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[29] **24**: colorless crystals, m.p. 203–205 °C (decomp); IR: $\tilde{\nu} = 2090$ cm^{-1} (C≡C); ^{1}H NMR (60 MHz, [D_5]pyridine): $\delta = 7.1$–8.0 (m, 30H, aromatic H); ^{13}C NMR (100.4 MHz, [D_5]pyridine): $\delta = 71.3$ (d, ^1J(P,C) = 186.2 Hz, C_α), 122.3 (d, ^1J(P,C) = 99.2 Hz, *ipso*-C, P-phenyl), 124.4 (s, *para*-C, B-phenyl), 127.3 (s, *ortho*-C, B-phenyl), 130.3 (d, ^3J(P,C) = 13.7 Hz, *meta*-C, P-phenyl), 133.3 (d, ^2J(P,C) = 12.2 Hz, *ortho*-C, P-phenyl), 134.8 (d, ^4J(P,C) = 3.0 Hz, *para*-C, P-phenyl), 135.5 (s, *meta*-C, B-phenyl), 157.6 (s, *ipso*-C, B-Phenyl); ^{31}P NMR (161.7 MHz, [D_5]pyridine): $\delta = 0.04$; ^{11}B NMR (128 MHz, C_6D_6): $\delta = -11.2$.

A Three-Dimensional Framework with Accessible Nanopores: $RbCuSb_2Se_4 \cdot H_2O$**

Jason A. Hanko and Mercouri G. Kanatzidis*

The synthesis of nonoxidic chalcogen-based open frameworks is motivated by the prospect of obtaining interesting semiconducting analogues of zeolites.[1] Planned syntheses of open-framework structures based on germanium and tin sulfides were reported in 1989.[2] This discovery led to a rapid expansion in this area, and compounds such as $[Et_4N]_2Cu_2Ge_4S_{10}$,[3] $[Me_4N]_2MGe_4S_{10}$ (M = Mn,[4,5] Fe,[5,6] Co,[5] Zn[5]), and $[Me_4N]_6(Cu_{0.44}Ge_{0.56}S_{0.73})Ge_4S_{10}$[7] were prepared. Hydrothermal synthesis is a common route to these materials. Solid-state lattices can be generated by the self-assembly of the appropriate molecular building blocks in the presence of organic template ions. Using this approach, we have demonstrated that $[EQ_3]^{3-}$ (E = As, Sb; Q = S, Se) units are versatile building blocks from which interesting compounds such as KBi_3S_5,[8] $[Ph_4P]InSe_{12}$,[9] $[Me_4N]HgAs_3S_6$,[10] $[Me_4N]RbBiAs_6S_{12}$,[11] and $[Co(en)_3]CoSb_4S_8$[12] can be made. A transition metal is not necessary for the formation of extended structures. Several of these germanium,[13] tin,[14–22] and antimony sulfide[23, 24] frameworks are also accessible by condensation of molecular building blocks.

Here we report on the new three-dimensional material $RbCuSb_2Se_4 \cdot H_2O$ (**1**), which was prepared by heating CuCl with Rb_3SbSe_3[25] and Ph_4PBr in H_2O at 130 °C. The black needlelike crystals are insoluble in common organic solvents. Compound **1** has a three-dimensional framework in which tetrahedral Cu centers are connected to both pyramidal $SbSe_3$ and square-pyramidal $SbSe_5$ units.[26] The novel feature of this framework is the presence of large channels running along the [010] direction (Figure 1). The channels have an irregular cross section with dimensions of 11.29 × 10.52 × 8.16 Å (Figure 2). Another unique feature is the presence of two kinds of $[SbSe_2]_n^{n-}$ chains which run parallel to the channels. One is a single $[SbSe_2]_n^{n-}$ chain of corner-sharing pyramids in which all of the terminal Se centers on the same side; the Sb–Se bond lengths range from 2.556(4) to 2.726(3) Å (av 2.66(5) Å), and the Se-Sb-Se angles from 95.5(1) to 99.1(1)°. The other contains associated double $\{[SbSe_2]_2\}_n^{2n-}$ chains with Sb–Se bond lengths in the range 2.585(4)–2.972(3) Å (av 2.83(8) Å) and Se-Sb-Se angles between 84.8(1) and 173.9(1)°. Such double chains are also found in Sb_2Se_3.[27] Figure 2 highlights the two different $[SbSe_2]_n^{n-}$ chains. The $[SbSe_2]_n^{n-}$ single chains are connected to the Cu atoms to give corrugated $CuSbSe_2$ sheets composed of alternating rows of tetrahedrally coordinated Cu and pyramidally coordinated Sb units. These sheets are held together by the $\{[SbSe_2]_2\}_n^{2n-}$ double chains, which complete the tetrahedral coordination sphere of the Cu atoms

