Se_2^{2-}, Se_5^{2-}, and Se_7^{2-} Ligands in $[NEt_4]_2[As_2Se_6]$, $[enH][AsSe_6]\cdot$2.2.2-cryptand, $[NEt_4][AsSe_8]$, and $[(en)_2In(SeAs(Se)Se_2)]\cdot$en

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The extraction in ethylenediamine (en) of “$AsSe_4$”, “$TlAsSe_4$”, and “$InAsSe_4$”, followed by reaction with cation sources or 2.2.2-cryptand, has led to the isolation of $[NEt_4]_2[As_2Se_6]$ (**1**), $[enH][AsSe_6]\cdot$2.2.2-cryptand (**2**), $[NEt_4][AsSe_8]$ (**3**), and $[(en)_2In(SeAs(Se)Se_2)]\cdot$en (**4**). These compounds contain $AsSe^+$ units coordinated to Se_2^{2-}, Se_5^{2-}, and Se_7^{2-} ligands in **1** and **4**, **2**, and **3**, respectively. The $[As_2Se_6]^{2-}$ anion features two $AsSe^+$ units joined by Se_2^{2-} ligands; the resultant As_2Se_4 ring exhibits a chair conformation. The $[AsSe_6]^-$ anion features an $AsSe^+$ unit coordinated in a bidentate fashion by a Se_5^{2-} ligand to create an $AsSe_5$ ring with a chair conformation. The $[AsSe_8]^-$ anion contains an $AsSe^+$ unit coordinated by a bidentate Se_7^{2-} ligand; the resultant $AsSe_7$ ring has a crown conformation. $[(en)_2In(SeAs(Se)Se_2)]$ features an octahedral In atom bridged by one Se^{2-} and one Se_2^{2-} ligand to an $AsSe^+$ unit; two bidentate en ligands complete the coordination about the In center.

Introduction

Activity in main-group chalcogenide chemistry has resulted in the synthesis of several interesting selenoarsenates, including $[AsSe_4]^{3-}$,[1] $[As_2Se_6]^{2-}$,[2−4] $[As_3Se_6]^{3-}$,[5] $[As_4Se_6]^{2-}$,[2] $[As_7Se_4]^{-}$,[6] and $[As_{10}Se_3]^{2-}$.[7] Several of these species have been obtained by the extraction of binary arsenic selenides. The extraction of solid-state metal chalcogenide phases often affords interesting compounds unobtainable by means of other experimental techniques.[3,8−21] We set out to investigate if yet more selenoarsenates could be isolated by means of extraction techniques. Here we report the syntheses and characterization of $[NEt_4]_2[As_2Se_6]$ (**1**), $[enH][AsSe_6]\cdot$2.2.2-cryptand (**2**), $[NEt_4][AsSe_8]$ (**3**), and $[(en)_2In(SeAs(Se)Se_2)]\cdot$en (**4**) formed from the extractions of $AsSe_4$, $TlAsSe_4$, and $InAsSe_4$, followed by reaction with cation sources or 2.2.2-cryptand. We also report some ^{77}Se NMR spectroscopic results that bear on what species are present in solution.

Experimental Section

All solvents were dried and degassed before use. Ethylenediamine (en) was distilled over CaH_2; NEt_4Br and 4,7,13,16,21,24-hexaoxa-1,-10-diazabicyclo[8.8.8]hexacosane (2.2.2-cryptand) were recrystallized from CH_3CN. ^{77}Se NMR spectra were obtained with a Varian 400 MHz Unity Plus spectrometer equipped with a deuterium lock, 10 mm tunable broad band probe, and a variable temperature apparatus. All ^{77}Se NMR resonances are referenced to the external standard $(CH_3)_2Se$ at $\delta = 0$ ppm. A sample was prepared for NMR measurements by filtering a fresh reaction mixture into an air-free 10 mm NMR tube or by performing the extraction directly in the NMR tube.

“$AsSe_4$”, “$TlAsSe_4$”, and “$InAsSe_4$” were synthesized from stoichiometric amounts of the constituent elements (Tl (Aldrich, pellets, 99.9%), In (Aesar, 325 mesh, 99.99%), As (Johnson Matthey, 200 mesh, 99.99%), and Se (Aldrich, 100 mesh, 99.5%)) under an N_2 atmosphere by rapid heating with a hydrogen/oxygen flame followed by rapid cooling. X-ray diffraction powder patterns of these materials were obtained with a Rigaku diffractometer. $TlAsSe_4$ and $AsSe_4$ are amorphous whereas $InAsSe_4$, though crystalline, has a powder pattern that does not match any calculated for reported ternary or binary indium−arsenic−selenide phases. The starting materials are stable in air, although most of the final products are air and moisture sensitive.

