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Preparation and Structures of the 2.2.2-Cryptand(1+) Salts of the $[Sb_2Se_4]^{2-}$, $[As_2S_4]^{2-}$, $[As_{10}S_3]^{2-}$, and $[As_4Se_6]^{2-}$ Anions

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2.2.2-Cryptand(1+) salts of the $[Sb_2Se_4]^{2-}$, $[As_2S_4]^{2-}$, $[As_{10}S_3]^{2-}$, and $[As_4Se_6]^{2-}$ anions have been synthesized from the reduction of binary chalcogenide compounds by K in NH_3(l) in the presence of the alkali-metal-encapsulating ligand 2.2.2-cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane), followed by recrystallization from CH_3CN. The $[Sb_2Se_4]^{2-}$ anion, which has crystallographically imposed symmetry 2, consists of two discrete edge-sharing $SbSe_3$ pyramids with terminal Se atoms cis to each other. The Sb−Se$_t$ bond distance is 2.443(1) Å, whereas the Sb−Se$_b$ distance is 2.615(1) Å (t = terminal; b = bridge). The Se$_b$−Sb−Se$_t$ angles range from 104.78(4) to 105.18(5)°, whereas the Se$_b$−Sb−Se$_b$ angles are 88.09(4) and 88.99(4)°. The ^{77}Se NMR data for this anion in solution are consistent with its X-ray structure (δ 337 and 124 ppm, 1:1 intensity, −30 °C, CH_3CN/CD_3CN). Similar to this $[Sb_2Se_4]^{2-}$ anion, the $[As_2S_4]^{2-}$ anion consists of two discrete edge-sharing AsS_3 pyramidal units. The As−S$_t$ bond distances are 2.136(7) and 2.120(7) Å, whereas the As−S$_b$ distances range from 2.306(7) to 2.325(7) Å. The S$_b$−As−S$_t$ angles range from 106.2(3) to 108.2(3)°, and the S$_b$−As−S$_b$ angles are 88.3(2) and 88.9(2)°. The $[As_{10}S_3]^{2-}$ anion has an 11-atom $As_{10}S$ center composed of six five-membered edge-sharing rings. One of the three waist positions is occupied by a S atom, and the other two waist positions feature As atoms with exocyclic S atoms attached, making each As atom in the structure three-coordinate. The As−As bond distances range from 2.388(3) to 2.474(3) Å. The As−S$_t$ bond distances are 2.181(5) and 2.175(4) Å, and the As−S$_b$ bond distance is 2.284(6) Å. The $[As_4Se_6]^{2-}$ anion features two $AsSe_3$ units joined by Se−Se bonds with the two exocyclic Se atoms trans to each other. The average As−Se$_t$ bond distance is 2.273(2) Å, whereas the As−Se$_b$ bond distances range from 2.357(3) to 2.462(2) Å. The Se$_b$−As−Se$_t$ angles range from 101.52(8) to 105.95(9)°, and the Se$_b$−As−Se$_b$ angles range from 91.82(7) to 102.97(9)°. The ^{77}Se NMR data for this anion in solution are consistent with its X-ray structure (δ 564 and 317 ppm, 3:1 intensity, 25 °C, DMF/CD_3CN).

Introduction

The use of nontraditional techniques to synthesize chalcogenometalates has led to the isolation of products and conformations unobtainable through the more conventional methods of nonaqueous solution chemistry. Some examples of these nontraditional synthetic routes include cathodic dissolution of electrodes composed of solid-state metal−chalcogenide phases,[1−6] extraction of ternary chalcogenides in ethylenediamine (en) and liquid ammonia,[7−10] and solventothermal reactions.[11−19] More recently, we have developed a chemical reduction method in which a metal chalcogenide is reduced by K in NH_3(l) in the presence of an encapsulating ligand.[20,21]

A recent review summarizes the progress of mixed group 15/group 16 chemistry.[22] Although a number of antimony selenides have been synthesized in the solid state,[23−27] selenoantimonates have only recently been synthesized by solution methods. These include $[PPh_4]_4[Sb_{12}Se_{20}]$[28] and $[PPh_4]_2[Sb_4Se_6]$.[6] The solution chemistry of chalcogenoarsenates has been more fruitful, for it has afforded compounds such as $[PPh_4]_2[As_2S_6]$,[29] $[enH_2]_3[As_3S_6]_2\cdot 6en$ (en = ethylenediamine),[30] $[pip]_2[As_4S_6]$ (pip = piperidine),[31] $[PPh_4]_4[As_7Se_4]$,[32] $[Sr(en)_4]_2[As_3$-

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Table 1. Selected Crystallographic Data for $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_4]$, $[K(2.2.2\text{-cryptand})]_2[As_2S_4]\cdot 2CH_3CN$, $[K(2.2.2\text{-cryptand})]_2[As_{10}S_3]$, and $[K(2.2.2\text{-cryptand})]_2[As_4Se_6]$

	$[K(2.2.2\text{-cryptand})]_2[Sb_2Se_4]$ (**1**)	$[K(2.2.2\text{-cryptand})]_2[As_2S_4]\cdot 2CH_3CN$ (**2**)	$[K(2.2.2\text{-cryptand})]_2[As_{10}S_3]$ (**3**)	$[K(2.2.2\text{-cryptand})]_2[As_4Se_6]$ (**4**)
chem formula	$C_{36}H_{72}K_2N_4O_{12}Sb_2Se_4$	$C_{40}H_{78}As_2K_2N_6O_{12}S_4$	$C_{36}H_{72}As_{10}K_2N_4O_{12}S_3$	$C_{36}H_{72}As_4K_2N_4O_{12}Se_6$
fw	1390.52	1188.34	1676.56	1604.61
a, Å	22.668(5)[a]	11.154(1)	11.698(2)	12.749(4)
b, Å	14.647(3)	12.066(1)	13.058(3)	20.990(11)
c, Å	17.687(4)	20.922(4)	21.606(4)	22.742(7)
α, deg	90	92.38(1)	95.57(3)	74.89(3)
β, deg	116.37(3)	92.02(1)	93.96(3)	81.16(2)
γ, deg	90	96.45(1)	108.94(3)	87.88(3)
V, Å^3	5261(2)	2793(1)	3089(1)	5806(1)
λ, Å	0.7093	1.54056	1.54056	1.54056
space group	C_{2h}^6-C2/c	$C_i^1-P\bar{1}$	$C_i^1-P\bar{1}$	$C_i^1-P\bar{1}$
Z	4	2	2	4
D(calcd), g cm^{-3}	1.755	1.413	1.802	1.836
T, K	113(2)	113(2)	113(2)	113(2)
μ, cm^{-1}	40	47	56	87
transmissn factors	0.746−0.868	0.467−0.804	0.100−0.455	0.071−0.316
$R(F)$[b]	0.069	0.117	0.085	0.064
$R_w(F^2)$[c]	0.1346	0.2589	0.218	0.1540