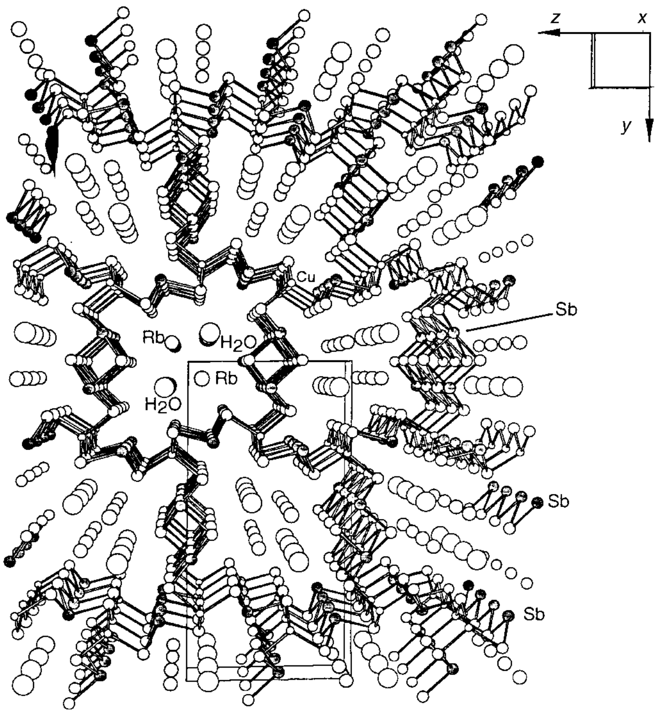

Figure 1. View of the structure of **1** along the *b* axis showing the channels occupied by the rubidium centers and water molecules.

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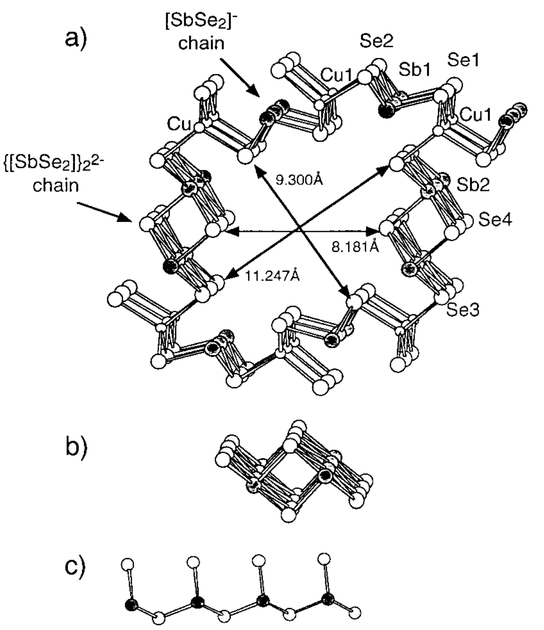

Figure 2. a) Section of the framework of **1** (Rb cation and water molecule omitted for clarity) with selected bond lengths [Å] and angles [°]: Cu(1)–Se(1) 2.489(3), Cu(1)–Se(1′) 2.489(3), Cu(1)–Se(2) 2.499(6), Cu(1)–Se(4) 2.480(5), Sb(1)–Se(1) 2.556(4), Sb(1)–Se(2) 2.726(3), Sb(1)–Se(2′) 2.726(3), Sb(2)–Se(3) 2.585(4), Sb(2)–Se(3′) 2.972(3), Sb(2)–Se(3″) 2.972(3), Sb(2)–Se(4) 2.823(3), Sb(2)–Se(4′) 2.823(3); Se(2)-Sb(1)-Se(1) 99.1(1), Se(2′)-Sb(1)-Se(1) 99.1(1), Se(2)-Sb(1)-Se(2′) 95.5(1), Se(3)-Sb(2)-Se(4) 89.7(1), Se(3)-Sb(2)-Se(3′) 84.8(1), Se(4)-Sb(2)-Se(4′) 91.2(1), Se(4)-Sb(2)-Se(4) 88.5(1), Se(3)-Sb(2)-Se(4) 91.3(1), Se(3)-Sb(2)-Se(4) 173.9(1), Se(4)-Cu(1)-Se(1) 110.6(1), Se(1)-Cu(1)-Se(1′) 108.4(1), Se(2)-Cu(1)-Se(4) 108.4(1), Se(2)-Cu(1)-Se(1) 109.4(1). b) View of the $[SbSe_2]_2^{2-}$ double chain. c) View of the $[SbSe_2]_n^{n-}$ single chain.

and form the three-dimensional framework. The Cu centers have a slightly distorted tetrahedral coordination environment. The Cu–Se bonds range from 2.480(5) to 2.499(6) Å, and the Se-Cu-Se angles from 108.4(1) to 110.6(1)°.