Synthesis of $[NEt_4]_2[As_2Se_6]$ (1). Compound **1** can be formed from the extraction of any of the three starting materials under similar conditions. The following is a representative example of the synthesis: en (30 mL) was added to a flask charged with $AsSe_4$ (0.30 g). The flask was sonicated for 8 h ($t = 60$ °C). The resulting dark red solution was filtered and layered with 6.0 mL of en saturated with NEt_4Br. The solution was then layered with toluene (20 mL), and large yellow crystals of **1** and small red needles of **3** formed after 2 days. The 170 mg of product is estimated to be about 100 mg of **1** and 70 mg of **3**; the corresponding yields of **1** and **3** (based on As) are then 59% and 22%, respectively. Separation of crystals of **1** from crystals

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Table 1. Crystal Data and Structure Refinement for $[NEt_4]_2[As_2Se_6]$ (**1**), $[enH][AsSe_6]\cdot$2.2.2-cryptand (**2**), $[NEt_4][AsSe_8]$ (**3**), and $[(en)_2In(SeAs(Se)Se_2)]\cdot en$ (**4**)

	$[NEt_4]_2[As_2Se_6]$	$[enH][AsSe_6]\cdot$2.2.2-cryptand	$[NEt_4][AsSe_8]$	$[(en)_2In(SeAs(Se)Se_2)]\cdot en$
chemical formula	$C_8H_{20}AsNSe_3$	$C_{20}H_{46}AsN_4O_6Se_6$	$C_8H_{20}AsNSe_8$	$C_6H_{20}AsInN_6Se_4$
fw	442.05	987.29	836.85	681.86
a, Å	7.465(5)	10.993(2)	9.153(4)	9.032(8)
b, Å	8.418(4)	19.660(10)	11.333(1)	11.290(8)
c, Å	12.873(4)	15.145(7)	10.407(2)	17.329(10)
α, deg	99.46(3)	90	90	90
β, deg	96.61(4)	95.66(6)	113.05(2)	90
γ, deg	114.67(5)	90	90	90
V, Å^3	709.7(6)	3257(2)	993.3(5)	1767(2)
λ, Å	1.54056	1.54056	1.54056	0.7093
space group	C_i^1-$P\bar{1}$	C_2^2-$P2_1$	C_{2h}^2-$P2_1/m$	D_2^4-$P2_12_12_1$
Z	2	4	2	4
D(calcd), g cm^{-3}	2.069	2.013	2.798	2.563
t, °C	−160(2)	−160(2)	−160(2)	−160(2)
μ, cm^{-1}	118	94	190	114
transm factors	0.178/0.616	0.395/0.571	0.517/0.706	0.402/0.504
$R_1(F)^a$	0.0581	0.0490	0.0879	0.0712
$R_w(F^2)^b$	0.1428	0.1361	0.1988	0.1470

^{a} $R_1(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $F_o^2 > 2\sigma(F_o^2)$. ^{b} $R_w(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$, $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$, $F_o^2 < 0$.

of **3** must be performed by hand, and hence accurate elemental analyses cannot be obtained. Semiquantitative analysis of single crystals of **1** by EDX gave consistent As/Se ratios of 1:3. ^{77}Se NMR: (manually separated crystals, 25 °C, CH_3CN) *δ* 461, 167 ppm (2:1 intensity); (manually separated crystals, 25 °C, en) *δ* 468, 144 ppm (2:1 intensity).

Synthesis of $[enH][AsSe_6]\cdot$2.2.2-cryptand (2). Crystals of **2** have only been isolated from the extraction of $TlAsSe_4$. Ethylenediamine (10 mL) was added to a flask charged with $TlAsSe_4$ (0.10 g). The flask was left overnight in a sonicator ($t = 60$ °C). The resulting orange-red solution was filtered, and 2.2.2-cryptand (5 mL of a saturated en solution) was added. The black powder (0.05 g) remaining in the reaction vessel was identified as Tl_2Se_2 from its X-ray diffraction powder pattern. The solution was layered with toluene (15 mL); a dark red oil resulted. The volume of the solution was subsequently reduced to ca. 1 mL, and the remaining residue was redissolved in CH_3CN (15 mL). This solution was layered with ether (60 mL) to produce large red needles of **2**. Yield: 38 mg, 18% (based on Se). ^{77}Se NMR (25 °C, CH_3CN): *δ* 779, 569, 418, 366 ppm (1:2:1:2 intensity).

