Inorg. Chem. **1997**, *36*, 3798−3800

Syntheses and Crystal Structures of $[K(2.2.2\text{-cryptand})]_2[(\mu\text{-O})\{\mu\text{-O}_2Si(CH_3)_2\}_2(GeSe)_2]$ and $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_6]$

Donna M. Smith, Chang-Woo Park, and James A. Ibers*

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

Received February 6, 1997

Introduction

Through our continuing attempts to solubilize solid-state binary chalcogenides,[1,2] we have isolated two previously unknown compounds, $[K(2.2.2\text{-cryptand})]_2[(\mu\text{-O})\{\mu\text{-O}_2Si(CH_3)_2\}_2(GeSe)_2]$ (**1**) and $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_6]$ (**2**).

The isolation of **1** was completely unexpected, as no Si-containing compound was knowingly involved in the reaction. Once the nature of **1** had been established from a single-crystal structure determination, it became clear that the Si-containing reactant was silicone grease. The compound is unique in containing a Se−Ge−O linkage. Whereas oxo−germanium chemistry has been widely studied,[3−6] few mixed oxo/chalcogenide/germanium compounds have been observed and the majority of these are sulfides. In addition to **1**, only the pentacarbonylbis[((2,4,6-tri-*tert*-butylphenyl)seleno)germylene]tungsten(0) complex[7] has Ge, Se, and O atoms within the same structural unit, although without the Se−Ge−O linkage seen in compound **1**.

Despite the number of selenoarsenates that are known, only relatively recently has the solution chemistry of the selenoantimonates been explored. The small number that have been reported include the anions of $[PPh_4]_2[Sb_4Se_6]$,[8] $[PPh_4]_4[Sb_{12}Se_{20}]$,[9] $[Ge(en)_3][enH][SbSe_4]$,[10] and $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_4]$.[11] The $[Sb_4Se_6]^{2-}$ anion has the known analogues $[Sb_4S_6]^{2-}$ [12] and $[As_4Q_6]^{2-}$, Q = S,[13] Se,[14] and Te;[15] the $[Sb_2Se_4]^{2-}$ anion has the known analogue $[As_2S_4]^{2-}$;[11] and the $[Sb_2Se_6]^{2-}$ anion reported here has the known analogue $[As_2Se_6]^{2-}$.[14]

Experimental Section

All manipulations were carried out under N_2 with the use of standard Schlenk techniques. Solvents were purchased from Baxter Scientific Products Inc., McGaw Park, IL, and were distilled, dried, and degassed before use. Ammonia gas (anhydrous, 99.95% purity) was purchased from Linde Gas Corp. The remaining reagents were purchased from Aldrich Chemical Co., Milwaukee, WI, and were used as received. 2.2.2-Cryptand was dissolved in acetonitrile and recrystallized by vacuum evaporation. SbSe and $GeSe_2$ were made by heating stoichiometric amounts of the elements in fused-silica tubes under an inert atmosphere. Purity of the known phase $GeSe_2$ was confirmed by X-ray powder diffraction methods. Although the phase diagram of the Sb−Se system indicates that SbSe is a congruently melting phase,[16] the product obtained here is a mixture of Sb_2Se_3 and Sb, as deduced from its X-ray powder diffraction pattern. ^{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 NMR chemical shifts are referenced to the external Ph_2Se_2 standard at $\delta = 460$ ppm that in turn is referenced to $(CH_3)_2Se$ at $\delta = 0$ ppm. No attempt was made to isolate all products from a given reaction. A reported yield is that before any purification attempts.

$[K(2.2.2\text{-cryptand})]_2[(\mu\text{-O})\{\mu\text{-O}_2Si(CH_3)_2\}_2(GeSe)_2]$ (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 liquid-N_2 temperature (−195 °C). The resulting blue solution was stirred at −77 °C until all the K had dissolved (30 min). Finely ground $GeSe_2$ (131 mg, 1.0 mmol) was added with stirring, and the solution turned yellow after 30 min. The solution was stirred at −77 °C for 6 h, and it was then allowed to warm to 20 °C overnight. The solid residue that remained after the NH_3 had evaporated was dissolved in CH_3CN (20 mL) to give a yellow solution as well as some undissolved powder. The nature of this powder could not be ascertained and taken into account in the calculation of the yield of **1**; hence it is likely that the stated yield is low. A small portion of the solution (5 mL) was filtered and layered with ether (10 mL) to afford after 3 days pale yellow hexagonal plates and blocks and some rhombohedral-shaped crystals. Crystals were manually separated, and the rhombohedral-shaped crystals were characterized as **1**. Yield: 30 mg; 19% (based on Ge).