Thermogravimetric analysis (TGA, Figure 3) showed two significant weight loss steps. A one-step mass loss of 2.65 % at 200 °C corresponds to the loss of the water molecule (calcd 2.47 %). This was followed by a one-step mass loss, with a shoulder, of 22.48 % at 380 °C, corresponding to the loss of two Se atoms (calcd 22.33 %). The X-ray diffraction pattern of the remaining powder, which had been heated to 600 °C, indicated the presence of a crystalline solid; however, it did not match that of Sb_2Se_3 or any known Cu/Se or Cu/Sb/Se phase. The thermal stability of the material after loss of the water molecule was investigated by interrupting the TGA at 300 °C and cooling to room temperature. The powder X-ray diffraction pattern of the residue did not match that of **1**, showing that the loss of the water molecule results in the collapse of the framework. Compound **1** exhibits topotactic ion-exchange properties, a key criterion for assessing the performance of the framework as a host. The facile removal of Rb^+ ions indicates substantial mobility of the alkali metal ions and water molecules in the tunnels. By using a mild solid-state exchange method developed by us,[28] the Rb^+ cations can readily be exchanged with other, smaller cations such as Li^+, Na^+, and NH_4^+, which were used in the form of their iodides. The degree of exchange was determined by energy dispersive spectrosopy (EDS). The compositions of the exchanged materials were $Rb_{0.2}Li_{0.8}CuSb_2Se_4$, $Rb_{0.2}Na_{0.8}CuSb_2Se_4$, and $Rb_{0.4}(NH_4)_{0.6}CuSb_2Se_4$, for the Li^+, Na^+, and NH_4^+ ions, respectively.

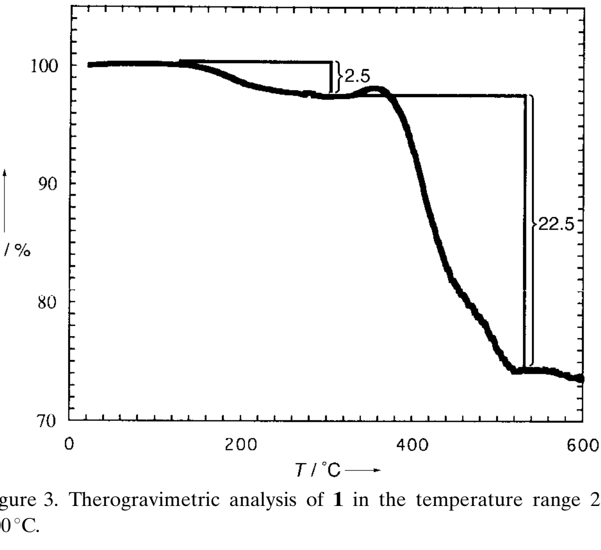

Figure 3. Therogravimetric analysis of **1** in the temperature range 25–600 °C.

The optical spectrum of **1** reveals the presence of a sharp optical gap of 1.32 eV, which suggests that the material is a semiconductor. The far-IR spectrum of **1** shows a broad absorption around 211 cm^{-1}, which can be tentatively assigned to Cu–Se stretching modes. The Raman spectrum of **1** displays a single strong band at about 233 cm^{-1}, which is assigned to Sb–Se stretching modes, and two shoulders at about 209 and 186 cm^{-1}, which are assigned to Cu–Se stretching vibrations.

Compound **1** has a unique structure and is the first example of a quaternary selenoantimonate with an open three-dimensional framework and proven ion-exchange properties.

Experimental Section

1 was synthesized by heating a mixture of CuCl (0.01 g, 0.10 mmol), Rb_3SbSe_3 (0.186 g, 0.30 mmol), Ph_4PBr (0.168 g; 0.40 mmol), and H_2O (0.2–0.5 mL) at 130 °C for 3 d in a sealed Pyrex tube. The product was isolated by washing with copious degassed methanol and dried with ether. The resulting product was a 50/50 mixture of black needles of $RbCuSb_2Se_4 \cdot H_2O$ and red platelets. The SEM/EDS analysis of the red platelets gave an average composition of $PCu_{2.0}Sb_{3.3}Se_{3.2}$, which suggests that they contains Ph_4P^+ ions.

