$Rb_2Au_6Sb_4S_{10}$: a novel sulfosalt with two different interpenetrating anionic frameworks: $[Au_3Sb_4S_8]^-$ and $[Au_3S_2]^-$

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The layered compound $Rb_2Au_6Sb_4S_{10}$ consisting of two interpenetrating $[Au_3Sb_4S_8]^-$ and $[Au_3S_2]^-$ frameworks was prepared from the reaction of Au with a polythioantimonate flux.

Polychalcoantimonate fluxes can be used for the synthesis of new ternary and quaternary thioantimonate and selenoantimonate compounds.[1–4] This method is complementary to conventional direct combination of the binary sulfides[5] or hydro(solvento)thermal synthesis.[6] The polychalcoantimonate fluxes are formed by the *in situ* fusion of $A_2Q/Sb/Q$ and contain $[Sb_xQ_y]^{n-}$ ligands (A = Na, K, Rb, Cs; Q = S, Se) as well as polychalcogenide ligands. The key feature of this method is that the polychalcoantimonate units form and coordinate to metal ions to build up extended lattices. Examples include A_2AgSbS_4 (A = K, Rb, Cs),[3,4] $Cs_3Ag_2Sb_3Q_8$ (Q = S, Se),[3,4] $KThSb_2Se_6$,[2] A_2AuSbS_4 (A = Rb, Cs)[3b] and $KHgSbS_3$.[7] Continuing our investigations of the coinage metals, particularly Au, we report here, the synthesis, structural characterization, and physical properties of a novel quaternary gold thioantimonate compound, $Rb_2Au_6Sb_4S_{10}$.‡ The novelty in this two-dimensional compound derives from the fact that its layers are comprised of two different and independent interwoven frameworks. The only other structurally characterized example of two interpenetrating frameworks is K_2PdSe_{10}.[8]

The strikingly complex structure of $Rb_2Au_6Sb_4S_{10}$§ is composed of two different interpenetrating layered frameworks, $[Au_3Sb_4S_8]^-$ and $[Au_3S_2]^-$, Fig. 1. As a result, $Rb_2[Au_3Sb_4S_8][Au_3S_2]$ is a more descriptive formula, and to the best of our knowledge, represents the first reported example of a compound in which a binary framework is interpenetrating with a ternary one. The $[Au_3Sb_4S_8]^-$ layer is strongly undulating and consists of infinite $[Sb_4S_7]^{2-}$ one-dimensional chains bound to $[Au_3S]^+$ units. The $[Sb_4S_7]^{2-}$ chain [Fig. 2(*a*)] is comprised of four condensed SbS_3 pyramids forming a twelve membered Sb–S ring. Two of the SbS_3 units share two corners leaving one terminal sulfide while the other two SbS_3 units share all three corners. The dimensions of the ring are 6.49(3) Å [Sb(4)–Sb(2)] by 7.83(3) Å [Sb(1)–Sb(3)]. The chains alternate above and below the layer in a staggered fashion [Fig. 2(*b*)]. The Sb atoms are in pyramidal coordination with Sb–S distances in the range from 2.21(6) to 2.65(6) Å [mean 2.46(3) Å] and compare well with those reported for $Cs_2Sb_4S_8$[1] and $Cs_3Ag_2Sb_3S_8$.[3,4] The discrete $[Au_3S]^+$ unit has a pyramidal sulfide linked to three linear Au^+ cations. The Au–S distances range from 2.28(4) to 2.46(5) Å and compare well with those found in $CsAu_3S_2$,[9a] $AAuS$[9b] (A = Na, K, Rb, Cs), $KAuS_5$[10] and $AAuSbS_4$[3] (A = Rb, Cs). The S–Au–S angles range from 170 to 174°.

