Inorg. Chem. **1996,** *35,* 4559−4562

Synthesis and Characterization of Two Group 15 Selenometalates: [NEt$_4$][BiSe$_2$] and [Ge(en)$_3$][enH][SbSe$_4$]

Michael A. Pell and James A. Ibers*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received February 22, 1996⊗

[NEt$_4$][BiSe$_2$] has been synthesized from the electrochemical reduction of “BiSnSe$_4$”, a microcrystalline mixture of Bi$_2$SnSe$_4$, SnSe$_2$, and Se, in an electrolyte solution of NEt$_4$Br in ethylenediamine. [Ge(en)$_3$][enH][SbSe$_4$] has been prepared from the dissolution in ethylenediamine of “GeSbSe$_4$”, a microcrystalline mixture of Sb$_2$Se$_3$, GeSe$_2$, and Se. The structures of both compounds have been determined by single-crystal X-ray methods. [NEt$_4$][BiSe$_2$] crystallizes in the rhombohedral space group C_{3v}^{6}-$R3c$ with six formula units in a cell of dimensions $a = 19.19(1)$ Å, $\alpha = 118.375(2)^\circ$, and $V = 2320(2)$ Å^3 ($T = 115$ K). Final agreement indices for [NEt$_4$][BiSe$_2$] are 0.113 for $R_w(F_o^2)$ for all 980 data and 0.054 for R_1 for the 787 reflections with $F_o^2 \geq 2\sigma(F_o^2)$ (65 variables). [Ge(en)$_3$][enH][SbSe$_4$] crystallizes in the triclinic space group C_i^1-$P\bar{1}$ with two formula units in a cell of dimensions $a = 8.82(2)$ Å, $b = 9.60(2)$ Å, $c = 14.20(3)$ Å, $\alpha = 104.84(7)^\circ$, $\beta = 92.66(7)^\circ$, $\gamma = 109.44(7)^\circ$, and $V = 1085.2(4)$ Å^3 ($T = 115$ K). Final agreement indices for [Ge(en)$_3$][enH][SbSe$_4$] are 0.241 for $R_w(F_o^2)$ for all 870 data and 0.101 for R_1 for the 393 reflections with $F_o^2 \geq 2\sigma(F_o^2)$ (90 variables). [NEt$_4$][BiSe$_2$] is the first example of a compound that contains a selenobismuthate; its structure features a one-dimensional [BiSe$_2^-$]$_n$ chain of apex-sharing [BiSe$_3^{3-}$] trigonal-pyramidal units. The structure of [Ge(en)$_3$][enH][SbSe$_4$] contains a tetrahedral [SbSe$_4$]$^{3-}$ anion (Sb^{V}) and a [Ge(en)$_3$]$^{2+}$ cation (Ge^{II}) as the $\Delta\lambda\lambda\delta$ conformer (and its enantiomer).

Introduction

Whereas the chemistry of the chalcogenides of the lighter group 15 elements is well developed,[1−11] that of Bi, the heaviest member, remains largely unknown. In fact, no selenobismuthates (selenobismuthate = [Bi$_x$Se$_y$]$^{z-}$) have been reported. The dearth of sulfidobismuthates is also apparent, as the sole known example is found in the remarkable compound [AsPh$_4$][Bi$_2$S$_{34}$].[12] We recently synthesized the group 14 anions [Sn$_4$Se$_{10}$]$^{4-}$ and [Ge$_2$Se$_6$]$^{4-}$ by means of electrochemical reduction of binary selenides.[13] Encouraged by the success of the cathodic dissolution technique for the synthesis of chalcogenometalates of the main-group elements,[14,15] we have begun the investigation of group 15 ternary systems. Here we report the synthesis of [NEt$_4$][BiSe$_2$] by means of the cathodic dissolution of “BiSnSe$_4$”, a microcrystalline mixture of Bi$_2$SnSe$_4$, SnSe$_2$, and Se. We have discovered several solid-state main-group selenides that are soluble in ethylenediamine (en) and hence unsuitable for a cathodic dissolution experiment in that solvent. Here we report the synthesis of [Ge(en)$_3$][enH][SbSe$_4$] through extraction in en of “GeSbSe$_4$”, a microcrystalline mixture of Sb$_2$Se$_3$, GeSe$_2$, and Se.