$[K(2.2.2\text{-cryptand})]_2[Sb_2Se_6]$ (2). NH_3 (30 mL) was condensed into a flask containing 2.2.2-cryptand (189 mg, 0.50 mmol) and K (20 mg; 0.50 mmol). Upon addition at −77 °C of SbSe (200 mg, 1.0 mmol) the solution changed from blue to dark red. Most of the orange-red residue that remained after the NH_3 had evaporated was soluble in CH_3CN (15 mL), and the solution was filtered and layered with ether (45 mL). On the basis of its X-ray diffraction pattern, the remaining gray powder (82 mg) was starting material. Red-orange blocks formed after 4 days. Yield: 125 mg, 84% (based on Se). ^{77}Se NMR (crystals dissolved to 0.05 mM in 100% CH_3CN; −40 °C): 456, 319 ppm.

Crystallographic Studies

Data from single crystals of **1** and **2** were collected on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from 25 reflections centered in the θ(Cu Kα_1) range 31−34° (**1**) and 30−35° (**2**) at 113(2) K. Six standard reflections were measured after every 1 h of X-ray exposure time. These standards showed an average decrease in intensity of 11% for **1** and 25% for **2**; the data were scaled accordingly. The peak profile data were processed[17] and were then corrected for absorption effects by the analytical method.[18]

In each instance the centrosymmetric space group was chosen on the basis of agreement between Friedel pairs; the structure was solved in that space group by direct methods with the use of the program

---

(1) Park, C.-W.; Salm, R. J.; Ibers, J. A. *Can. J. Chem.* **1995**, *73*, 1148−1156.
(2) Park, C.-W.; Salm, R. J.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1879−1880.
(3) Puff, H.; Braun, K.; Franken, S.; Riza-Kök, T.; Schuh, W. *J. Organomet. Chem.* **1987**, *335*, 167−178.
(4) Puff, H.; Franken, S.; Schuh, W.; Schwab, W. *J. Organomet. Chem.* **1983**, *254*, 33−41.
(5) Puff, H.; Braun, K.; Franken, S.; Riza-Kök, T.; Schuh, W. *J. Organomet. Chem.* **1988**, *349*, 293−303.
(6) Puff, H.; Franken, S.; Schuh, W. *J. Organomet. Chem.* **1983**, *256*, 23−30.
(7) du Mont, Wolf-W.; Lange, L.; Pohl, S.; Saak, W. *Organometallics* **1990**, *9*, 1395−1399.
(8) Sportouch, S.; Thumim, J.; Tillard-Charbonnel, M.; Belin, C. *New J. Chem.* **1995**, *19*, 133−135.
(9) Martin, T. M.; Wood, P. T.; Kolis, J. W. *Inorg. Chem.* **1994**, *33*, 1587−1588.
(10) Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 4559−4562.
(11) Smith, D. M.; Park, C.-W.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 6682−6687.
(12) Martin, T. M.; Schimek, G. L.; Pennington, W. T.; Kolis, J. W. *J. Chem. Soc., Dalton Trans.* **1995**, 501−502.
(13) Porter, E. J.; Sheldrick, G. M. *J. Chem. Soc. A* **1971**, 3130−3132.
(14) Ansari, M. A.; Ibers, J. A.; O'Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Polyhedron* **1992**, *11*, 1877−1881.
(15) Eisenmann, B.; Zagler, R. *Z. Naturforsch., B: Chem. Sci.* **1987**, *42*, 1079−1082.
(16) Scott, W. W., Jr. In *Binary Alloy Phase Diagrams*, 2nd ed.; Massalski, T. B., Okamota, H., Subramanian, P. R., Kacprzak, L., Eds.; ASM: Materials Park, OH, 1990.
(17) Blessing, R. H. *Crystallogr. Rev.* **1987**, *1*, 3−58.
(18) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014−1018.