Synthesis of $[NEt_4][AsSe_8]$ (3). Crystals of **3** can be obtained from extractions of any of the starting materials under similar conditions, but they are always mixed with **1**, as noted above EDX analysis of several crystals of **3** gave consistent As/Se ratios of 1:8. ^{77}Se NMR (mixture of crystals of **1** and **3**, 25 °C, en): *δ* 466, 150 ppm (2:1) corresponding to **1**; 656, 591, 476, 335, 327, 319, 275, 182 ppm.

Synthesis of $[(en)_2In(SeAs(Se)Se_2)]\cdot en$ (4). En (10 mL) was added to a flask charged with dark gray $InAsSe_4$ (0.13 g). The mixture was sonicated for 8 h, and the resulting red-brown solution was separated from a yellow powder by filtration. The solution was layered with 2.2.2-cryptand (yield: 35 mg, 20% (based on In)). EDX analysis of **4** gave an In/As/Se ratio of 1:1:4. Compound **4** is moderately air stable. Since it is insoluble in all the common solvents analysis by ^{77}Se NMR spectroscopy was precluded.

Crystal Structure Determinations. Details are presented in Table 1. The refinement of the structure of **1** was straightforward. Crystals of **2** are of marginal quality for data collection. Only 5167 unique reflections were obtained from the chosen crystal. No solution could be found in space group C_{2h}^2-$P2_1/m$; averaging among Friedel pairs is significantly better in $P2_1$ ($R_{int} = 0.029$) than in $P2_1/m$ ($R_{int} = 0.060$). The final refinement of 496 variables in space group $P2_1$ involves anisotropic displacement parameters for As and Se atoms only. The structure contains two unique $[enH]^+$ cations, two unique $[AsSe_6]^-$ anions, and two unique 2.2.2-cryptand adducts. The MISSYM algorithm[22] in the PLATON suite of programs[23] did not detect any additional symmetry relating the unique structural units. Each $[AsSe_6]^-$ anion is disordered over two sites, the distributions being 0.631(5): 0.369(5) and 0.679(6):0.321(6). In the penultimate cycle of refinement, the value of the Flack parameter was 0.76(5). Accordingly, the structure was refined as a twin, the final ratio of the two components being 0.76(5):0.24(5). In **3** the $[NEt_4]^+$ cation is disordered over the crystallographically imposed mirror plane. In **4** all atoms were refined with anisotropic displacement parameters except for atoms N(1), N(2), C(1), and C(3) which failed to remain positive definite

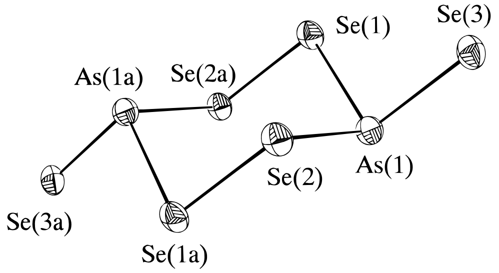

Figure 1. Structure of the $[As_2Se_6]^{2-}$ anion in $[NEt_4]_2[As_2Se_6]$ (**1**). The anion has an imposed center of symmetry. Here and in succeeding figures, the 50% probability displacement ellipsoids are shown.

Further details of the crystal structure determinations are given in the Supporting Information.

Results

The structure of the $[As_2Se_6]^{2-}$ anion of **1**, which has a crystallographically imposed center of symmetry, contains two As^{3+} centers, each coordinated by a terminal Se^{2-} anion and joined together by bridging Se_2^{2-} units. Alternatively, the anion may be described as two trigonal-pyramidal $AsSe_3$ units joined through Se−Se bonds (Figure 1). The As_2Se_4 ring exhibits a chair conformation. The $[As_2Se_6]^{2-}$ anion has been previously characterized as the $[PPh_4]^+$ [2] and $[A(2.2.2\text{-cryptand})]^+$ salts (A = Na,[3] K[4]). The metrical details (Table 2) for the anion of **1** are consistent with those reported for the other salts of $[As_2Se_6]^{2-}$.