Experimental Section

Syntheses and NMR Measurements. Ethylenediamine (Aldrich, 99%) was distilled twice from CaH$_2$ before use. Other solvents were distilled and degassed prior to use. All manipulations were carried out under an N$_2$ atmosphere with the use of standard Schlenk techniques. NEt$_4$Br was recrystallized from acetonitrile.

^{77}Se NMR spectra were recorded on a Varian 400 MHz Unity Plus spectrometer equipped with a 10 mm tunable broad-band probe and a deuterium lock. Chemical shifts are referenced to the secondary external standard Ph$_2$Se$_2$ at $\delta = 460$ ppm. The chemical shift scale is based on (CH$_3$)$_2$Se at $\delta = 0$ ppm.

Preparation of [NEt$_4$][BiSe$_2$]. [NEt$_4$][BiSe$_2$], which is extremely air- and moisture sensitive, was synthesized from the cathodic dissolution of a compound of nominal composition BiSnSe$_4$ by the technique developed by Warren et al.[14,15] The cathode was fabricated by melting stoichiometric amounts of Bi (Johnson Matthey, 99.9996%), Sn (Johnson Matthey, 99.5%), and Se (Aldrich, 99.5%) in a fused silica tube under an Ar atmosphere with the use of an H$_2$/O$_2$ flame. BiSnSe$_4$ is a microcrystalline mixture of Bi$_2$SnSe$_4$, SnSe$_2$, and Se.[16,17] Cu wire was silver soldered to the cylindrical melt before the entire assembly was inserted into a fused silica jacket and fastened with epoxy. Ni wire (Aldrich, 99%) was used for the sacrificial anode. The electrochemical reduction was carried out in a solution of en saturated with NEt$_4$Br electrolyte. The current was held constant at 300 μA with the

---

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1996.

(1) O’Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1992**, *31*, 888−894.

(2) Eisenmann, B.; Zagler, R. *Z. Naturforsch., B: Chem. Sci.* **1987**, *42*, 1079−1082.

(3) Sheldrick, W. S.; Kaub, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40*, 1020−1022.

(4) O’Neal, S. C.; Pennington, W. T.; Kolis, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 710−712.

(5) Ansari, M. A.; Ibers, J. A.; O’Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Polyhedron* **1992**, *11*, 1877−1881.

(6) Haushalter, R. C. *J. Chem. Soc., Chem. Commun.* **1987**, 196−197.

(7) Warren, C. J.; Haushalter, R. C.; Bocarsly, A. B. *Chem. Mater.* **1994**, *6*, 780−783.

(8) Belin, C. H. E. *J. Am. Chem. Soc.* **1980**, *102*, 6036−6040.

(9) Warren, C. J.; Ho, D. M.; Haushalter, R. C.; Bocarsly, A. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1646−1648.

(10) Konno, T.; Yonenobu, K.; Hidaka, J.; Okamoto, K. *Inorg. Chem.* **1994**, *33*, 861−864.

(11) Tan, K.; Ko, Y.; Parise, J. B. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1994**, *50*, 1439−1442.

(12) Müller, A.; Zimmermann, M.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 273.

(13) Park, C.; Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, in press.

(14) Warren, C. J.; Ho, D. M.; Bocarsly, A. B.; Haushalter, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 6416−6417.

(15) Warren, C. J.; Haushalter, R. C.; Bocarsly, A. B. *J. Alloys Compd.* **1995**, *229*, 175−205.

(16) Hirai, T.; Takeda, Y.; Kurata, K. *J. Less-Common Met.* **1967**, *13*, 352−356.

(17) Sher, A. A.; Odin, I. N.; Novoselova, A. V. *Russ. J. Inorg. Chem.* **1986**, *31*, 575−579.