[a] The cell parameters were obtained from a refinement constrained so that $\alpha = \gamma = 90°$. [b] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $F_o^2 > 2\sigma(F_o^2)$. [c] $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$; $w^{-1} = \sigma^2(F_o^2)$, $F_o^2 < 0$.

$Se_6]Cl$,[33] $Na_3AsSe_4\cdot 9H_2O$,[34] and $[PPh_4]_2[As_2Se_6]$.[35] Interestingly, most of these compounds were synthesized from similar starting materials. Different reaction conditions lead not only to the isolation of different products but also to different conformers. Here we report the synthesis, crystal structures, and spectroscopic data for $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_4]$ (**1**), $[K(2.2.2\text{-cryptand})]_2[As_2S_4]\cdot 2CH_3CN$ (**2**), $[K(2.2.2\text{-cryptand})]_2[As_{10}S_3]$ (**3**), and $[K(2.2.2\text{-cryptand})]_2[As_4Se_6]$ (**4**).

Experimental Section

All manipulations were carried out under a N_2 atmosphere with the use of standard Schlenk-line techniques. Anhydrous diethyl ether was purchased from Baxter Scientific Products Inc., McGaw Park, IL, and acetonitrile (anhydrous, 99.8% purity) was obtained from Aldrich Chemical Co., Milwaukee, WI. Both solvents were dried, distilled, and degassed before use. Sb (100 mesh, 99.5%) and Se (100 mesh, 99.5%) were purchased from Aldrich Chemical Co., As (100 mesh, 99%) was purchased from Strem Chemical Co., Newbury Port, MA, and S (99.6%) was obtained from Mallinckrodt Inc., Paris, KY. The NH_3 gas (anhydrous, 99.5%) was purchased from Linox, Hinsdale, IL. The remaining reagents were purchased from Aldrich Chemical Co. 2.2.2-Cryptand was recrystallized from acetonitrile.

The known phases Sb_2Se_3, As_4S_4, and As_4Se_4 were prepared by the fusion of stoichiometric amounts of the elements in fused-silica tubes under an inert argon atmosphere. Purity of the samples was confirmed by X-ray powder diffractometry. These materials were finely ground with a mortar and pestle before use. ^{77}Se NMR spectra were obtained with the use of a Varian 400 MHz Unity Plus spectrometer equipped with a 10-mm tunable broad-band probe, a variable-temperature apparatus, and a deuterium lock. All ^{77}Se chemical shifts are referenced to an external Ph_2Se_2 standard at δ 460 ppm, which in turn is referenced to $(CH_3)_2Se$ at δ 0 ppm. No attempt was made to isolate all product from a given reaction. Yields are raw values before any purification attempts.

Synthesis of $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_4]$ (1). NH_3 (60 mL) was condensed into a flask containing 2.2.2-cryptand (753 mg, 2.0 mmol) and K (80 mg, 2.0 mmol) at −195 °C. The resulting blue solution was stirred until all the K had dissolved (30 min). Upon the addition of finely ground Sb_2Se_3 (480 mg, 1.0 mmol), the solution became orange-red. After the solution was stirred at −78 °C for 6 h, it was warmed to 25 °C overnight. The solid residue that remained after the evaporation of the NH_3 was dissolved in CH_3CN (20 mL) to give an orange-red solution. The solution was filtered and then layered with diethyl ether (60 mL) to afford orange rectangular blocks after 5 days. Yield: 0.52 g, 37% based on Sb. ^{77}Se NMR (−30 °C, CH_3CN/CD_3CN): δ 337, 124 ppm (1:1 intensity). These same two peaks are the only ones observed from the initial solution and from the solution obtained from dissolution of the raw product.

Synthesis of $[K(2.2.2\text{-cryptand})]_2[As_2S_4]\cdot 2CH_3CN$ (2) and $[K(2.2.2\text{-cryptand})]_2[As_{10}S_3]$ (3). Compounds **2** and **3** were synthesized on a smaller scale than for **1** and with a slight excess of K. NH_3 (20 mL) was condensed into a flask containing 2.2.2-cryptand (189 mg, 0.5 mmol) and K (28 mg, 0.7 mmol) at −195 °C. Upon the addition of As_4S_4 (110 mg, 0.25 mmol), the solution changed from blue to yellow-brown; it was stirred at −78 °C for several hours. The evaporation of NH_3 left a rust-colored solid that was dissolved in CH_3CN (20 mL) and filtered. The solution was layered with diethyl ether (30 mL) to afford **3** as red needles together with a yellow powder. The filtrate, when layered with more ether (30 mL), yielded small yellow-orange plates of **2** after several days. Approximate yields: 15% for the red needles and 30% for the yellow-orange plates.

