2)^1	2.543(3)
Sn(1)−Se(2)	2.552(3)
Sn(1)−Se(3)	2.555(3)
Sn(2)−Se(5)	2.429(7)
Sn(2)−Se(1)	2.558(3)
average NEt_4^+ distances:	
N−C	1.557(6)
C−C	1.51(2)
Se(4)−Sn(1)−Se(2)^1	106.50(12)
Se(4)−Sn(1)−Se(2)	108.97(11)
Se(2)^1−Sn(1)−Se(2)	109.22(9)
Se(4)−Sn(1)−Se(3)	111.87(12)
Se(2)^1−Sn(1)−Se(3)	110.01(10)
Se(2)−Sn(1)−Se(3)	110.17(10)
Se(5)−Sn(2)−Se(1)	108.77(11)
Se(1)−Sn(2)−Se(1)^2	110.17(10)

[a] Symmetry transformations used to generate equivalent atoms: (1) $-y + 1/2, x + 1/2, -z - 1/2$; (2) $-z -1, -x -1, y$.

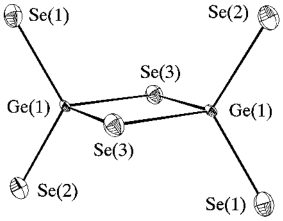

Figure 1. The $[Ge_2Se_6]^{4-}$ anion. Here and in Figure 2 displacement ellipsoids are drawn at the 50% probablility level.

calculations and were idealized. All non-hydrogen atoms were refined anisotropically. The final refinement led to a value of $R_w(F_o^2)$ of 0.116 for all data and to a value of R_1 of 0.055 for the 1958 data having $F_o^2 \geq 2\sigma(F_o^2)$.

The unit cell of $[NEt_4]_4[Sn_4Se_{10}]$ was determined from a least-squares analysis of the setting angles of 32 reflections automatically centered at 115 K on a Picker diffractometer. The observed Laue symmetry and the systematic extinctions (hhl, $l = 2n + 1$; $h00$, $h = 2n + 1$) are consistent with the cubic space groups $T_d^4-P\bar{4}3n$ and $O_h^3-Pm\bar{3}n$. Six standard reflections monitored every 100 reflections showed no significant change during data collection. The data were processed[26] and corrected for absorption[27] by methods standard to this laboratory. Intensity statistics and comparison of Friedel pairs strongly favored the noncentrosymmetric space group $P\bar{4}3n$. The positions of the heavy atoms were found with the direct methods program SHELXS.[28] Subsequent full-matrix least-squares refinements on F_o^2 with use of the program SHELXL[29] and ensuing difference electron density maps led to the modeling of the cations. The structure contains two unique anions: one with $\bar{4}$ (S_4) symmetry and one with 23 (T) symmetry. Requirements of charge balance dictate that if one of the cations is in a general position (and, in fact, it is and is ordered), then another cation must be on a 3-fold axis. While only one β-C atom of this NEt_4^+ cation need be disordered, in fact only the N atom could be located. Inspection of difference electron density maps suggested the positions of tetrahedral α-C atoms but at unreasonable N−C bonding distances. Carbon atoms were subsequently constrained along these tetrahedral vectors at reasonable distances. No attempt was made to model the β-C atoms or to assign hydrogen atom positions. The positions of the hydrogen atoms in the ordered cation were determined from geometrical calculations and were idealized. All Sn and Se atoms were refined anisotropically. The final refinement led to a value of $R_w(F_o^2)$ of 0.123 for all data and to a value of R_1 of 0.057 for the 1138 data having $F_o^2 \geq 2\sigma(F_o^2)$.

Crystal data and some experimental details are given in Table 1. Final positional parameters of all non-hydrogen atoms are given in Tables 2 and 3 for $[NEt_4]_2[enH]_2[Ge_2Se_6]$ and $[NEt_4]_4[Sn_4Se_{10}]$, respectively. Selected bond distances and angles for the $[Ge_2Se_6]^{4-}$ anion are given in Table 4; those for the $[Sn_4Se_{10}]^{4-}$ anion are given in Table 5. Further crystallographic details are available as supporting information.

Results and Discussion

There have been many recent structural investigations of germanium and tin chalcogenometalates.[32−40] Whereas the diborane-type $[M_2Q_6]^{4-}$ anion (M = Ge, Q = S;[41] M = Sn, Q

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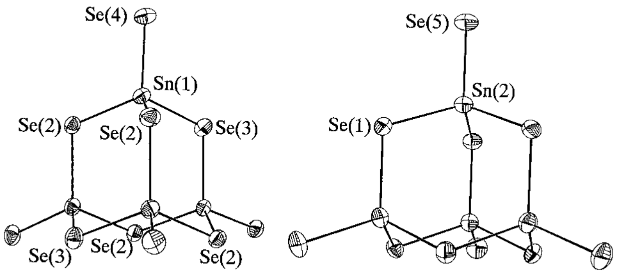

Figure 2. The two unique $[Sn_4Se_{10}]^{4-}$ anions in the $[NEt_4]_4[Sn_4Se_{10}]$ structure. The anion on the left has crystallographically imposed symmetry $\bar{4}$, whereas the anion on the right has imposed symmetry 23.

