4178 *Inorg. Chem.* **1999,** *38,* 4178−4180

$RbAg_2As_3Se_6$: A Unique Three-Dimensional Silver-Selenoarsenate Framework $^{3}_{\infty}[Ag_2As_3Se_6]^-$, Assembled from $[As_3Se_6]^{3-}$ Rings and "$Ag_2{}^{2+}$" Dumbbell Units

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Received May 17, 1999

The growing class of ternary and quaternary phases with group 15/16 anions is now a substantial subclass of solid-state chalcogenide compounds.[1] The most successful discovery techniques have been solventothermal[2] as well as molten salt[3] methods, giving access to a large number of $[Pn_xQ_y]^{n-}$ anions (Pn = P, As, Sb; Q = S, Se, Te), which function as building blocks. The simplest building block hereby is the pyramidal $[PnQ_3]^{3-}$ unit (Pn = As, Sb), and its stepwise condensation ability plays an important role in the stabilization of new networks. The Ag−As−Se reaction system has proved to be very flexible and versatile presenting a variety of compositions and arrangements, depending on the various reaction parameters. Initial investigations showed $K_5Ag_2As_3Se_9$ to be the main product in a reaction of K_3AsSe_3 with $AgBF_4$ in MeOH at 110 °C for 1 week.[4] Subsequent studies, however, indicated that the products greatly depend on the reaction time and temperature. For example, a similar reaction for 3 days at 130 °C provides $K_2AgAs_3Se_6$,[5] while stopping the reaction after only 2 h gives the solvated compound $K_3AgAs_2Se_5 \cdot 0.25MeOH$.[5] The products show different degrees of condensation of $[AsSe_3]^{3-}$ units, which can be a function of reaction time, besides other parameters, e.g. the initial pH influencing the reaction rate. This diversity of results prompted us to try similar studies with the slightly more voluminous Rb^+ cation. Thus, the reaction among RbCl, $AgBF_4$, and Li_3AsSe_3 under otherwise identical conditions used for $K_2AgAs_3Se_6$ led to the isostructural $Rb_2AgAs_3Se_6$.[5] In the very early stages of the reaction, however, we identified an intermediate product, $RbAg_2As_3Se_6$,[6a,b] which is structurally very unusual and represents a unique three-dimensional (3D-) silver-selenoarsenate framework.

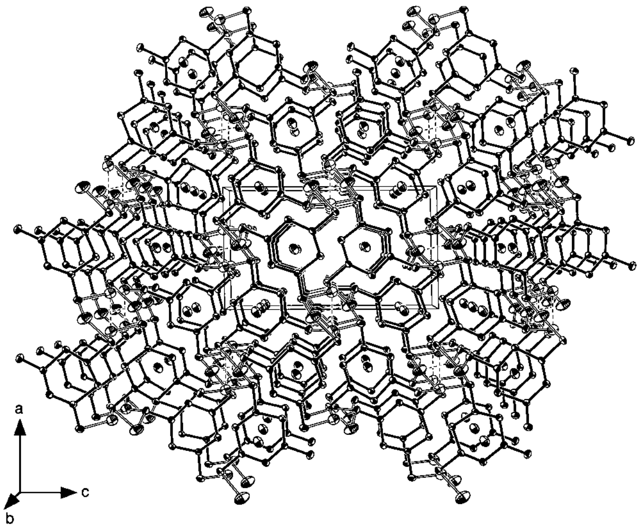

Figure 1. Unit cell of $RbAg_2As_3Se_6$ viewed down the [010] direction, showing the framework $^{3}_{\infty}[Ag_2As_3Se_6]^-$ (50% probability thermal vibrational ellipsoids).

$RbAg_2As_3Se_6$ is built up of $[As_3Se_6]^{3-}$ rings and distorted trigonal planar coordinated Ag^+ atoms. The resulting $^{3}_{\infty}[Ag_2As_3Se_6]^-$ framework is shown in Figure 1. The $[As_3Se_6]^{3-}$ anions consist of a six-membered As_3Se_3 ring in a chair conformation, with alternating As/Se_b positions (b = bridging), see Figure 2. Every As atom is bonded to an additional terminal Se_t atom (t = terminal), which lie in equatorial position to the ring. It shows a pseudo-C_{3v} symmetry, although its center is lying on a general position within the crystal structure. The rings are formally obtained by condensation of three $[AsSe_3]^{3-}$ units, accompanied by a ring closure reaction and elimination of Se^{2-}.[5] This ring structure also occurs in free uncoordinated form in $[Sr(en)_4]_2(As_3Se_6)Cl$,[8] with comparable metric parameters. The $[As_3Se_6]^{3-}$ rings are arranged parallel within the ac-plane. Distorted trigonal planar coordinated Ag^+ ions connect the rings together to form a 3D framework (Figures 1 and 2). Two crystallographically distinguishable Ag^+ atoms are present, both are coordinated by three Se_t atoms of the $[As_3Se_6]^{3-}$ rings. It is