The structure of the $[AsSe_6]^-$ anion in compound **2** comprises a trigonal-pyramidal As^{3+} center coordinated by a terminal Se^{2-} ligand and a bidentate Se_5^{2-} ligand (Figure 2). The $AsSe_5$ ring has a chair conformation with annular angles (ranging from 94.3(2) to 107.9(8)°) similar to those of the As_2Se_4 ring of **1**.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for the $[As_2Se_6]^{2-}$ Anion in Various Salts

	$[NEt_4]^{+}$ [a]	$[PPh_4]^{+}$ [b]	[Na(2.2.2-crypt)]$^{+}$ [c]	[K(2.2.2-crypt)]$^{+}$ [d]
As(1)−Se(3)	2.293(1)	2.271(2)	2.276(2)	2.268(4)
As(1)−Se(2)	2.415(2)	2.411(2)	2.412(2)	2.438(3)
As(1)−Se(1)	2.415(2)	2.421(2)	2.416(2)	2.417(3)
Se(1)−Se(2)	2.352(1)	2.353(2)	2.345(2)	2.350(3)
Se(3)−As(1)-Se(2)	95.07(4)	97.4(1)	95.10(8)	96.39(12)
Se(3)−As(1)-Se(1)	98.88(6)	99.2(1)	96.51(8)	93.81(12)
Se(2)−As(1)-Se(1)	101.48(6)	100.3(1)	101.32(7)	102.87(11)
Se(2)−Se(1)-As(1)	97.62(6)	100.9(1)	101.09(7)	100.21(11)
Se(1)−Se(2)-As(1)	100.59(4)	101.7(1)	101.04(8)	100.89(11)

[a] Present work. [b] Reference 2. [c] Reference 3. [d] Reference 4.

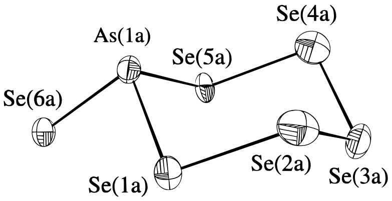

Figure 2. Structure of one of the $[AsSe_6]^-$ anions in [enH][$AsSe_6$]·2.2.2-cryptand (**2**).

Bidentate Se_5^{2-} species have been previously observed chelating C,[24] Ti,[25,26] Fe,[27,28] Cu,[29] Zn,[30] Se,[31−33] Zr,[26] Pd,[34] Te,[35] and Hf [26] centers. Of these structures, only $[PPh_4]_4[Cu_2Se_{14}]$ features a Se_5^{2-} ligand attached to a three-coordinate center.[29] The unit cell of **2** contains two unique $[AsSe_6]^-$ anions, two unique 2.2.2-cryptand adducts, and two unique $[enH]^+$ cations. To achieve charge balance it is necessary that the en be monoprotonated. The $[enH]^+$ species has been observed in several other chalcogenide compounds.[36−38]

The $[AsSe_8]^-$ anion of **3** contains a trigonal-pyramidal As^{3+} center coordinated by a terminal Se^{2-} ligand and a bidentate Se_7^{2-} ligand (Figure 3). The $[AsSe_8]^-$ anion has crystallographically imposed *m* symmetry. The anion is very similar to the $[SAsS_7]^-$ anion in $[PPh_4][AsS_8]$.[39] However, the sulfide compound was made from the reaction of $[PPh_4][As_2SCl_5]$ with K_2S_5 in CH_3CN. The $[AsSe_8]^-$ anion contains the first example of a bidentate Se_7^{2-} chain. Structures containing tridentate[40] and bidentate[41] S_7^{2-} ligands, in addition to the $[AsS_8]^-$ anion, have been reported. An uncoordinated Se_7^{2-} chain has been structurally characterized.[42] The compound $Re_2I_2(CO)_6(Se_7)\cdot 0.5C_7H_{16}$ features a Se_7 *ring* that bridges two Re centers.[43] The present $AsSe_7$ ring has a crown conformation similar to the Q_8 (Q = S, Se, Te) rings in S_8,[44−46] α-Se,[47,48] β-Se,[49,50] Cs_3Te_{22},[51] and the BiS_7 rings in Bi_2S_{34} $[(S_7)_2Bi(S_6)Bi(S_7)_2]$.[41] Metrical details are given in Table 3.

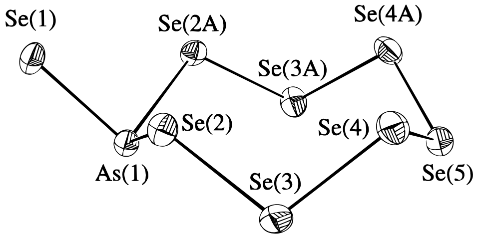

Figure 3. $[AsSe_8]^-$ anion in $[NEt_4][AsSe_8]$ (**3**). The anion has imposed *m* symmetry.