S0020-1669(97)00137-7 CCC: $14.00

Table 1. Crystal Data and Structure Refinement for $[K(2.2.2\text{-cryptand})]_2[(\mu\text{-O})\{\mu\text{-O}_2Si(CH_3)_2\}_2(GeSe)_2]$ (**1**) and $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_6]$ (**2**)

	compound	
	$[K(2.2.2\text{-cryptand})]_2[(\mu\text{-O})\text{-}\{\mu\text{-O}_2Si(CH_3)_2\}_2(GeSe)_2]$	$[K(2.2.2\text{-cryptand})]_2\text{-}[Sb_2Se_6]$
chem formula	$C_{40}H_{84}Ge_2K_2N_4O_{12}Se_2Si_2$	$C_{36}H_{72}K_2N_4O_{12}Sb_2Se_6$
fw	1330.59	1548.44
a, Å	11.587(1)	11.152(2)
b, Å	12.766(1)	11.889(2)
c, Å	20.903(2)	12.399(3)
α, deg	107.15(1)	66.06(3)
β, deg	92.11(1)	87.14(3)
γ, deg	90.66(1)	69.29(3)
V, Å^3	2951(1)	1397(1)
space group	$C_i^1\text{-}P\bar{1}$	$C_i^1\text{-}P\bar{1}$
Z	2	1
D(calc), g·cm^{-3}	1.497	1.841
μ, cm^{-1} [a]	49	139
transm factors	0.383−0.640	0.155−0.287
T, K	113(2)	113(2)
$R(F)$ [b]	0.046	0.049
$R_w(F^2)$ [c]	0.115	0.168

[a] For Cu Kα radiation ($\lambda = 1.5418$ Å). [b] $R = \sum||F_o| - |F_c||/\sum F_o$. [c] $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$, $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$, $F_o^2 < 0$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[K(2.2.2\text{-cryptand})]_2[(\mu\text{-O})\{\mu\text{-O}_2Si(CH_3)_2\}_2(GeSe)_2]$ (**1**)

Se(1)−Ge(1)	2.219(1)	Si(1)−O(16)	1.634(3)
Se(2)−Ge(2)	2.204(1)	Si(1)−O(14)	1.636(3)
Ge(1)−O(13)	1.783(3)	Si(1)−C(38)	1.846(6)
Ge(1)−O(14)	1.785(3)	Si(1)−C(37)	1.847(5)
Ge(1)−O(15)	1.786(4)	Si(2)−O(17)	1.626(4)
Ge(2)−O(13)	1.779(3)	Si(2)−O(15)	1.629(3)
Ge(2)−O(17)	1.787(3)	Si(2)−C(39)	1.844(5)
Ge(2)−O(16)	1.791(3)	Si(2)−C(40)	1.874(5)

O(13)−Ge(1)−O(14)	102.79(14)	O(16)−Si(1)−O(14)	110.6(2)
O(13)−Ge(1)−O(15)	101.8(2)	O(16)−Si(1)−C(38)	108.0(2)
O(14)−Ge(1)−O(15)	102.8(2)	O(14)−Si(1)−C(38)	110.4(2)
O(13)−Ge(1)−Se(1)	116.70(9)	O(16)−Si(1)−C(37)	110.3(2)
O(14)−Ge(1)−Se(1)	115.68(10)	O(14)−Si(1)−C(37)	109.9(2)
O(15)−Ge(1)−Se(1)	115.04(10)	C(38)−Si(1)−C(37)	107.6(3)
O(13)−Ge(2)−O(17)	102.86(14)	O(17)−Si(2)−O(15)	110.4(2)
O(13)−Ge(2)−O(16)	102.29(13)	O(17)−Si(2)−C(39)	108.3(2)
O(17)−Ge(2)−O(16)	100.2(2)	O(15)−Si(2)−C(39)	109.7(2)
O(13)−Ge(2)−Se(2)	116.98(9)	O(17)−Si(2)−C(40)	108.8(2)
O(17)−Ge(2)−Se(2)	116.05(11)	O(15)−Si(2)−C(40)	110.0(2)
O(16)−Ge(2)−Se(2)	116.04(10)	C(39)−Si(2)−C(40)	109.6(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Anion of $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_6]$ (**2**)

Sb(1)−Se(1)	2.428(2)	Se(2)−Se(3a)	2.349(2)
Sb(1)−Se(2)	2.610(2)	Se(3)−Se(2a)	2.349(2)
Sb(1)−Se(3)	2.616(2)		

Se(1)−Sb(1)−Se(2)	97.35(5)	Se(3a)−Se(2)−Sb(1)	98.71(5)
Se(1)−Sb(1)−Se(3)	95.83(5)	Se(2a)−Se(3)−Sb(1)	100.30(6)
Se(2)−Sb(1)−Se(3)	98.48(4)		

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

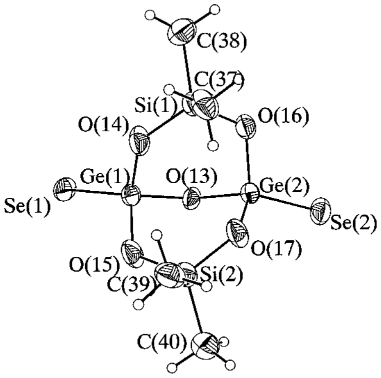

Figure 1. View of the $[(\mu\text{-O})\{\mu\text{-O}_2Si(CH_3)_2\}_2(GeSe)_2]^{2-}$ anion. Here and in the succeeding figure 50% probability displacement ellipsoids are shown.