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[26] a) Crystal structure analysis of **1**: $T = -148\,^{\circ}\mathrm{C}$, orthorhombic, space group *Pnma* (no. 62), $a = 11.0765(1)$, $b = 4.0369(2)$, $c = 21.4629(8)$ Å, $V = 956.73(5)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 5.027\ \mathrm{g\,cm^{-3}}$, crystal dimensions $0.24 \times 0.01 \times 0.01$ mm, $\mu(\mathrm{Mo_{K\alpha}}) = 27.92\ \mathrm{cm^{-1}}$, $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å), Siemens SMART Platform CCD diffractometer, data collection at 10 s per frame; Lorentzian, polarization, and empirical absorption corrections[26b] were applied (min./max. transmission = 0.719); index ranges $-12 \leq h \leq 13$, $-22 \leq l \leq 26$, $-3 \leq k \leq 5$, $2\theta_{\max} = 55.1^{\circ}$; of 5058 measured reflections, 1150 were independent ($R_{\mathrm{int}} = 0.179$). The structure was solved by direct methods and refined with the SHELXTL-5[26c] package of programs, refinement on F^2, 59 variables, $R = 0.0767$, $wR2 = 0.1518$, GOF = 1.150, min./max. reidual electron density $+4.443/-2.691\ \mathrm{e\,Å^{-3}}$ for data with $F_o^2 > 2\sigma(F_o^2)$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: int. code +(49)7247-808-666 (Frau S. Höhler-Schlimm); E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407337; b) H. R. Blessing, *Acta. Crystallogr. Sect. A* **1995**, *51*, 175–189. c) G. M. Sheldrick, SHELXTL: Version 5, Siemens Analytical X-ray Instruments Inc., Madison, WI 53719, **1994**.

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Generation and Trapping Reactions of a Formal 1:1 Complex between Singlet Carbon and 2,2′-Bipyridine[**]

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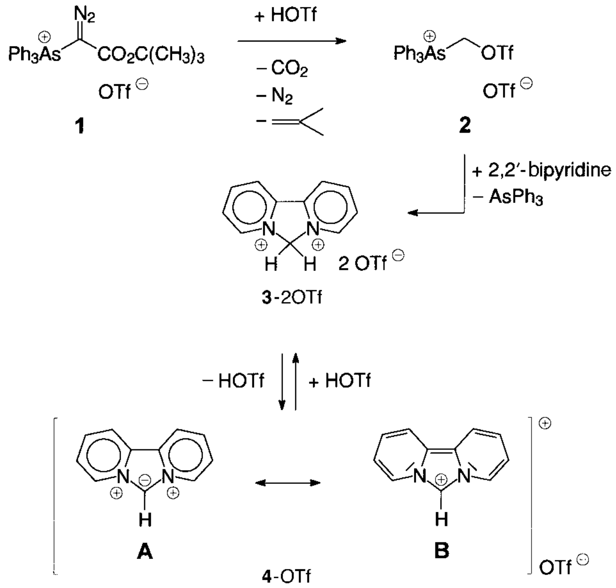
Dedicated to Professor George A. Olah
on the occasion of his 70th birthday

2,2′-Bipyridine is a classical chelating ligand for metals as well as nonmetals in different oxidation states and bonding types.[1,2] However, to our knowledge analogous complexes are unknown for all oxidation states of carbon. Here we report a first compound of this kind. In 1994 we described the first S_N reactions at the α-carbon atom of aryliodonio diazo compounds.[3] Using $AsPh_3$ as nucleophile, we obtained the diazo compound **1**, which served as starting material for the new class of compounds.

The reaction of **1** with trifluoromethanesulfonic acid (HOTf, Scheme 1) afforded the arsonium salt **2** in high yield as the result of an acid-induced fragmentation of the *tert*-butyl ester functionality, followed by a proto-dediazonation.[4] Compound **2** is a potent 1,1-bis(electrophile) which reacted with a host of neutral nucleophiles to form symmetrical and unsymmetrical geminal bis(onio)-substituted salts.[5] Accordingly, the reaction of **2** with 2,2′-bipyridine provided the cyclic bis(onio)-substituted salt **3**-2 OTf, a bis(azonia) analogue of fluorene. Under the reaction conditions, this C–H-acidic



Scheme 1. Synthesis of **3**-2 OTf and its deprotonation to **4**-OTf.

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