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Anion of $[NEt_4][AsSe_8]$ (**3**)[a]

As(1)−Se(1)	2.276(6)	Se(1)−As(1)-Se(2)	88.85(16)
As(1)−Se(2)	2.409(4)	Se(2)−As(1)-Se(2)′	103.85(17)
Se(2)−Se(3)	2.336(5)	Se(3)−Se(2)-As(1)	108.52(18)
Se(3)−Se(4)	2.350(5)	Se(2)−Se(3)-Se(4)	104.05(17)
Se(4)−Se(5)	2.320(4)	Se(5)−Se(4)-Se(3)	105.78(19)
		Se(4)−Se(5)-Se(4)′	108.3(2)

[a] The primed atoms are at x, $-y + 1/2$, z.

Compound **4**, $[(en)_2In(SeAs(Se)Se_2]\cdot en$, features an octahedral In atom bridged by one Se^{2-} and one Se_2^{2-} ligand to an $AsSe^+$ unit; two bidentate en ligands complete the coordination about the In center (Figure 4). For the crystal chosen the conformation of the In-containing molecule is $\Delta\lambda\lambda\delta$. Because of the en solvate, ambiguity exists in assigning formal charges to the metal atoms: $[(en)_2In^{III}(SeAs^{III}(Se)Se_2)]\cdot en$, $[(en)_2In^{I}(SeAs^{V}(Se)Se_2)]\cdot en$, and $[enH_2][(en)_2In^{I}(SeAs^{III}(Se)Se_2)]$ are all possible descriptions, with the first seeming to us to be the most reasonable. Thus,

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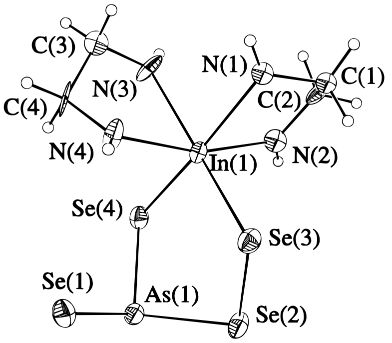

Figure 4. Structure of $[(en)_2In(SeAs(Se)Se_2)]$ in (**4**).

Table 4. Bond Distances (Å) and Angles (deg) for $[(en)_2In(SeAs(Se)Se_2)]\cdot en$ (**4**)

In(1)−N(2)	2.268(16)	N(1)−In(1)−N(3)	82.3(6)
In(1)−N(4)	2.297(15)	N(2)−In(1)−Se(4)	93.7(4)
In(1)−N(1)	2.315(16)	N(4)−In(1)−Se(4)	96.2(4)
In(1)−N(3)	2.337(16)	N(1)−In(1)−Se(4)	165.7(4)
In(1)−Se(4)	2.631(3)	N(3)−In(1)−Se(4)	88.6(5)
In(1)−Se(3)	2.661(3)	N(2)−In(1)−Se(3)	100.6(4)
As(1)−Se(1)	2.302(3)	N(4)−In(1)−Se(3)	88.4(4)
As(1)−Se(4)	2.357(3)	N(1)−In(1)−Se(3)	88.4(4)
As(1)−Se(2)	2.425(3)	N(3)−In(1)−Se(3)	162.5(4)
Se(2)−Se(3)	2.330(3)	Se(4)−In(1)−Se(3)	103.04(9)
		Se(1)−As(1)−Se(4)	107.30(11)
N(2)−In(1)−N(4)	164.8(6)	Se(1)−As(1)−Se(2)	104.41(12)
N(2)−In(1)−N(1)	75.7(6)	Se(4)−As(1)−Se(2)	101.39(11)
N(4)−In(1)−N(1)	92.5(6)	Se(3)−Se(2)−As(1)	104.19(11)
N(2)−In(1)−N(3)	91.5(6)	Se(2)−Se(3)−In(1)	98.26(11)
N(4)−In(1)−N(3)	77.2(6)	As(1)−Se(4)−In(1)	101.47(10)

the In−Se distances (Table 4) in **4** (μ_2-Se, 2.631(3) Å; μ_2-Se$_2$, 2.661(3) Å) are comparable to the distances (2.643(1)−2.657(1) Å) observed for $In(C_{12}H_{15}N_2OSe)_3$,[52] which also features octahedrally coordinated In^{III} atoms. Moreover, the As−Se distances (Se$_t$, 2.302(3) Å, μ_2-Se: 2.357(3) Å, μ_2-Se$_2$: 2.425(3) Å) are comparable to those in other arsenic(III) selenide complexes.[2,53]