Synthesis of $[K(2.2.2\text{-cryptand})]_2[As_4Se_6]$ (4). NH_3 (30 mL) was condensed into a flask containing 2.2.2-cryptand (376 mg, 1.0 mmol) and K (42 mg, 1.0 mmol) at −195 °C. After the addition of As_4Se_4 (616 mg, 0.5 mmol), the solution changed from blue to yellow-brown. The solution was stirred at −78 °C for several hours. The evaporation of NH_3 left a rust-colored solid that was dissolved in CH_3CN (20 mL) and filtered. The solution was layered with diethyl ether (30 mL) to afford red-orange blocks. Yield: 336 mg, 42% based on As. ^{77}Se NMR (25 °C, DMF/CD_3CN): δ 564 and 317 ppm (3:1 intensity). Anal. Calcd for $C_{36}H_{72}As_4K_2N_4O_{12}Se_6$: C, 26.95; H, 4.52; N, 3.49. Found: C, 26.04; H, 3.96; N, 3.10.

Crystal Structure Determinations. Intensity data were collected at 113(2) K with Mo Kα radiation on a Picker diffractometer for **1** and with Cu Kα radiation on an Enraf-Nonius CAD4 diffractometer for **2**−**4**. The number of reflections used to obtain unit cell parameters and the 2θ ranges involved were as follows: **1**, 30, 20−34°; **2**, 25, 50−59°; **3**, 25, 50−60°; **4**, 25, 50−60°. In each study six standard reflections were monitored. These remained constant, except for the data collection for **2** where a 10% drop in intensities was observed. Those data were corrected for this decline. Continuous scan data were collected for **1** and processed in the standard way,[36] whereas profile data were collected for **2**−**4** and processed.[37] All

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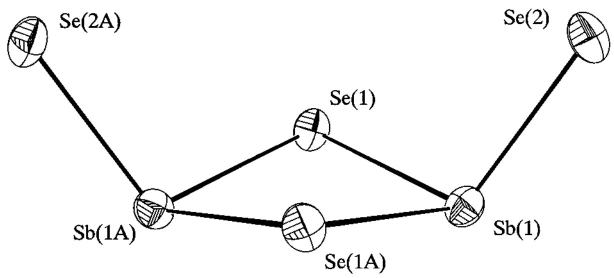

Figure 1. View of the anion in [K(2.2.2-cryptand)]$_2$[Sb$_2$Se$_4$]. Here and in Figures 3, 5, and 6 the 50% probability displacement ellipsoids are shown.

Table 2. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Anions

atom	*x*	*y*	*z*	$U_{eq}{}^a/U_{iso}$
[K(2.2.2-cryptand)]$_2$[Sb$_2$Se$_4$] (**1**)				
Sb(1)	−0.00013(4)	0.06325(5)	0.35350(5)	0.0228(2)
Se(1)	0.09091(5)	0.09197(7)	0.30352(7)	0.0236(3)
Se(2)	−0.00151(6)	0.20123(8)	0.43031(7)	0.0293(3)
[K(2.2.2-cryptand)]$_2$[As$_2$S$_4$]·2CH$_3$CN (**2**)				
As(1)	0.1091(3)	0.2131(2)	0.84215(13)	0.0428(9)
As(2)	−0.1575(3)	0.1083(2)	0.78506(13)	0.0421(9)
S(1)	0.2703(6)	0.2120(5)	0.7901(3)	0.049(2)
S(2)	0.0055(6)	0.0357(5)	0.8314(3)	0.042(2)
S(3)	−0.0352(6)	0.2727(5)	0.7726(3)	0.047(2)
S(4)	−0.1904(6)	0.0250(5)	0.6938(3)	0.055(2)
[K(2.2.2-cryptand)]$_2$[As$_{10}$S$_3$] (**3**)				
As(1)	1.2034(2)	0.5914(2)	0.19467(10)	0.0519(6)
As(2)	1.0056(2)	0.5881(2)	0.14796(9)	0.0554(6)
As(3)	0.9901(2)	0.7255(2)	0.22838(10)	0.0498(6)
As(4)	0.7236(2)	0.4837(2)	0.23415(10)	0.0473(6)
As(5)	0.8611(2)	0.4187(2)	0.17118(8)	0.0449(6)
As(6)	0.9837(2)	0.36206(14)	0.24842(8)	0.0369(5)
As(7)	0.8536(2)	0.3441(2)	0.33352(8)	0.0371(5)
As(8)	0.8295(2)	0.5244(2)	0.33819(9)	0.0417(5)
As(9)	1.0282(2)	0.6514(2)	0.32561(8)	0.0433(5)
As(10)	1.1386(2)	0.5271(2)	0.29396(9)	0.0436(5)
S(1)	1.2681(4)	0.7673(4)	0.2229(2)	0.0451(12)
S(2)	0.7825(5)	0.6602(4)	0.2152(2)	0.0481(13)
S(3)	0.6795(4)	0.2545(3)	0.2797(2)	0.0328(10)
[K(2.2.2-cryptand)]$_2$[As$_4$Se$_6$] (**4**)				
As(1)	1.18072(10)	0.68300(6)	1.13328(7)	0.0559(4)
As(2)	1.08977(12)	0.68109(7)	1.29208(8)	0.0673(5)
As(3)	1.22458(13)	0.58793(7)	1.28451(8)	0.0708(5)
As(4)	0.96002(13)	0.52516(7)	1.32591(7)	0.0653(4)
As(5)	0.50677(9)	0.95337(6)	0.73700(6)	0.0452(3)
As(6)	0.35747(9)	0.84725(7)	0.67581(6)	0.0464(3)
As(7)	0.45504(9)	0.77721(6)	0.76125(5)	0.0399(3)
As(8)	0.18577(9)	0.78538(7)	0.81555(7)	0.0570(4)
Se(1)	1.25875(12)	0.74367(7)	1.04012(8)	0.0817(5)
Se(2)	1.14370(12)	0.76046(7)	1.19863(9)	0.0746(5)
Se(3)	0.93549(11)	0.63883(7)	1.26904(7)	0.0634(4)
Se(4)	1.0187(2)	0.53504(8)	1.41254(7)	0.0845(5)
Se(5)	1.12080(12)	0.51022(7)	1.25859(6)	0.0639(4)
Se(6)	1.32753(11)	0.63338(7)	1.18756(9)	0.0757(5)
Se(7)	0.64248(10)	1.02674(7)	0.71183(7)	0.0656(4)
Se(8)	0.46363(10)	0.94411(7)	0.63859(6)	0.0614(4)
Se(9)	0.21346(10)	0.88774(7)	0.73536(7)	0.0566(4)
Se(10)	0.22501(10)	0.70876(7)	0.76003(7)	0.0624(4)
Se(11)	0.35207(10)	0.79298(7)	0.85221(6)	0.0573(4)
Se(12)	0.59925(8)	0.84834(6)	0.75341(6)	0.0459(3)