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(6) (a) $RbAg_2As_3Se_6$ was synthesized from a 4:1:3 mixture of RbCl (72 mg, 0.60 mmol), $AgBF_4$ (30 mg, 0.15 mmol) and Li_3AsSe_3 (150 mg, 0.45 mmol), which was sealed, together with 1 mL of methanol, under vacuum in a Pyrex tube and heated to 130 °C for 2 h, followed by fast cooling to room temperature. After washing the product with acetone and H_2O and drying it with ether, dark red needles of $RbAg_2As_3Se_6$ were obtained (∼9%) as a minor product, together with red needles of $RbAsSe_2$ (50%).[7] The X−ray diffraction pattern of the pulverized sample showed that at least one other new phase is present. $RbAg_2As_3Se_6$ is stable in air and not soluble in alcohols or water. Physical/chemical characterization was performed as follows; semiquantitative microprobe analysis on single crystals: $Rb_{0.55}Ag_{2.24}As_{3.00}Se_{6.00}$; optical absorption spectrum: band gap ∼ 1.85 eV; infrared spectrum: absorptions at 222 (m), 260 (w), 269 (w), 299 (w) cm^{-1}, Raman spectrum: 112 (m), 129 (w), 143 (m), 214 (m), 225 (w), 258 (s), 274 (s) cm^{-1} (s = strong, m = medium, w = weak); differential thermal analysis (25−500 °C): incongruent melting point at ∼308 °C (amorphous powder pattern after reaction). (b) A full sphere of data were collected at 25 °C on a Siemens SMART Platform CCD from a crystal of 0.12 × 0.02 × 0.02 mm dimensions with a 30 s/frame collection speed and Mo Kα ($\lambda = 0.710\,73$ Å). The completeness of data collection in the range $2\theta = 4.7$ to 57.44° was 90.3%. The SMART software[6c] was used for data acquisition and SAINT[6d] for data extraction and reduction. Absorption correction was performed with SADABS.[6e] Structure solution and refinement was performed with the SHELXTL package of crystallographic programs.[6f] Crystal data (25 °C): monoclinic, space group $P2_1/n$ (No. 14), $a = 9.9401(15)$ Å, $b = 7.5714(11)$ Å, $c = 17.201(3)$ Å, $\beta = 90.728(3)°$, V= 1294.5(3) Å^{3,} $Z = 4$; $\rho_{calc} = 5.130$ g/cm^3; μ(Mo Kα)= 311.91 cm^{-1}; index ranges $-12 \leq h \leq 13$, $-9 \leq k \leq 9$, $-21 \leq l \leq 22$; data collected, 11 940; unique data, 3029 ($R_{int} = 0.1013$); no. of data, $F_o{}^2 \geq 4s(F_o{}^2)$: 1664; no. of variables, 109; max/min trans, 0.5743/0.1176; final R1/wR2 [$I > 2s(I)$] = 0.0499/0.0800; GoF = 0.913; max diff peak/hole, +1.324/−1.662 e Å^{-3}. (c) *SMART*, Version 5: Siemens Analytical X−ray Systems, Inc.; Madison, WI, 1998. (d) SAINT, Version 4: Siemens Analytical Systems, Inc.: Madison, WI, 1994−1996. (e) Sheldrick, G. M. *SADABS*; University of Göttingen, Germany. (f) Sheldrick G. M. *SHELXTL*, Version 5.1; Siemens Analytical Systems, Inc.: Madison, WI, 1997.

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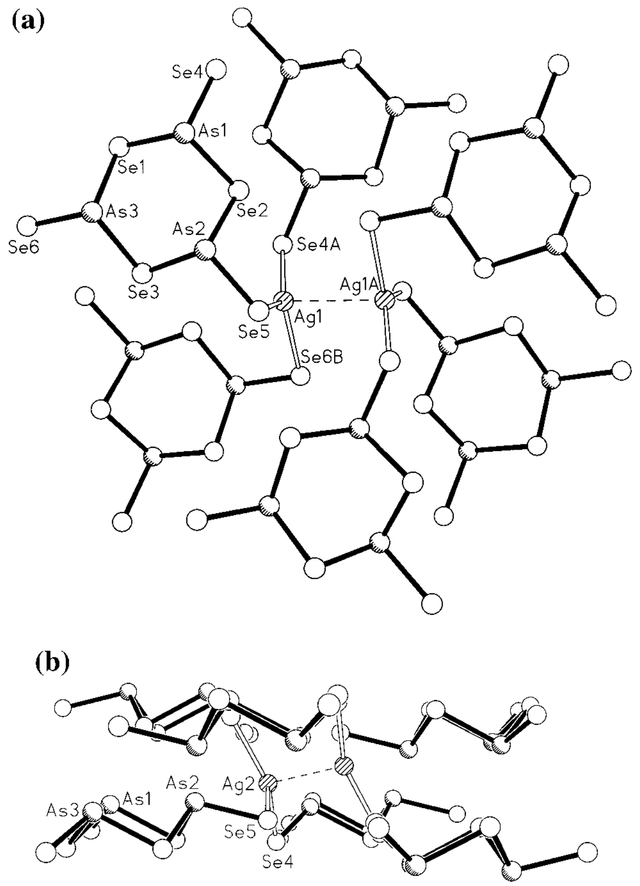