S0020-1669(96)00181-4 CCC: $12.00

voltage varying to a maximum of 5 V. Black needles were observed in the cathodic chamber after 4 days. No evidence for the incorporation of Sn was gathered from energy dispersive X-ray analysis (EDX) measurements on single crystals isolated from the electrochemical cell. Attempts to synthesize [NEt$_4$][BiSe$_2$] in a stoichiometric fashion from BiSe$_2$ resulted in the formation of a different selenobismuthate.[18]

Preparation of [Ge(en)$_3$][enH][SbSe$_4$]. A cathode of nominal composition GeSbSe$_4$ was obtained by melting of the constituent powders Ge (Johnson Matthey, 99.999%), Sb (Johnson Matthey, 99.5%), and Se, and the electrochemical cell was set up in the same fashion as described above. GeSbSe$_4$ is a microcrystalline mixture of Sb$_2$Se$_3$, GeSe$_2$, and Se.[19] When it was realized that the cathode was dissolving in the en solution, the cathodic dissolution experiment was aborted and GeSbSe$_4$ was ground into a powder. The powder was dissolved in fresh en, and the solution was sonicated overnight. The solution was then filtered and layered with diethyl ether. Very small orange-yellow needles crystallized after 7 days. EDX measurements confirmed the presence of Ge, Sb, and Se in a 1:1:4 ratio. ^{77}Se NMR data: $\delta = -384$ ppm (25 °C, CD$_3$CN/en). [Ge(en)$_3$][enH][SbSe$_4$] is moderately air sensitive.

Crystallographic Study of [NEt$_4$][BiSe$_2$]. Single crystals of [NEt$_4$][BiSe$_2$] were mounted in a glovebag in an N$_2$ atmosphere and rapidly transferred to the cold stream of a Picker diffractometer. Lattice constants were determined from a least-squares analysis of the setting angles of 32 reflections in the range $29° < 2\theta(\mathrm{Mo}K\alpha_1) < 34°$ at 115 K. Laue symmetry $\bar{3}m$ and the systematic extinctions (hhl, $l = 2n + 1$; hhh, $h = 2n + 1$) are consistent with the space groups C_{3v}^6-$R3c$ and D_{3d}^6-$R\bar{3}c$. No significant changes were observed in the intensities of six standard reflections monitored every 100 reflections throughout data collection. Data were processed[20] and corrected for absorption[21] by methods standard to this laboratory. The structure was solved with the use of the direct methods program SHELXS[22] and refined on F_o^2 with the full-matrix least-squares program SHELXL.[23] All heavy atoms were refined anisotropically. The positions of the hydrogen atoms were determined from geometrical calculations and were idealized. Only in the polar space group $R3c$ could a chemically sensible solution be found. In the penultimate cycle of refinement the value of the Flack parameter[24] was 0.26(3). Accordingly, the structure was refined as a twin, the final ratio of the two components being 0.74(3) to 0.26(3). This final refinement on F_o^2 for 980 data and 65 variables converged to a value of $R_w(F_o^2)$ of 0.113 for all data and to a value of R_1 of 0.054 for those 787 data having $F_o^2 \geq 2\sigma(F_o^2)$.

Crystallographic Study of [Ge(en)$_3$][enH][SbSe$_4$]. All crystals of [Ge(en)$_3$][enH][SbSe$_4$] examined were marginally large enough for the collection of diffraction data. A crystal was chosen and mounted in a glovebag in an N$_2$ atmosphere and rapidly transferred to the cold stream of a Picker diffractometer. Lattice constants were determined from a least-squares analysis of the setting angles of 17 reflections in the range $20° < 2\theta(\mathrm{Mo}\ K\alpha_1) < 26°$ at 115 K. No significant changes were observed in the intensities of six standard reflections monitored every 100 reflections throughout data collection. Data processing and structure solution in the centrosymmetric space group C_i^1-$P\bar{1}$ followed the procedures outlined above. Owing to the weak, limited data set, all atoms were refined isotropically. The final refinement on F_o^2 for 870 data and 90 variables converged to a value of $R_w(F_o^2)$ of 0.241 for all data and to a value of R_1 of 0.101 for those 393 data having $F_o^2 \geq 2\sigma(F_o^2)$.