[a] $U_{eq} = \sum_i \sum_j (U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j)$.

data sets were corrected for absorption by means of the analytical method.[38]

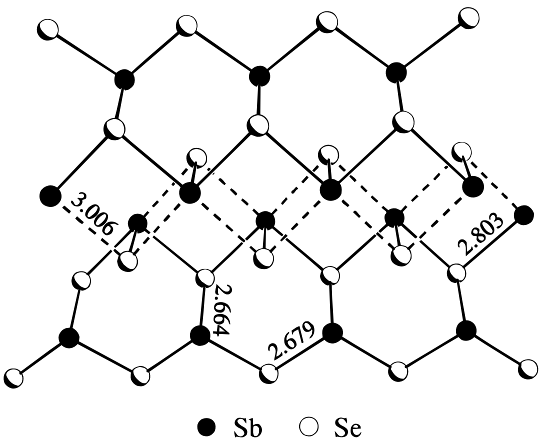

Figure 2. View of the structure of Sb$_2$Se$_3$ from ref 41.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [K(2.2.2-cryptand)]$_2$[Sb$_2$Se$_4$] (**1**) and the *cis*-[Sb$_2$Se$_4$]$^{2-}$ Unit in Ba$_4$Sb$_4$Se$_{11}$[a]

	[K(2.2.2- cryptand)]$_2$-[Sb$_2$Se$_4$]	Ba$_4$Sb$_4$Se$_{11}$
Sb(1)−Se(2)	2.443(1)	2.540(1)
Sb(1)−Se(1)	2.615(1)	2.778(1)
Sb(1)−Se(1)#1[b]	2.655(2)	2.778(1)
Sb(1)1−Se(2)#1	2.443(1)	2.584(1)
Se(1)−Sb(1)#1	2.655(2)	2.588(1)
Se(2)−Sb(1)−Se(1)	105.18(5)	92.7
Se(2)−Sb(1)−Se(1)#1	104.78(4)	92.7
Se(1)−Sb(1)−Se(1)#1	88.99(4)	85.7
Sb(1)−Se(1)−Sb(1)#1	88.09(4)	89.6
Se(1)−Sb(1)#1−Se(2)#1	105.18(5)	97.1
Se(1)−Sb(1)#1−Se(1)#1	88.99(4)	94.3

[a] Reference 42. For clarity and ease of comparison atoms Sb(2), Sb(3), Se(2), Se(2a), Se(4), and Se(8) in Ba$_4$Sb$_4$Se$_{11}$ have been changed to Sb(1), Sb(1)#1, Se(1), Se(1)#1, Se(2)#1, and Se(2). [b] Symmetry transformation used to generate equivalent atoms: #1, $-x$, y, $-z + {}^1/_2$.

Space groups were determined from systematic absences and agreement among Friedel pairs. The structures were solved from direct methods with the use of the program SHELXS,[39] and they were refined by full-matrix least-squares methods with the program SHELXL-93.[40] Methylene hydrogen atoms were assigned to calculated positions and refined according to a riding model. Torsional angles were then refined as additional least-squares parameters. Methyl hydrogen atoms were placed at positions of maximum residual electron density with the constraints of normal tetrahedral angles and C−H distances. The structures were fully ordered, except for one of the four independent cations in compound **4**. This cation exhibits disorder along two of the N(C$_2$H$_4$O)$_2$C$_2$H$_4$N chains. Most of the atoms in the chains were disordered over two positions. The occupancies of the two positions for a given atom were constrained to be unity.

Crystallographic details are given in Tables 1 and S1 (Supporting Information). Final atomic coordinates and equivalent isotropic displacement parameters for the anions are given in Table 2. Other tabulations may be found in the Supporting Information.

Results and Discussion

[K(2.2.2-cryptand)]$_2$[Sb$_2$Se$_4$] consists of well-separated cations and anions. The [Sb$_2$Se$_4$]$^{2-}$ anion (Figure 1), which has crystallographically imposed symmetry 2, features two edge-sharing SbSe$_3$ pyramidal units. It can also be described as an Sb$_2$Se$_4$ four-membered ring with the terminal Se atoms cis to each other. The Sb−Se$_b$ distances are 2.615(1) and 2.655(2)

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(37) Blessing, R. H. *Crystallogr. Rev.* **1987**, *1*, 3−58.

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(39) Sheldrick, G. M. SHELXTL PC Version 4.1: An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990.

(40) Sheldrick, G. M. *J. Appl. Crystallogr.*, in press.

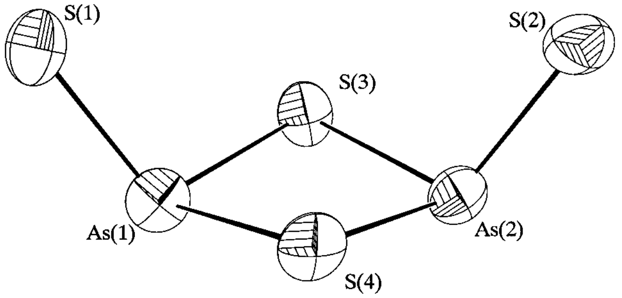

Figure 3. View of the anion in $[K(2.2.2\text{-cryptand})]_2[As_2S_4]\cdot 2CH_3CN$.