Figure 2. Coordination of the Ag···Ag dumbbell units in $RbAg_2As_3Se_6$ with the six-membered $[As_3Se_6]^{3-}$ ring revealing a chair conformation. (a) Ag1···Ag1 from [010] direction; (b) Ag2···Ag2 from [100] direction. The trigonal planar coordination environments in both units are very similar, with the latter (Ag2) being more distorted toward a linear $AgSe_2$ coordination. The distances (Å) of the $AgSe_3$ triangle atoms from its least-squares plane are as follows: for (a) Ag1, +0.1226; Se, 4−0.0447; Se5, −0.0481; Se6, −0.0297; (b) Ag2, +0.2881; Se4, −0.1190; Se5, −0.0455; Se6, −0.1236. Selected bond distances [Å] and angles [deg] are (a) Ag1···Ag1, 3.033(3); Ag1−Se4, 2.582(2); Ag1−Se5, 2.565(2); Ag1−Se6, 2.720(2); Se6−Ag1−Se4, 104.17(6); Se4−Ag1−Se5, 139.89(7); Se5−Ag1−Se6, 114.65(7). (b) Ag2···Ag2, 2.927(4); Ag2−Se4, 2.574(2); Ag2−Se5, 2.850(2); Ag2−Se6, 2.547(2); Se6−Ag2−Se4, 149.69(9); Se4−Ag2−Se5, 97.25(6); Se5−Ag2−Se6, 104.26(6). The Ag−Ag−Se angles range from 66.70° to 114.65°. Bond distances and angles within the $[As_3Se_6]^{3-}$ ring: As1−Se1, 2.412(2); As1−Se2, 2.430(2); As1−Se4, 2.349(2); As2−Se2, 2.412(2); As2−Se3, 2.433(2); As2−Se5, 2.358(2); As3−Se1, 2.438(2); As3−Se3, 2.420(2); As3−Se6, 2.345(2); Se−As−Se angles range from 95.13° to 102.81°; As−Se−As angles, from 89.49° to 91.06°.

worth mentioning that all Ag^+ atoms exhibit relatively short Ag···Ag distances (see Figure 2), with Ag2···Ag2 at 2.927(4) Å and Ag1···Ag1 at 3.033(3) Å. The former value is comparable with the Ag−Ag distance of 2.89 Å in the element structure.[9] Considering that one of the three $Ag-Se_t$ bonds is significantly longer than the other two, these short Ag···Ag interactions presumably cause the distortion[10] of the trigonal planar $AgSe_3$ coordination toward a linear $AgSe_2$ coordination, see Figure 2.