Table 1. Crystal Data and Structure Refinement for [NEt$_4$][BiSe$_2$] and [Ge(en)$_3$][enH][SbSe$_4$]

	compd	
	[NEt$_4$][BiSe$_2$]	[Ge(en)$_3$][enH][SbSe$_4$]
chem formula	C$_8$H$_{20}$BiNSe$_2$	C$_8$H$_{33}$GeN$_8$SbSe$_4$
fw	497.15	751.60
a (Å)	19.19(1)[a]	8.82(2)
b (Å)	19.19(1)	9.60(2)
c (Å)	19.19(1)	14.20(3)
α (deg)	118.375(2)	104.84(7)
β (deg	118.375(2)	92.66(7)
γ (deg)	118.375(2)	109.44(7)
V (Å^3)	2320(2)	1085.2(4)
ρ(calcd) (g/cm^3)	2.135	2.30
space group	C_{3v}^6-$R3c$	C_i^1-$P\bar{1}$
Z	6	2
μ (cm^{-1})	161	93
T of data collcn (K)[b]	115(2)	115(2)
$R_w(F^2)$[c] (all data)	0.113	0.241
R_1 ($F_o^2 > 2\sigma(F_o^2)$)[c]	0.054	0.101
transm factors[d]	0.122−0.394	0.712−0.884

[a] The cell parameters were obtained from a refinement constrained so that $a = b = c$ and $\alpha = \beta = \gamma$. [b] The low-temperature system is based on a design by Huffman.[38] The diffractometer was operated with the Indiana University PCPS system.[39] [c] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ 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 absorption program AGNOST was used for the absorption correction.[21]

Table 2. Positional Parameters and Equivalent Isotropic Displacement Parameters for [NEt$_4$][BiSe$_2$]

atom	x	y	z	U(eq)[a] (Å^2)
Bi(1)	1.0003(2)	0.5396(2)	0.5735(2)	0.0491(7)
N(1)	0.254(4)	−0.500(5)	−0.317(5)	0.050(10)
Se(1)	0.7309(6)	0.4026(5)	0.3618(5)	0.057(2)
Se(2)	0.6888(6)	0.1247(6)	0.2005(6)	0.058(2)
C(1)	0.138(6)	−0.657(6)	−0.400(6)	0.061(14)
C(2)	0.432(6)	−0.386(6)	−0.190(6)	0.09(2)
C(3)	0.306(8)	−0.372(8)	−0.184(8)	0.13(2)
C(4)	0.141(8)	−0.580(9)	−0.474(8)	0.14(2)
C(5)	−0.040(6)	−0.795(7)	−0.525(7)	0.12(2)
C(6)	0.561(7)	−0.219(7)	−0.093(7)	0.15(3)
C(7)	0.412(9)	−0.296(9)	−0.038(9)	0.17(3)
C(8)	0.098(12)	−0.685(13)	−0.578(12)	0.30(6)

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

No additional symmetry was found in either structure with the MISSYM algorithm[25] in the PLATON package of programs.[26] No unusual features were observed in the final difference electron density map of either structure.

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, and selected bond distances and angles are given in Tables 4 and 5 for [NEt$_4$][BiSe$_2$] and [Ge(en)$_3$][enH][SbSe$_4$], respectively. Further crystallographic details are available as Supporting Information.

Results and Discussion

The crystal structure of [NEt$_4$][BiSe$_2$] consists of the packing of NEt$_4^+$ cations and [BiSe$_2^-$]$_n$ one-dimensional anionic chains of apex-sharing [BiSe$_3^{3-}$] trigonal pyramids. The closest cation−anion distance of 2.83 Å is between atom H(4A) on an α-carbon atom of NEt$_4^+$ and atom Se(2). In addition to its three Se^{2-} ligands, each Bi^{3+} cation has an extended interaction of

---

(18) Pell, M. A.; Ibers, J. A. Unpublished work. Crystals of this material differ in habit and color from the those of [NEt$_4$][BiSe$_2$]. However, they are weakly diffracting and no structure has yet been determined.

(19) Orlova, G. M.; Martynova, N. S.; Khomenko, A. V. *Russ. J. Inorg. Chem.* **1982**, *27*, 275−278.

(20) Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273−3277.

(21) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014−1018.

(22) Sheldrick, G. M. SHELXTL PC Version 5.0 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data. Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994.