SHELXS,[19] and the structure was refined by full-matrix least-squares methods with the program SHEL93.[20] Methylene hydrogen atoms were assigned to calculated positions and refined according to a riding model. Methyl hydrogen atoms were placed at positions of maximum residual electron density with the constraints of normal tetrahedral angles and C−H bond lengths. Crystallographic details are given in Tables 1 and in the Supporting Information. Tables 2 and 3 provide metrical details. Other tabulations are given in the Supporting Information.

Whereas the refinement of the structure of **2** was routine, deduction of the nature of **1** presented an interesting crystallographic challenge. The basic connectivity of the structure, including the presence of two unique, unambiguous K(2.2.2-cryptand) (1+) cations, was clear from the initial structural solution, but the nature of the atoms in the anion, charge 2−, was not. Referring to Figure 1, where the final structure of the anion is illustrated, one sees that there are four heavy scatterers, Ge(1), Ge(2), Se(1), and Se(2). Because $GeSe_2$ was a reactant and because of their heights relative to C in the direct-methods solution, the assumption was made that the heavy scatterers were some combination of Ge and Se; their approximately equal scattering power necessitated that stereochemical and metrical arguments be used to identify them. Refinement of the structure with these four atoms assigned to Ge led to "Ge−Ge" distances of 2.204(1) and 2.219(1) Å. These may be compared with the following typical bond lengths: Ge−Ge, 2.46 Å ($Ph_8Ge_2Si_2O_3$[21]), Ge−Se_t, 2.29 Å ($Tl_4Ge_4Se_{10}$[22]), 2.33 Å ($[NEt_4]_2[enH]_2[Ge_2Se_6]$[23]), Se−$Se_t$, 2.23 and 2.29 Å ($[K(2.2.2\text{-cryptand})]_2[Se_7]\cdot H_2O$[24]). Thus Ge−Ge linkages were eliminated. Since there appears to be no precedent for a terminal Ge atom, this leaves Se−Ge or Se−Se for the linkages corresponding to Se(1)−Ge(1) and Se(2)−Ge(2) in Figure 1. Subsequent refinement of the Ge/Se fragments and the cations led to a difference electron density map that showed the same connectivity seen initially but with somewhat more reliable peak heights. The two major difference peaks had heights corresponding to a second-row element; these peaks, which correspond to atoms Si(1) and Si(2) of Figure 1, were assigned to Si. The assignment of bridging O atoms and terminal CH_3 groups on these Si atoms was made on the basis of bond lengths and angles. The average Si−O and Si−C bond lengths (1.629(3) and 1.853(5) Å, respectively) for **1** are comparable with those seen in 1,3,5,7-tetraoxo-2,6-disila-4,8-digermocine (1.636(4) and 1.878(6) Å, respectively),[25] which also has an O_2SiR_2 bridge. The bridging atom, denoted O(13) in Figure 1, had a peak height that was nearly the same as those assigned to the oxygen atoms of the SiO_2 groups; hence, it was assigned as oxygen. Considerations of charge balance then lead to +IV for the atoms denoted Ge(1) and Ge(2) in Figure 1. As Se(IV) seems much less likely than Ge(IV) and since compounds with Ge−O−Ge linkages are common,[3−5, 21] these atoms were assigned to Ge to complete the structure shown in Figure 1. The coexistence of both O and O_2SiR_2 bridges between two group 14 metals has a precedent in (*μ-O,O′*-di-*tert*-butylsilanediyldihydroxo)bis(*μ*-hydroxo)hexachlorodistannane.[25] Refinement of the structure depicted in Figure 1 afforded reasonable

---

(19) 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.

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

(21) Puff, H.; Riza-Kök, T.; Nauroth, P.; Schuh, W. *J. Organomet. Chem.* **1985**, *281*, 141−148.

(22) Eulenberger, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36*, 521−523.

(23) Park, C.-W.; Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 4555−4558.