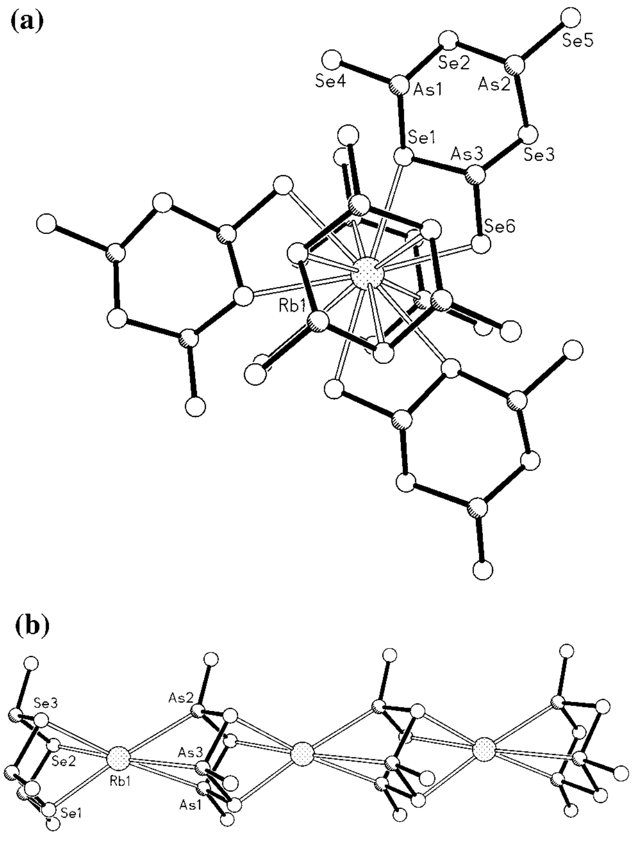

Figure 3. (a) Coordination of the Rb^+ cation in $RbAg_2As_3Se_6$ (distances [Å] are as follows: Rb−As, 3.839(2)−4.009(2); Rb−Se, 3.527(2)−3.898(2)). (b) The crown-like coordination forms polar $^{1}_{\infty}[Rb(As_3Se_6)]^{2-}$ columns running down the *b* axis of the unit cell.

The Rb^+ cation is embedded in octahedral holes made of two $[As_3Se_6]^{3-}$ rings, which coordinate in an unusual crown-ether like manner, see Figure 3. Such crown-ether like coordination modes of alkali metals with chalcogen containing ring molecules are known from several examples, e.g. $[Rb(Se_8)]^+$ or $[Cs(Te_8)]^+$ columns in Rb_2PdSe_{16}[11] and Cs_4Te_{28},[12] respectively. The unique feature of the Rb^+ bonding in $RbAg_2As_3Se_6$ is that the coordination mode is *asymmetric* in that one ring coordinates with its Se_b atoms, while the other one with its As atoms. The coordination number of twelve is completed by three Se_t and three Se_b atoms of additional $[As_3Se_6]^{3-}$ units. Considering the crown-ether like coordination mode and its asymmetry, the structure of $RbAg_2As_3Se_6$ can be described more vividly as *polar* $^{1}_{\infty}[Rb(As_3Se_6)]^{2-}$ columns running down the *y* direction of the unit cell and held together by Ag^+···Ag^+ dumb-bell units (see Figures 2B and 1). However, the compound is not polar, since the three neighbors of each column are arranged in an antiparallel manner. Therefore the presence of formally "Ag_2^{2+}" in $RbAg_2As_3Se_6$ is more significant than in other silver-selenidoarsenates, where these contacts are rather forced by other structure units, e.g. by small Ag_2Se_2 four-membered rings in $A_2AgAs_3Se_6$ (A = K, Rb).[5] In $(Me_4N)_2Ag_2Ge_4S_{10}$, isolated adamantane units $[Ge_4S_{10}]^{4-}$ are also connected into a framework $^{3}_{\infty}[Ag_2Ge_4S_{10}]^{2-}$ by Ag_2^{2+} units, but due to a lower coordination number of the Ag atoms to only two S_t atoms of the adamantane clusters, the Ag···Ag contacts are much stronger than in our case (2.761 Å).[13]

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(10) The anisotropy of the temperature factors for Ag2 is significantly greater than for Ag1, with its strongest component being along the Ag···Ag direction, i.e. about double of the components in the other two main directions of the ellipsoid. This is a common feature in Ag-containing compounds with d^{10}···d^{10} interactions and has been attributed to anharmonic thermal vibrations of these atoms.

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$RbAg_2As_3Se_6$ is somewhat comparable to $(Me_4N)_2Rb[Bi(As_3S_6)_2]$[14] in that the "$Ag_2^{2+}$" units are replaced by octahedrally coordinated Bi^{3+} atoms. Since only half of the linking atoms are present, and the rings are arranged differently in the crystal structure, the linkage leads to $^2_\infty[Bi(As_3S_6)_2]^{3-}$ double layers.

$RbAg_2As_3Se_6$ is a kinetic product which forms early in the methanolothermal reaction. An important and interesting part of selenoarsenate chemistry are the possible different condensation pathways of the initial $[AsSe_3]^{3-}$ units. Short reaction times can lead to products in which only a few condensation steps have occurred, whereas prolonged times seem to favor products with infinite condensation, such as $^1_\infty[AsSe_2]^-$ chains. However, packing forces between the various components and the pH of the medium are also important factors in determining the choice of a structure type. The combination of these factors produces a complex multidimensional parameter system whose exploration is still unmapped, rendering the prediction of new compositions and structure types rather difficult.

Acknowledgment. Support from the National Science Foundation CHE 96-33798 (Chemistry Research Group) and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Part of this work was carried out using the facilities of the Center for Electron Optics of Michigan State University. M.W. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral research fellowship.

Supporting Information Available: Tables of crystallographic details, anisotropic thermal ellipsoid plots, a figure of the unit cell of $RbAg_2As_3Se_6$ from [100] direction, fractional atomic coordinates, isotropic and anisotropic thermal parameters, and interatomic distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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