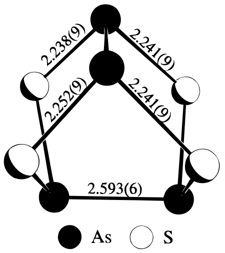

Figure 4. View of the structure of As_4S_4 from ref 50.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $K(2.2.2\text{-cryptand})]_2[As_2S_4]\cdot 2CH_3CN$ (**2**) and $Ba_2As_2S_5$

	$[K(2.2.2\text{-cryptand})]_2$-$[As_2S_4]\cdot 2CH_3CN$	$Ba_2As_2S_5$[a]
As(1)−S(1)	2.136(7)	2.227(8)
As(1)−S(2)	2.314(6)	2.483(8)
As(1)−As(3)	2.325(7)	2.359(8)
As(2)−S(2)	2.306(7)	2.335(8)
As(2)−S(3)	2.308(6)	2.362(8)
As(2)−S(4)	2.120(7)	2.260(8)
S(1)−As(1)−S(2)	107.7(2)	103.8(3)
S(1)−As(1)−S(3)	106.4(3)	107.6(3)
S(2)−As(1)−S(3)	88.3(2)	85.3(3)
S(2)−As(2)−S(3)	88.9(2)	88.7(3)
S(4)−As(2)−S(2)	106.2(3)	99.4(3)
S(4)−As(2)−S(3)	108.2(3)	100.4(3)
As(1)−S(2)−As(2)	89.9(2)	91.6(3)
As(1)−S(3)−As(3)	89.6(2)	94.1(3)

[a] Reference 51. For the sake of comparison, S(8), S(9), and S(10) have been changed to S(3), S(2), and S(1), respectively.

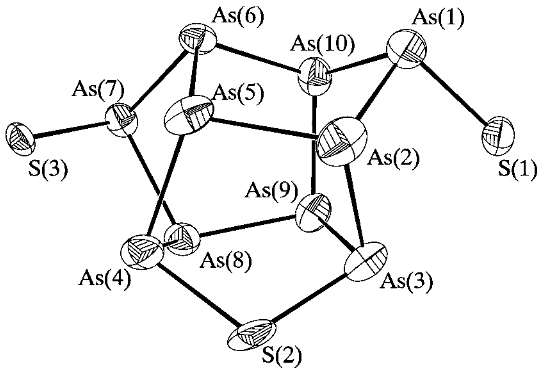

Figure 5. View of the anion in $[K(2.2.2\text{-cryptand})]_2[As_{10}S_3]$.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[K(2.2.2\text{-cryptand})]_2[As_{10}S_3]$ (**3**), $[PPh_4]_2[As_{10}Se_3]$,[a] $[PPh_4]_2[As_{10}Te_3]$,[b] and $[K(2.2.2\text{-cryptand})]_3[As_{11}]$[c]

	$[As_{10}S_3]^{2-}$	$[As_{10}Se_3]^{2-}$	$[As_{10}Te_3]^{2-}$	$[As_{11}]^{3-}$
As(1)−Q(1)	2.181(5)	2.326(8)	2.550(5)	
As(1)−As(2)	2.445(3)	2.456(4)	2.438(6)	2.369(9)
As(1)−As(10)	2.458(3)	2.468(4)	2.431(6)	2.369(7)
As(2)−As(5)	2.430(3)	2.444(6)	2.440(6)	2.452(7)
As(2)−As(3)	2.433(3)	2.439(5)	2.423(6)	2.440(7)
As(3)−Q(2)	2.284(6)	2.390(6)	2.611(4)	2.377(8)
As(3)−As(9)	2.469(3)	2.464(6)	2.457(6)	2.440(7)
As(4)−Q(2)	2.268(5)	2.414(4)	2.605(5)	2.385(7)
As(4)−As(8)	2.414(3)	2.433(4)	2.423(6)	2.424(7)
As(4)−As(5)	2.474(3)	2.476(5)	2.461(6)	2.437(8)
As(5)−As(6)	2.447(3)	2.449(5)	2.469(6)	2.474(7)
As(6)−As(10)	2.388(3)	2.414(7)	2.405(6)	2.436(7)
As(6)−As(7)	2.448(3)	2.441(5)	2.432(6)	2.406(7)
As(7)−Q(3)	2.175(4)	2.333(4)	2.534(5)	
As(7)−As(8)	2.453(3)	2.446(4)	2.423(6)	2.357(7)
As(8)−As(9)	2.429(3)	2.452(4)	2.451(6)	2.481(7)
As(9)−As(10)	2.456(3)	2.459(4)	2.465(6)	2.435(8)
Q(1)−As(1)−As(2)	93.8(2)	95.8(2)	95.7(2)	
Q(1)−As(1)−As(10)	100.0(2)	102.1(2)	102.0(2)	
As(2)−As(1)−As(10)	97.6(1)	96.6(2)	97.2(2)	96.4(3)
As(5)−As(2)−As(3)	104.1(1)	105.1(2)	107.6(2)	100.5(2)
As(5)−As(2)−As(1)	105.3(1)	103.0(2)	100.8(2)	105.3(3)
As(3)−As(2)−As(1)	93.7(1)	96.3(2)	97.1(2)	99.5(3)
Q(2)−As(3)−As(2)	92.7(2)	93.1(2)	92.2(2)	98.2(3)
Q(2)−As(3)−As(9)	100.1(2)	101.3(2)	100.7(2)	105.5(2)
As(2)−As(3)−As(9)	102.3(1)	102.0(2)	101.0(2)	100.2(3)
Q(2)−As(4)−As(8)	94.7(2)	93.1(2)	92.7(2)	100.3(3)
Q(2)−As(4)−As(5)	99.5(2)	100.4(2)	100.7(2)	103.8(2)
As(8)−As(4)−As(5)	102.9(1)	101.9(2)	101.3(2)	100.4(3)
As(2)−As(5)−As(6)	101.8(1)	103.2(2)	103.4(2)	102.8(3)
As(2)−As(5)−As(4)	102.5(1)	103.2(2)	104.9(2)	103.7(2)
As(6)−As(5)−As(4)	103.7(1)	103.5(2)	103.0(2)	104.0(2)
As(10)−As(6)−As(7)	97.3(1)	95.5(2)	94.1(2)	101.5(3)
As(10)−As(6)−As(5)	104.8(1)	103.4(2)	102.4(2)	99.8(2)
As(7)−As(6)−As(5)	99.3(1)	102.2(2)	103.7(2)	102.5(3)
Q(3)−As(7)−As(6)	98.9(1)	101.5(2)	102.5(2)	
Q(3)−As(7)−As(8)	96.2(1)	93.2(2)	94.4(2)	
As(6)−As(7)−As(8)	98.0(1)	98.0(2)	98.2(2)	96.8(2)
As(4)−As(8)−As(9)	103.8(1)	105.4(2)	106.9(2)	100.4(2)
As(4)−As(8)−As(7)	92.5(1)	94.7(2)	96.6(2)	99.4(3)
As(9)−As(8)−As(7)	105.8(1)	103.5(2)	101.2(2)	105.3(3)
As(8)−As(9)−As(10)	101.9(1)	102.1(2)	102.7(2)	104.1(2)
As(8)−As(9)−As(3)	102.9(1)	102.8(2)	105.3(2)	103.2(2)
As(10)−As(9)−As(3)	103.9(1)	103.7(2)	103.2(2)	103.1(2)
As(6)−As(10)−As(9)	104.6(1)	104.4(2)	103.5(2)	100.4(3)
As(6)−As(10)−As(1)	96.2(1)	95.5(2)	94.3(2)	100.0(3)
As(9)−As(10)−As(1)	100.3(1)	102.9(2)	104.2(2)	105.4(3)
As(4)−Q(2)−As(3)	107.3(2)	103.3(2)	97.9(2)	97.3(3)