(23) Sheldrick, G. M. *J. Appl. Crystallogr.*, manuscript in preparation.

(24) Flack, H. D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *39*, 876−881.

(25) Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264−269.

(26) Spek, A. L. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, C34.

Table 3. Positional Parameters and Equivalent Isotropic Displacement Parameters for [Ge(en)$_3$][enH][SbSe$_4$]

atom	*x*	*y*	*z*	*U*(eq) (Å^2)
Sb(1)	0.3821(8)	0.0747(8)	0.2289(5)	0.015(3)
Ge(1)	0.713(2)	−0.313(2)	0.3163(11)	0.068(5)
Se(1)	0.3929(12)	0.1861(12)	0.0889(8)	0.020(4)
Se(2)	0.2619(13)	−0.2123(12)	0.1637(8)	0.027(4)
Se(3)	0.6655(12)	0.1609(12)	0.3079(7)	0.016(4)
Se(4)	0.2108(13)	0.1782(12)	0.3382(8)	0.026(4)
C(1)	−0.059(9)	−0.343(9)	−0.104(6)	0.00(3)
C(2)	0.050(9)	−0.195(9)	−0.070(6)	0.00(3)
C(3)	1.061(13)	−0.198(13)	0.447(8)	0.08(4)
C(4)	0.966(9)	−0.365(9)	0.446(6)	0.00(3)
C(5)	0.735(11)	−0.449(11)	0.097(7)	0.03(3)
C(6)	0.585(11)	−0.377(10)	0.108(7)	0.05(4)
C(7)	0.463(9)	−0.195(8)	0.431(6)	0.00(3)
C(8)	0.406(10)	−0.392(9)	0.396(6)	0.00(3)
N(1)	−0.046(8)	−0.421(8)	−0.210(5)	0.02(2)
N(2)	0.229(7)	−0.165(7)	−0.075(5)	0.02(2)
N(3)	0.970(8)	−0.190(9)	0.346(6)	0.05(3)
N(4)	0.782(7)	−0.408(7)	0.434(5)	0.00(2)
N(5)	0.730(8)	−0.496(7)	0.190(5)	0.02(2)
N(6)	0.674(8)	−0.233(8)	0.190(5)	0.03(3)
N(7)	0.655(8)	−0.137(8)	0.428(5)	0.03(3)
N(8)	0.462(7)	−0.437(7)	0.310(5)	0.00(2)

Table 4. Interatomic Distances (Å) and Angles (deg) for [NEt$_4$][BiSe$_2$]

	Distances		
Bi(1)−Se(2)^1	2.590(5)	Bi(1)−Se(1)^1	2.832(5)
Bi(1)−Se(1)	2.668(5)	Bi(1)−Se(2)	3.207(5)
	Average NEt$_4^+$ Distances		
N−C	1.57(4)	C−C	1.42(3)
	Angles		
Se(2)^1−Bi(1)−Se(1)	107.8(2)	Se(1)−Bi(1)−Se(2)	87.04(14)
Se(2)^1−Bi(1)−Se(1)^1	97.0(2)	Se(1)^1−Bi(1)−Se(2)	162.41(14)
Se(1)−Bi(1)−Se(1)^1	91.3(2)	Bi(1)−Se(1)−Bi(1)^2	89.22(14)
Se(2)^1−Bi(1)−Se(2)	100.2(2)	Bi(1)^2−Se(2)−Bi(1)	82.87(13)

[a] Symmetry transformations used to generate equivalent atoms: (1) $x + ^1/_2, z + ^1/_2, y + ^1/_2$; (2) $x - ^1/_2, z - ^1/_2, y - ^1/_2$.