Discussion

$[NEt_4]_2[As_2Se_6]$ (**1**) and $[NEt_4][AsSe_8]$ (**3**) can be isolated from the extraction of each of the three mixtures AsSe$_4$, TlAsSe$_4$, and InAsSe$_4$ in en by the addition of NEt$_4$Br and toluene. The inclusion of the second metal in the starting mixture may allow for the formation of other products, as $[enH][AsSe_6]\cdot$2.2.2-cryptand (**2**) is not isolated from the extraction of AsSe$_4$. The extracted en solution of TlAsSe$_4$ ultimately leads to crystals of **2** whereas a similar treatment of the extracted en solution of AsSe$_4$ yields only crystals of $[enH]_2[As_2Se_6]$.[54]

Limited insight into the formation chemistry has been obtained from a series of ^{77}Se NMR experiments (Table 5) on both the final products and the en extractions. The absence of J_{As-Se} or J_{Se-Se} coupling makes direct peak assignment difficult; assignments are based on intensities and analogies to spectra for other selenoarsenates. The ^{77}Se NMR spectrum of crystals of $[NEt_4]_2[As_2Se_6]$ (**1**) redissolved in en has two resonances at $\delta = 468$ and 144 ppm; when the crystals are redissolved in CH$_3$CN these resonances are at $\delta = 461$ and 167 ppm. Cation choice also appears to have little effect on the resonances, as these are found at $\delta = 466$, 169 ppm for $[K(18\text{-crown-6})]_2[As_2Se_6]$ redissolved in CH$_3$CN.[4]

Table 5. ^{77}Se NMR Chemical Shifts (ppm) for **1**−**3** and the Different Reaction Mixtures (25 °C)

compound or reaction mixture	chemical shift	solvent
$[NEt_4]_2[As_2Se_6]$	468, 144	en
	461, 167	CH$_3$CN
$[enH][AsSe_6]$	779, 569, 418, 366	en
$[NEt_4][AsSe_8]$	656, 591, 476, 335, 327, 319, 275, 182	en
$[K(18\text{-crown-6})]_2[As_2Se_6]^a$	466, 169	CH$_3$CN
$K_2Se_3^b$	278, 308	en
$K_2Se_4^b$	608, 321	en
AsSe$_4$	468, 181, 140	en
As$_2$Se$_3$	462, 174, 135	en
TlAsSe$_4$	470, 182, 142	en
InAsSe$_4$	444,^{c} 181, 99^c	en
As + 4Se	180	en
As$_4$Se$_4^d$	568, 422, 338, 205, 216	en

[a] Reference 4. [b] Reference 55. [c] Broad resonance. [d] These were previously reported to occur at 465, 180, and 139 ppm (see ref 2); the reason for the discrepancy is not known.

Crystals of $[enH][AsSe_6]$ (**2**) dissolved in en display four ^{77}Se NMR resonances ($\delta = 779$, 569, 418, 366 ppm), consistent with the four unique Se atom environments observed in the crystal structure. However, the ^{77}Se NMR spectrum of a mixture of crystals of **1** and $[NEt_4][AsSe_8]$ (**3**) dissolved in en shows six peaks ascribable to **3**, whereas only five are expected. Either the anion does not retain its structure in solution or there is another product present. None of these resonances matches those observed for Se$_n^{2-}$ species.[55,56] At first glance, the absence of multiple resonances in the ^{77}Se NMR spectra along with the similarity of resonance locations for each reaction mixture (Table 5) suggests that the predominant soluble selenoarsenate species generated are the same for all the extractions. Isolation of a given product is then dependent on the choice of cation and layering solvent, as in the In/Se$_n^{2-}$ family of compounds.[57] If this were the case, one would expect to be able to isolate the same products from reaction mixtures treated in the same manner. For most of the extractions this is true; however, **2** is isolated only from the extraction of TlAsSe$_4$ and **3** is not isolated from the extraction of As$_2$Se$_3$. This suggests that while the predominant species are the same for each extraction, other polyselenide species, undetected by ^{77}Se NMR spectroscopy, are also present and have a bearing on which products are isolated from the reaction mixtures.

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Supporting Information Available: Tables, in CIF format, of crystallographic details, atomic coordinates, displacement parameters, and bond distances and angles. Access information is given on any current masthead page.

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