[a] References 57 and 58. Atoms As(1), As(2), As(3), As(4), As(5), As(6), As(7), As(8), As(9), As(10), Se(1), Se(2), and Se(3) have been changed to As(9), As(6), As(5), As(3), As(7), As(8), As(10), As(4), As(1), As(2), Q(3), Q(1), and Q(2), respectively, for ease of comparison. [b] Reference 56. Atoms As(1), As(2), As(3), As(5), As(6), As(7), As(8), As(9), As(10), Te(1), and Te(2) have been changed to As(3), As(9), As(8), As(2), As(5), As(1), As(10), As(6), As(7), Q(2), and Q(1), respectively. [c] Reference 8. Atoms As(1), As(2), As(4), As(6), As(7), As(8), As(9), As(10), and As(11) have been changed to As(9), As(10), As(8), As(2), As(4), As(6), As(1), As(7), and Q(2), respectively.

Å, and the Sb−Se$_t$ distances are 2.443(1) Å. Although Sb_2Se_3[41] has an extended structure (Figure 2), the Sb_2Se_4 fragment exists within the framework with bridging Sb−Se distances of 3.006 and 2.803 Å and an Sb−Se$_t$ distance of 2.589 Å (no errors reported). The isolated $[Sb_2Se_4]^{2-}$ anion could be formed conceptually from Sb_2Se_3 by the breaking of four Sb−Se bonds and the re-forming of one such bond. Interestingly, the electrochemical reduction of Sb_2Se_3 yields $[PPh_4]_2[Sb_4Se_6]$;[6] it has an Sb−Se$_t$ distance of 2.46(7) Å and an Sb−Se$_b$ distance of 2.58(1) Å.

With the exception of the $[As_2S_4]^{2-}$ anion discussed below, there apparently are no reported group 15 sulfur or tellurium analogues of the $[Sb_2Se_4]^{2-}$ anion. The cis $[Sb_2Se_4]^{2-}$ unit does occur in the solid-state compound $Ba_4Sb_4Se_{11}$[42] along with a trans unit and a trigonal $SbSe_3$ pyramid. The distances and angles for the anion in $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_4]$ differ from those in the similar *cis*-$[Sb_2Se_4]^{2-}$ unit of $Ba_4Sb_4Se_{11}$ (Table

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(41) Voutsas, G. P.; Papazoglou, A. G.; Rentzeperis, P. J.; Siapkas, D. *Z. Kristallogr.* **1985**, *171*, 261−268.

Table 6. Average Bond Distances (Å) and Angles (deg) for Several Sulfidoarsenates

	[K(2.2.2-cryptand)]$_2$-[As_2S_4]·2CH_2CN (**2**)	$PbAs_2S_4$[a]	[PPh_4]$_2$[As_2S_6][b]	[enH_2]$_3$[As_3S_6]$_2$•en[c]	[pip]$_2$[As_4S_6][d]	[K(2.2.2-cryptand)]$_2$-[$As_{10}S_3$] (**3**)
As−S_t	2.128(7)	2.25(2)	2.122(3)	2.16(1)	2.183(9)	2.178(6)
As−S_b	2.323(7)	2.59(2)	2.305(3)	2.29(2)	2.266(9)	2.284(6)
S_b−As−S_t	107.9(4)	108.1(5)	100.8(2)	100.1(5)	99.6(3)	
S_b−As−S_b	88.6(3)	92.3(4)	98.3(2)	99.5(4)	99.1(2)	

[a] Reference 53. [b] Reference 29. [c] Reference 30. [d] Reference 31.

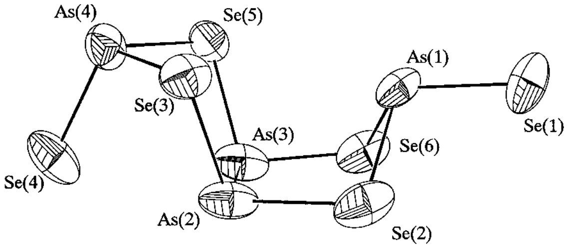

Figure 6. View of one of the anions in [K(2.2.2-cryptand)]$_2$[As_4Se_6].