The second framework, which is interwoven with the one described above is a $[Au_3S_2]^-$ layer. The $[Au_3S_2]^-$ layer is puckered with twelve-membered Au–S rings in an *anti*-B_2O_3 motif {ring dimensions: 6.91(2) Å [Au(4)$\cdots$Au(4)] by 7.19(3) Å [Au(3)$\cdots$Au(3)]}. Fig. 3(*a*) highlights the pyramidal sulfide and the puckered nature of the layer and Fig. 3(*b*) shows a perpendicular view. The Au–S distances are in the range from 2.25(4) to 2.46(5) Å and the S–Au–S angles range from 165 to 178°. The $[Au_3S_2]^-$ layered structure is similar but not identical to that observed in $CsAu_3S_2$.[9a]

Upon further inspection, it was observed that the Au^+ centers in $Rb_2Au_6Sb_4S_{10}$ aggregate to form a column that runs along the *c*-axis. There are two types of Au$\cdots$Au interactions: those at $\leqslant$3.25 Å and those between 3.25 and 3.6 Å. Fig. 3(*c*) shows a view perpendicular to these Au-based columns. In Fig. 3(*c*) the interactions $\leqslant$3.25 Å are represented as solid lines while the Au$\cdots$Au interactions between 3.25 and 3.60 Å are represented as dashed lines. The layers are separated by ten-coordinate $Rb(1)^+$ [Rb(1)–S (mean) 3.59(3) Å] and eight-coordinate Rb(2) $[Rb(2)^+$ [Rb(2)–S (mean) 3.50(3) Å].

The optical spectrum of $Rb_2Au_6Sb_4S_{10}$ reveals the presence of a sharp optical gap of 1.37 eV, suggesting the material is a semiconductor.

The far-IR spectrum¶ of $Rb_2Au_6Sb_4S_{10}$ displays absorptions at *ca*. 377 and 350 cm^{-1} which can be tentatively assigned to Sb–S stretching modes in the 'Sb_2S_4'-like backbone of the $[Au_3Sb_4S_8]^-$ framework.[1,3] Absorptions in the range 381–347 cm^{-1} are tentatively assigned to the Sb–S vibrational stretching modes by analogy with the $Cs_2Sb_4S_8$[1] and $Cs_3Ag_2Sb_3S_8$.[3] Absorptions below 347 cm^{-1} are assigned to Au–S vibrations as compared to Rb_2AuSbS_4.[3] By comparison with $KAuS_5$ the absorption at *ca*. 323 cm^{-1} is assigned as an Au–S stretching vibration.[10] The Raman spectrum¶ of $Rb_2Au_6Sb_4S_{10}$ displays absorptions in the range 377–350 cm^{-1} which are assigned to