(24) Müller, V.; Dehnicke, K.; Fenske, D.; Baum, G. *Z. Naturforsch., B: Chem. Sci.* **1991**, *46*, 63−67.

(25) Mazzah, A.; Haoudi-Mazzah, A.; Noltemeyer, M.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1991**, *604*, 93−103.

anisotropic displacement parameters for all atoms, a strong confirmation that the assignment of atom types is correct. Subsequent EDX analysis of the crystal used in data collection confirmed the presence of Si, Se, and Ge.

Discussion

The anion in $[K(2.2.2\text{-cryptand})]_2[(\mu\text{-}O)\{\mu\text{-}O_2Si(CH_3)_2\}_2(GeSe)_2]$ (Figure 1) can be formed conceptually by the linking of two GeSe units with one O and two O_2SiMe_2 bridges. The Ge atoms are coordinated to three O atoms and one Se_t (t = terminal) atom. The $Ge-O_b$ (b = bridging) bond lengths in **1** range from 1.779(3) to 1.791(3) Å (Table 2) and are comparable to the $Ge-O_b$ bond lengths of 1.779(1) and 1.775(1) Å in $Ph_8Ge_2Si_2O_3$[21] and 1.75(1)−1.77(1) Å in $(t\text{-}BuGe)_6O_8Cl_2$.[3] The presence of Si in **1** almost certainly comes from the adventitious reaction of an intermediate with silicone grease. As the Schlenk tube was kept upright, it is likely the grease dissolved as solvent was added to the reaction mixture. Attempts to remake the compound by adding silicone grease directly to the reaction mixture were unsuccessful. Reaction of silicone grease with an organometallic intermediate has been reported as the source of Si in the synthesis of $[K(OSiMe_2)_7][K\{C(SiMe_3)_2[SiMe_2(HC{=}CH_2)]\}_2]$[26] and $K_3[K(Me_2SiO)_7][InH(CH_2CMe_3)_3]_4$.[27]

The reduction of SbSe by K in $NH_3(l)$ affords the $[Sb_2Se_6]^{2-}$ anion (Figure 2); this anion comprises two $SbSe_3$ pyramids joined to form a Sb_2Se_4 ring in the chair conformation with exocyclic Se atoms attached to the Sb atoms. The anion has crystallographically imposed $\bar{1}$ symmetry. The $Sb-Se_t$ bond length (Table 3) of 2.428(2) Å is comparable to the $Sb-Se_t$ bond lengths of 2.443(1) and 2.46(7) Å in $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_4]$[11] and $[PPh_4]_2[Sb_4Se_6]$,[8] respectively. The $Sb-Se_b$ bond lengths are 2.610(2) and 2.616(2) Å and are comparable to the $Sb-Se_b$ bond length of 2.615(1) Å in $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_4]$.

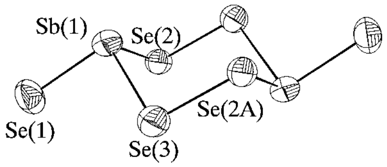

Figure 2. View of the $[Sb_2Se_6]^{2-}$ anion.

^{77}Se NMR chemical shifts for $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_6]$ are observed at 456 and 319 ppm (CH_3CN, −40 °C). Although no J_{Sb-Se} or J_{Se-Se} coupling is observed, integration of the resonances suggests that the one at 456 ppm corresponds to the Se_b nucleus. These chemical shifts are similar to those observed for $[PPh_4]_2[As_2Se_6]$ (457 and 363 ppm; DMF, 25 °C).[14]

Acknowledgment. This research was funded by the National Science Foundation, Grant No. CHE-9531232.

Supporting Information Available: Tables giving structure determination summaries, positional coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths and angles, and hydrogen-atom coordinates and displacement parameters for compounds **1** and **2** (19 pages). Ordering information is given on any current masthead page.

IC970137Z

---

(26) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2679−2680.

(27) Churchill, M. R.; Lake, C. H.; Chao, Sun-H. L.; Beachley, O. T., Jr. *J. Chem. Soc., Chem. Commun.* **1993**, 1577−1578.

Additions and Corrections

1997, Volume 36

Suraj P. Narula,* Ravi Shankar, Manish Kumar, Raj K. Chadha, and Christoph Janiak: Structure and Reactivity of 1-Isothiocyanatosilatrane: The First Silatrane with a Direct Si−NCS Bond.

Page 1268. The name of the last coauthor, Christoph Janiak, was inadvertently misspelled in the byline and should correctly read as given above.

IC9705608

S0020-1669(97)00560-0