Table 5. Interatomic Distances (Å) and Angles (deg) for [Ge(en)$_3$][enH][SbSe$_4$]

	Distances		
Sb(1)−Se(3)	2.467(12)	Ge(1)−N(7)	2.22(7)
Sb(1)−Se(4)	2.472(13)	Ge(1)−N(5)	2.22(6)
Sb(1)−Se(1)	2.478(12)	Ge(1)−N(4)	2.25(6)
Sb(1)−Se(2)	2.497(13)	N(1)−C(1)	1.52(9)
Ge(1)−N(8)	2.12(6)	N(2)−C(2)	1.51(8)
Ge(1)−N(3)	2.14(7)	C(1)−C(2)	1.37(8)
Ge(1)−N(6)	2.18(7)		
	Average Ge(en)$_3^{2+}$ Distances		
N−C	1.52(4)	C−C	1.65(5)
	Angles		
Se(3)−Sb(1)−Se(4)	112.6(4)	Se(3)−Sb(1)−Se(2)	111.3(4)
Se(3)−Sb(1)−Se(1)	106.0(4)	Se(4)−Sb(1)−Se(2)	111.5(4)
Se(4)−Sb(1)−Se(1)	106.4(4)	Se(1)−Sb(1)−Se(2)	108.7(4)

3.207(5) Å with the terminal Se^{2-} anion of an adjacent Bi^{3+} cation along the same chain. The nonbridging Se^{2-} anion alternates sides along the [BiSe$^+$] polymer backbone in a zigzag or syndiotactic fashion (Figure 1). The Bi−Se bond lengths are 2.590(5), 2.668(5), and 2.832(5) Å. Bi−Se bond distances of 2.704(3) and 2.713(2) Å have been reported for Ph$_2$BiSePh[27] and [{Cp(CO)$_2$Mo}$_2$SeBiCl]·THF,[28] respectively. The Se−Bi−Se bond angles are 91.3(2), 97.0(2), and 107.8(2)°. The Bi−Se(1)−Bi bond angle is 89.2(3)°. A similar polymeric structure has been observed in the compound [Ba(en)$_4$][SbSe$_2$]$_2$, where the Se−Sb−Se angles span 91.1(1)−112.3(1)° and the Sb−Se−Sb angles are 96.7(1) and 102.5(1)°.[29]

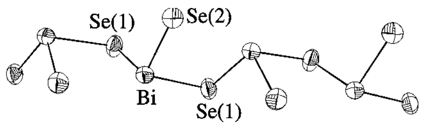

Figure 1. The [BiSe$_2^-$]$_n$ chain. Displacement ellipsoids are drawn at the 50% probability level.

No ^{77}Se resonances in the range 2000 to −1000 ppm were observed for crystals of [NEt$_4$][BiSe$_2$] dissolved in en (25 °C) or in CD$_3$CN (−50 °C). A possible reason is that resonances are broadened by coupling with ^{209}Bi (100% abundant, spin $^9/_2$). It is unlikely that the [BiSe$_2^-$]$_n$ polymer exists in solution.

The crystal structure (Figure 2) of [Ge(en)$_3$][enH][SbSe$_4$] consists of the packing of [SbSe$_4$]$^{3-}$ tetrahedral anions and [Ge(en)$_3$]$^{2+}$ and [enH]$^+$ cations. That the ethylenediamine in the structure is protonated was inferred from considerations of charge balance and a reasonable oxidation state for the Ge cation (i.e., Ge^{2+} or Ge^{4+}). Monoprotonated enH cations have been previously observed in chalcogenide systems.[30,31] The proton H(2C) was assigned to atom N(2) rather than to atom N(1) as a closer cation−anion interaction (2.52(2) Å) results. The N(2)−H(2C)···Se(1) angle is 153.4(5)°. The assignment of oxidation states is non-trivial, with reasonable formulations being [Ge^{II}(en)$_3$][enH][Sb^{V}Se$_4$] and [Ge^{IV}(en)$_3$][enH][Sb^{III}Se$_4$]. We favor the former on the basis of the Sb−Se distances of 2.47(1)−2.50(1) Å, which agree well with those of the related Sb^V compounds [Ba(en)$_3$]$_2$[Ba(en)$_4$][SbSe$_4$]$_2$ (2.438(9)−2.497(10) Å) and K$_3$SbSe$_4$ (2.473(4) and 2.475(2) Å);[32] Sb^{III}−Se bond distances tend to be longer, as in [SbSe$_2$]$^{2-}$ [29] (2.457(3), 2.591(3), and 2.624(3) Å) and [Sb$_{12}$Se$_{20}$]$^{4-}$ [33] (2.544(4)−2.796(5) Å). The [Ge(en)$_3$]$^{2+}$ cation, which has not been characterized structurally before, exists as the Δλλδ conformer (and its enantiomer). Although this is not the energetically favored conformer, it is the statistically favored species.[34,35] The octahedral environment about the Ge is distorted with N−Ge−N bond angles ranging from 77(3) to 97(3)°. The Ge−N bond distances span 2.12(6)−2.25(6) Å and are longer than those observed in (glycyl-L-methioninato)dimethylgermanium(IV) (1.889(4) and 2.103(4) Å).[36]