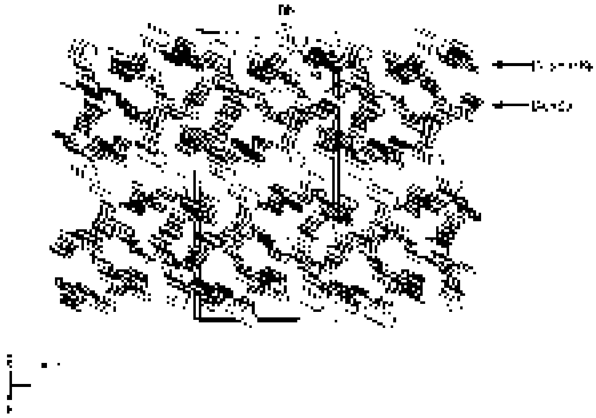

Fig. 1 Structure of $Rb_2Au_6Sb_4S_{10}$ viewed down the *c*-axis. Selected distances (Å) and angles (°) with esds in parentheses: Au(1)–S(3) 2.32(1), Sb(1)–S(6) 2.43(2), Au(1)–S(5) 2.30(1), Sb(1)–S(8) 2.47(1) (×2), Au(2)–S(2) 2.28(2), Sb(2)–S(5) 2.54(2), Au(2)–S(4) 2.30(2), Sb(2)–S(1) 2.48(1) (×2), Au(3)–S(3) 2.32(1), Sb(3)–S(6) 2.58(2), Au(3)–S(7) 2.31(1), Sb(3)–S(1) 2.48(1) (×2), Au(4)–S(3) 2.29(2), Sb(4)–S(4) 2.40(2), Au(4)–S(7) 2.30(2), Sb(4)–S(8) 2.47(1) (×2), Au(1)–Au(3) 3.192(3), Au(1)–Sb(1) 3.393(5), Au(1)–Au(4) 3.060(4), Au(1)–Sb(3) 3.233(5), Au(2)–Au(4) 3.593(1), Au(2)–Sb(2) 3.091(6), Au(1)–Au(1′) 3.588(4), Au(2)–Au(3) 3.389(4), Au(3)–Au(3′) 3.461(5), Au(3)–Au(4) 3.558(3); S(2)–Au(1)–S(5) 170.9(7), S(1)–Sb(3)–S(1′) 89.4(7), S(2)–Au(2)–S(4) 173.9(8), S(1)–Sb(3)–S(6) 95.6(5), S(3)–Au(3)–S(7) 178.4(7), S(1′)–Sb(3)–S(6) 95.6(5), S(3)–Au(4)–S(7) 170.0(8).

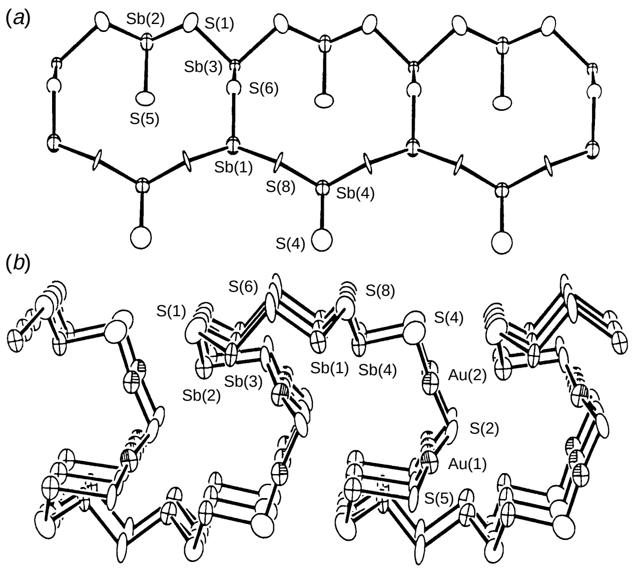

Fig. 2 (*a*) ORTEP view of the $[Sb_4S_7]^{2-}$ chain with labelling; (*b*) ORTEP view of the complete $[Au_3Sb_4S_8]^-$ framework with labelling

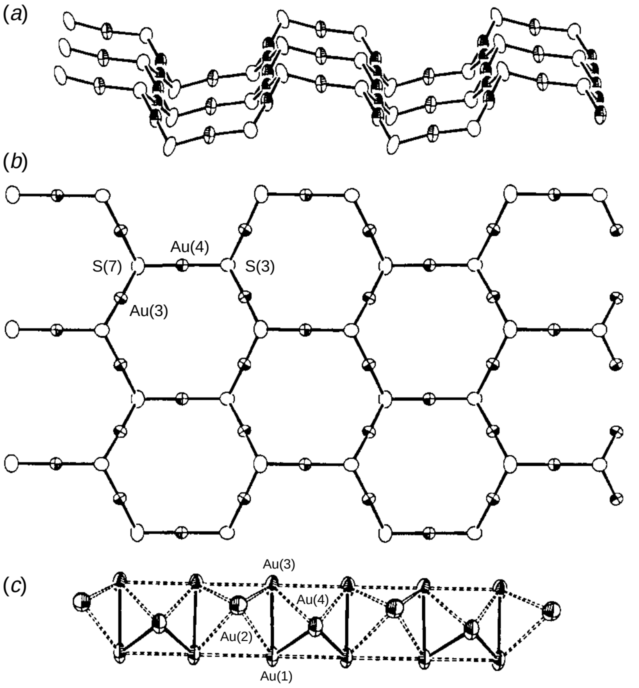

Fig. 3 (*a*) ORTEP view of the $[Au_3S_2]^-$ layer highlighting the pyramidal sulfides in the undulating layer; (*b*) perpendicular view of the $[Au_3S_2]^-$ layer with labelling; (*c*) Au···Au interactions of the Au column

Sb–S modes and the absorptions below 350 cm^{-1} are assigned to Au–S stretching vibrations.