Table 7. Selected Bond Distances (Å) and Angles (deg) for the Two Independent Anions in [K(2.2.2-cryptand)]$_2$[As_4Se_6] (**4**) and the Anion in [PPh_4]$_2$[As_4Se_6]

	anion 1[a]	anion 2[b]	[PPh_4]$_2$[As_4Se_6][c]
As(1)−Se(1)	2.267(2)	2.264(2)	2.265(2)
As(1)−Se(2)	2.462(2)	2.430(2)	2.466(2)
As(1)−Se(6)	2.451(2)	2.442(2)	2.443(2)
As(2)−Se(2)	2.357(3)	2.367(2)	2.341(2)
As(2)−Se(3)	2.370(2)	2.367(2)	2.333(2)
As(2)−As(3)	2.577(2)	2.570(2)	2.561(2)
As(3)−Se(5)	2.379(2)	2.377(2)	2.347(2)
As(3)−Se(6)	2.367(3)	2.374(2)	2.359(2)
As(4)−Se(3)	2.434(2)	2.419(2)	2.406(2)
As(4)−Se(4)	2.272(2)	2.288(2)	2.279(2)
As(4)−Se(5)	2.425(2)	2.425(2)	2.425(2)
Se(1)−As(1)−Se(2)	105.95(9)	102.26(7)	104.9(1)
Se(1)−As(1)−Se(6)	105.30(8)	104.99(7)	102.0(1)
Se(2)−As(1)−Se(6)	91.45(7)	91.82(7)	90.8(1)
Se(2)−As(2)−Se(3)	100.41(8)	99.53(7)	106.9(1)
Se(2)−As(2)−As(3)	101.63(9)	99.97(7)	102.4(1)
Se(3)−As(2)−As(3)	101.80(8)	102.97(7)	102.0(1)
Se(5)−As(3)−Se(6)	100.22(8)	99.67(8)	107.6(1)
Se(5)−As(3)−As(2)	101.87(8)	100.77(7)	101.6(1)
Se(6)−As(3)−As(2)	101.34(8)	102.63(6)	100.5(1)
Se(4)−As(4)−Se(3)	101.52(8)	101.68(7)	103.0(1)
Se(4)−As(4)−Se(5)	104.08(9)	101.52(8)	101.2(1)
Se(3)−As(4)−Se(5)	93.93(8)	94.08(7)	93.6(1)
As(1)−Se(2)−As(2)	96.99(8)	99.55(7)	100.8(1)
As(2)−Se(3)−As(4)	95.95(7)	93.24(7)	104.1(1)
As(3)−Se(5)−As(4)	95.79(8)	94.82(7)	104.5(1)
As(1)−Se(6)−As(3)	97.16(8)	98.27(7)	100.9(1)

[a] Anion 1 refers to atoms As(1)−As(4) and Se(1)−Se(6) in [K(2.2.2-cryptand)]$_2$[As_4Se_6]. [b] Anion 2 refers to atoms As(5)−As(8) and Se(7)−Se(12). The atom names have been changed to facilitate comparison. As(5), As(6), As(7), and As(8) become As(1), As(3), As(2), and As(4), respectively. Se(7), Se(8), Se(9), Se(10), Se(11), and Se(12) become Se(1), Se(6), Se(5), Se(4), Se(3), and Se(2), respectively. [c] Reference 35. Here Se(3), Se(4), and Se(6) are now Se(6), Se(3), and Se(4), respectively.

3), probably because the Ba^{2+} cation is coordinated to Se atoms. Several compounds with similar formulas but different structures have been isolated by solid-state techniques. $SnSb_2Se_4$,[43] as determined by high-resolution electron microscopy, has an extended structure built from ribbons of edge-sharing MSe_5 square pyramids (M = randomly distributed Sn and Sb atoms). In $BaSb_2Se_4$[44] one Sb atom is in a tetrahedral environment, whereas the other is in a trigonal-bipyramidal environment. The Sb−Se_b bond lengths range from 2.61(8) Å in the tetrahedron to 2.85(15) Å in the trigonal bipyramid. $CsSb_2Se_4$[45] has a structure similar to $BaSb_2Se_4$. Other antimony selenides synthesized by solid-state techniques include [Ba(en)$_4$][$SbSe_2$]$_2$ (en = ethylenediamine),[46] Cu_3SbSe_3 and Tl_3SbSe_3,[27,47] [Ba(en)$_2$]$_3$[$SbSe_3$]$_2$,[48] M_3SbSe_4 (M = Na, K, Cu),[26,49] [Ba(en)$_4$]$_2$-[Ba(en)$_3$][$SbSe_4$]$_2$,[49] $RbSb_3Se_5$,[11] and $Cs_3Sb_5Se_9$.[24] The majority of these compounds consist of isolated cations and anions with average Sb−Se_t distances of 2.4 Å and average Sb−Se_b distances of 2.6 Å. In almost every instance the Sb atom is in a pyramidal environment.

The ^{77}Se NMR spectrum of [K(2.2.2-cryptand)]$_2$[Sb_2Se_4] has resonances at δ 124 and 337 ppm. Thus, there are two distinct Se environments, as there are in the solid state. Although Sb has two spin-active nuclei (^{121}Sb, spin $^5/_2$, 57% abundance; ^{123}Sb, spin $^7/_2$, 43% abundance), we observed no J_{Sb-Se} coupling even at low temperatures and hence we cannot assign these resonances to Se_t and Se_b.