= S,[42] Se,[36,43] Te[34,44]) has been pervasive in both Sn and Ge systems, the adamantane-type $[Ge_4Q_{10}]^{4-}$ anion (Q = S,[45−48] Se,[49] Te[40]) seems to be endemic to Ge systems but is also found among chalcogenosilicolates.[47,50−52]

The crystal structure of $[NEt_4]_2[enH]_2[Ge_2Se_6]$ consists of separated cations and anions. The shortest cation−anion interaction of 2.458(3) Å occurs between the atoms H(3D) of the protonated ethylenediamine and Se(1). The Se(1)···H(3D)−C(3) bond angle is 176.2(8)°. A nominal interaction is thus inferred, since the sum of the van der Waals radii for Se and H is 3.2 Å.[53]

The $[Ge_2Se_6]^{4-}$ anion, which has a crystallographically imposed center of symmetry, consists of two symmetry-related edge-sharing $GeSe_4$ tetrahedra (Figure 1). The tetrahedra are mildly distorted in order to increase the separation between the Ge^{4+} centers (3.337(3) Å). The Se−Ge−Se bond angles range from 94.46(5)° between bridging Se atoms to 119.04(7)° between terminal Se atoms. The $Ge-Se_b$ bond distances are 2.456(2) and 2.459(2) Å; the $Ge-Se_t$ bond distances are 2.329(2) and 2.334(2) Å.

The $[Ge_2Se_6]^{4-}$ anion is a new member of the $[M_2Q_6]^{4-}$ series (M = Ge, Q = S; M = Sn, Q = S, Se, Te). It is somewhat surprising that in this active area of research this anion has been prepared for the first time through the cathodic dissolution technique. Structurally, the $[Ge_2Se_6]^{4-}$ anion is closely related to the $[Ge_2Se_8]^{4-}$ anion where the two Ge^{4+}-centered tetrahedra are bridged by two $(Se_2)^{2-}$ ligands instead of condensing to share a common edge.[49] The motif of edge-sharing Ge^{4+}-centered tetrahedra is observed in the binary compound $GeSe_2$.[54] In this two-dimensional solid-state compound, the slabs feature Ge_2Se_6 units that stitch together infinite chains of corner-sharing tetrahedra. The $Ge-Se_b$ bond lengths (2.349(5)−2.369(5) Å) and the $Se_b-Ge-Se_b$ bond angles (99.4(1) and 99.7(1)°) in this Ge_2Se_6 unit are comparable to those in $[NEt_4]_2[enH]_2[Ge_2Se_6]$. Amusingly, the isomeric isolated $[Ge_2Se_6]^{6-}$ unit has been observed in the solid-state compound $K_6Ge_2Se_6$.[55] In this structure the anion has a Ge−Ge bond with Ge in the +3 oxidation state and a 2.477(1) Å Ge−Ge bond distance. The Ge−Se bond distances are 2.353(2) and 2.368(2) Å, comparable to the $Ge-Se_t$ distances in the title compound.

The crystal structure of $[NEt_4]_4[Sn_4Se_{10}]$ consists of two crystallographically unique $[Sn_4Se_{10}]^{4-}$ anions (Figure 2) and two unique cations. One cation is in a general position, and the other has crystallographically imposed symmetry 3 and hence is disordered. One of the anions has crystallographically imposed symmetry 23 while the other has imposed symmetry $\bar{4}$. Both anions are ordered. There is a short interaction of 2.691(4) Å between atoms Se(2) and H(21A); the Se(2)··· H(21A)−C(21) angle is 170.1(15)°. The adamantane-like structure of the anion stems from four Sn^{4+}-based tetrahedra sharing the corners with three other similar tetrahedra through Se^{2-} bridges. The fourth tetrahedral site is occupied by a terminal Se^{2-} ligand. Se−Sn−Se bond angles range from 106.50(12) to 111.87(12)°. The $Sn-Se_b$ bond distances span 2.543(3) to 2.558(3) Å; $Sn-Se_t$ distances are 2.429(7) Å and 2.432(4) Å. Very recently, $[2,2,2\text{-Crypt-K}]_4[Sn_4Se_{10}]$ has been synthesized and its structure determined.[56] The $Sn-Se_b$ and $Sn-Se_t$ bond distances in $[2,2,2\text{-Crypt-K}]_4[Sn_4Se_{10}]$ span 2.533(2) to 2.562(2) Å and 2.416(2) to 2.433(2) Å, respectively; the Se−Sn−Se bond angles range from 103.55(7) to 113.06(6)°. There is thus excellent agreement in the two determinations of the metrical aspects of the $[Sn_4Se_{10}]^{4-}$ anion.[57] The shortening of the $M-Se_t$ bond has been observed in other group 14 adamantanes, for example in $[NEt_4]_4[Ge_4Te_{10}]$[40] and in $[NMe_4]_4[Ge_4S_{10}]$,[45] and is also observed in related oxide structures.[58]

Although many structures are known in which Sn is tetrahedrally coordinated to Se,[43,59,60] the Sn center is always five- or six-coordinate in the binary selenides;[61−63] it is six-coordinate in *β*-Sn.[64] X-ray powder diffraction studies suggest that Sn_2Se_3, the starting material of the electrochemical reduction, is a new phase. Whether it is a source of tetrahedral Sn remains to be determined.

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Supporting Information Available: Tables listing detailed crystallographic data, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for both compounds (8 pages). Ordering information is given on any current masthead page.

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