DTA data, followed by careful XRD analysis of the residues, show that $Rb_2Au_6Sb_4S_{10}$ melts incongruently at *ca.* 442 °C. Examination of the residue by powder XRD revealed that the compound decomposes to an amorphous material and Au metal.

In conclusion, $Rb_2Au_6Sb_4S_{10}$ represents the first example of a sulfosalt with two different interpenetrating anionic frameworks. Although one of the frameworks $[Au_3S_2]^-$ can exist by itself, efforts to isolate the second framework alone are in progress.

Financial support from the National Science Foundation DMR-9527347 is gratefully acknowledged. M. G. K. is an A. P. Sloan Foundation, and a Camille and Henry Dreyfus Teacher Scholar 1993–98. The authors are grateful to the X-ray Crystallography Laboratory of the University of Minnesota and to Dr Victor G. Young, Jr. for collecting the single crystal X-ray data set. This work made use of the SEM facilities of the Center for Electron Optics at Michigan State University.

Notes and References

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‡ $Rb_2Au_6Sb_4S_{10}$ was synthesized from a mixture of Rb_2S (0.102 g, 0.5 mmol), Au (0.098 g, 0.5 mmol), Sb (0.031 g, 0.25 mmol) and S (0.064 g, 2 mmol) sealed under vacuum in a Pyrex tube and heated to 350 °C for 4 days followed by cooling to 150 °C at 4 °C h^{-1}. The excess $Rb_x[Sb_yS_z]$ flux was removed by washing with DMF to reveal analytically pure black needles in low yield (20% yield based on Sb). The crystals are air- and water-stable. Microprobe analysis carried out on several randomly selected crystals gave an average composition of $RbAu_{4.6}Sb_{2.7}S_9$. This technique tends to underestimate the amount of Rb.

§ *Crystallography*: A Siemens SMART Platform CCD diffractometer equipped with Mo-Kα was used for a crystal of 0.400 × 0.010 × 0.005 mm. An empirical radiation (λ = 0.710 73 Å) absorption correction was applied to the data during data processing. *Crystal data* at −120 °C: a = 12.4402(2), b = 26.0790(4), c = 6.9614(1) Å, U = 2258.3(7) Å^3, Z = 4, D_c = 4.043 g cm^{-3}, space group *Pnnm* (no. 63), μ = 48.83 cm^{-1}, index ranges $-14 \leqslant h \leqslant 14$, $-31 \leqslant k \leqslant 28$, $-8 \leqslant l \leqslant 8$; total data 15609; unique data 2340 (R_{int} = 0.146), data with $F_o^2 > 3\sigma(F_o^2)$ 1181; no. of variables, 124; final R, R_w = 0.080, 0.096; GOF 2.66; max. peak in difference electron density map = 7.97 e$^-$ Å^{-3}. The structure was solved with SHELXS-86 and refined with the TEXSAN Structure Analysis Package (Molecular Structure Corporation, 1985) of crystallographic programs. CCDC 182/760.

¶ Far-IR (CsI matrix) gave absorptions at *ca.* 381w, *ca.* 359w (sh), 347m, 325m, 306w, 295w, 270s and 233w cm^{-1}. Raman spectra (ground crystals) gave absorptions at *ca.* 377w, 350s, 323m, 285w, 266m and 250s cm^{-1}.

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Received in Bloomington, IN, USA, 17th June 1997; 7/04254J

Typeset and printed by Black Bear Press Limited, Cambridge, England