The anion of [K(2.2.2-cryptand)]$_2$[As_2S_4]•2CH_3CN (Figure 3) has a structure similar to **1**, with two edge-sharing AsS_3 trigonal pyramids having terminal S atoms cis to one another. The As−S_t bond distances are 2.136(7) and 2.120(7) Å, slightly shorter than a normal As−S bond distance of 2.243(5) Å as seen in As_4S_4,[50] and hence are indicative of some multiple-bond character. The As−S_b bonds range from 2.306(7) to 2.325(7) Å. The S_b−As−S_b bond angles are 88.3(2) and 88.9(2)°, while the S_t−As−S_b angles range from 106.2(3) to 108.2(3)°. The compound could conceptually be formed from As_4S_4 (Figure 4)[50] by the cleavage of both As−As bonds and two As−S bonds followed by the formation of three As−S bonds. The [As_2Q_4]$^{2-}$ (Q = S, Se) structural unit has precedence in the solid-state compounds $Ba_2As_2S_5$[51] and $Ba_2As_2Se_5$.[52] Both compounds contain two isolated AsQ_3 pyramids and an As_2Q_4 four-membered ring with the terminal chalcogen atoms trans to each other. In $Ba_2As_2Se_5$ one of the ring-bound As atoms is coordinated to the $AsSe_3$ pyramids through long As−As interactions of 2.848(8) and 3.014(8) Å. A normal As−As bond length of 2.57(1) Å is seen in **4**. Bond distances for [K(2.2.2-cryptand)]$_2$[As_2S_4]•2CH_3CN (**2**) are compared with those for

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(42) Cordier, G.; Cook, R.; Schäfer, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 324−325.

(43) Smith, P. P. K.; Parise, J. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1985**, *41*, 84−87.

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(46) König, T.; Eisenmann, B.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1982**, *488*, 126−132.

(47) Olsen, A.; Goodman, P.; Whitfield, H. J. *J. Solid State Chem.* **1985**, *60*, 305−315.

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(49) Eisenmann, B.; Zagler, R. *Z. Naturforsch., B: Chem. Sci.* **1989**, *44*, 249−256.

(50) Porter, E. J.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1972**, 1347−1349.

(51) Cordier, G.; Schwidetzky, C.; Schäfer, H. *Rev. Chim. Miner.* **1983**, *20*, 877−883.

(52) Cordier, G.; Schwidetzky, C.; Schafer, H. *Rev. Chim. Miner.* **1985**, *22*, 93−100.

$Ba_2As_2S_5$ in Table 4. The structures of $PbAs_2S_4$,[53] $Tl_2As_2S_4$,[54] and $SrAs_2S_4$[55] possess chains of corner-sharing AsS_3 pyramids very different from the edge-sharing AsS_3 trigonal pyramids observed in **2**.

The $[As_{10}S_3]^{2-}$ anion (Figure 5) in $[K(2.2.2\text{-cryptand})]_2[As_{10}S_3]$ (**3**) has the same structure as the anions in $[PPh_4]_2[As_{10}Te_3]$[56] and $[PPh_4]_2[As_{10}Se_3]$.[57] It is based on the $[As_{11}]^{3-}$ [8] anion, where one of the waist As atoms is replaced by the atom S(2) and the other As atoms in the waist are coordinated by the exocyclic atoms S(1) and S(3). Comparison of the As−As bond angles for $[As_{10}Q_3]^{2-}$ and $[As_{11}]^{3-}$ are presented in Table 5. Once again, the $As-S_b$ bond distances are longer than the $As-S_t$ bond distances.

A number of other sulfidoarsenates have been synthesized through nontraditional techniques. Included among these compounds are $[PPh_4]_2[As_2S_6]$,[29] $[pip]_2[As_4S_6]$ (pip = piperidine),[31] and $[enH_2]_3[As_3S_6]\cdot 6en$.[30] Average bond distances and angles in the anions in these compounds are compared with those in $[K(2.2.2\text{-cryptand})]_2[As_2S_4]\cdot 2CH_3CN$ (**2**) and $[K(2.2.2\text{-cryptand})]_2[As_{10}S_3]$ (**3**) in Table 6. Note that despite the number of similar starting materials used in previous syntheses of such sulfidoarsenates it is only with the present synthetic route that compounds **2** and **3** have been isolated.

It is striking that the use of As_4Se_4 as a starting material affords a wide variety of different selenoarsenates. The present compound $[K(2.2.2\text{-cryptand})]_2[As_4Se_6]$ (**4**) was synthesized from the reaction of As_4Se_4 with 3 equiv K in NH_3(l) in the presence of 2.2.2-cryptand. Reaction of As_4Se_4 with K_2Se_3 in the presence of PPh_4^+ in DMF yields $[PPh_4]_2[As_2Se_6]$.[35] $[Na(2.2.2\text{-cryptand})]_2[As_2Se_6]$[9] can be synthesized by dissolving $NaAs_2Se_3$ (made by fusing As_4Se_4 with Se and Na at 700 °C) in en in the presence of 2.2.2-cryptand. Reaction of As_4Se_4 with 8 equiv of K in en leads to the isolation of $[PPh_4]_2[As_{10}Se_3]$.[57] In a similar reaction (although details are lacking) the reaction of As_4Se_4 with K in en in the presence of PPh_4Br affords $[PPh_4]_2[As_7Se_4]$.[32] $[PPh_4]_2[As_4Se_6]$[35] has been synthesized in two different ways, starting with As_4Se_4: dissolution of As_4Se_4 in en in the presence of PPh_4Br and also reduction of As_4Se_4 with 2 equiv of K in DMF.

The crystal structure of $[K(2.2.2\text{-cryptand})]_2[As_4Se_6]$ (**4**) contains four crystallographically independent cations and two crystallographically independent anions. The anions are very similar in structure, and one is shown in Figure 6. It could be considered a basket having one of the arms turned downward in a trans fashion. On the other hand, $[PPh_4]_2[As_4Se_6]$ has a basket structure with two terminal $As-Se_t$ bonds acting as the handle in a cis fashion. The bond distances and angles for the anions in these two compounds are similar (Table 7), but the ^{77}Se NMR data are not. Resonances at 564 and 317 ppm (25 °C, DMF/CD_3CN, 3:1 intensity) are observed for the $K(2.2.2\text{-cryptand})^+$ salt, whereas resonances at 465 and 180 ppm (25 °C, DMF) are observed for the PPh_4^+ salt. No As−Se coupling is observed in either case. There is no evidence from the ^{77}Se NMR data for a conformational change in the anion of **4** between 120 and −70 °C.

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Supporting Information Available: Tables giving structure determination summaries, positional coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond distances and angles, and hydrogen atom coordinates and displacement parameters for compounds **1**−**4** (47 pages). Ordering information is given on any current masthead page.

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