A single resonance is observed in the ^{77}Se spectrum of [Ge(en)$_3$][enH][SbSe$_4$] at −384 ppm, consistent with the [SbSe$_4$]$^{3-}$ anion retaining its tetrahedral structure in solution. No other ^{77}Se NMR data have been reported for Sb^V systems; the Sb^{III} compound [K(2.2.2.-crystand)]$_2$[Sb$_2$Se$_4$] has ^{77}Se resonances at 124 and 337 ppm.[37]

---

(27) Calderazzo, F.; Morvillo, A.; Pelizzi, G.; Poli, R.; Ungari, F. *Inorg. Chem.* **1988**, *27*, 3730−3733.

(28) Merzweiler, K.; Brands, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1992**, *47*, 978−982.

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

(30) Böttcher, P.; Buchkremer-Hermanns, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1987**, *42*, 267−271.

(31) Böttcher, P.; Buchkremer-Hermanns, H. *J. Less-Common Met.* **1988**, *137*, 1−11.

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

(33) Martin, T. M.; Wood, P. T.; Kolis, J. W. *Inorg. Chem.* **1994**, *33*, 1587−1588.

(34) Mason, S. F. *Molecular Optical Activity and the Chiral Discriminations*; Cambridge University Press: Cambridge, U.K., 1982.

(35) Sudmeier, J. L.; Blackmer, G. L.; Bradley, C. H.; Anet, F. A. L. *J. Am. Chem. Soc.* **1972**, *94*, 757−761.

(36) Pruet, H.; Vornefeld, M.; Huber, F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *45*, 1504−1506.

(37) Smith, D. M.; Ibers, J. A. Unpublished results.

(38) Huffman, J. C. Ph.D. Dissertation, Indiana University, 1974.

(39) Huffman, J. C.; Streib, W. E. Unpublished work, 1990.

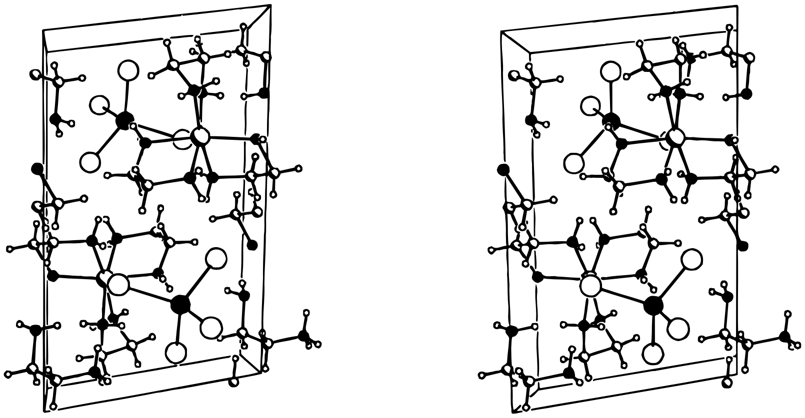

Figure 2. Stereoview of the unit cell of [Ge(en)$_3$][enH][SbSe$_4$] along [010]. Atoms are drawn as circles of arbitrary size.

Acknowledgment. This work was supported by NSF Grants DMR 91-14934 and CHE 92-24469. Use was made of MRL Central Facilities supported by the National Science Foundation at the Materials Research Center of Northwestern University under Grant No. DMR 91−20521.

Supporting Information Available: Tables listing detailed crystallographic data, bond lengths and angles, anisotropic displacement parameters, and hydrogen-atom coordinates (11 pages). Ordering information is given on any current masthead page.

IC960181Z