

Tl₂Au₄S₃: $x = 4/3$ member of the series A_{2-x}Au_xQ. Preparation and an analysis of its gold–gold bonding

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Tl₂Au₄S₃ was synthesized by reacting gold with reactive fluxes of Tl₂S and S; its crystal structure is characterised by sheets of buckled 16-membered rings of Au and S with short Au–Au contacts between the sheets; the Au–Au bonding has been analysed through high-level band structure calculations.

The chemistry of ternary gold chalcogenides continues to attract interest because of the richness of structures displayed by them. Thus even in the simple formulation AAuQ, the anionic species found include linear, molecular AuQ₂ units in KAuQ (Q = S, Se),¹ AuQ chains in AAuQ (A = Rb, Cs and Q = S, Se, Te),² planar hexagonal Au–Te networks in AAuTe (A = Na, K),² etc. The unique feature of many of these compounds is the presence of short Au–Au distances arising from mixing of gold 5d, 6s and 6p levels; these are usually described in terms of d¹⁰–d¹⁰ interactions. Computational difficulties abound in handling an element such as gold whose electronic structure is influenced by relativistic effects, and there seem to be few high-level band structure calculations detailing the nature of bonding between gold atoms in extended solids. Much of the previous theoretical work on d¹⁰–d¹⁰ interactions has focussed on molecular systems with the exception of some alkali-metal aurides.³

We have noted short Au–Au distances in many quaternary gold chalcogenides from the A–Au–X–Q systems where X (= Ge, Sn, P, As) is a main group element that forms chalcogeno anions.⁴ Gold chalcogenides and related systems have been studied extensively during the past few years.^{4–9} In the course of these investigations we have found the first ternary gold chalcogenide with thallium (replacing the alkali metal).[‡] The compound Tl₂Au₄S₃ turns out to be the $x = 4/3$ member of the series A_{2-x}Au_xQ. With A = alkali metal and Q = chalcogen, the members with $x = 1/2$,⁶ $5/6$,⁷ $1/2$,² $6/5$,⁸ and $3/2$ ⁹ have been previously characterised. To understand the nature of the short Au–Au contacts in the title compound, we have used scalar-relativistic TB-LMTO band-structure calculations in conjunction with an analysis of the crystal orbital hamiltonian population (COHP) which we present here. Apart from the bonding situation, these compounds are of interest because they display direct band gaps suggesting uses such as in infrared detection.

The crystal structure of Tl₂Au₄S₃ is shown in Fig. 1. It is characterised by buckled sheets comprising 16-membered rings of Au and S arranged in an alternating manner. The confirmation of the rings are boat-like. The S–Au–S units in the ring are linear or nearly so. Acute Au(1)–S(1)–Au(2) angles [91.8(3)°] at the corners of the rings lead to an Au–Au distance of 3.350(1) Å within the rings. However, the stacking of the sheets along *c* results in an intersheet Au–Au distance of 3.010(1) Å. These distances are emphasised in the [100] projection by light grey lines. The Tl atoms are in a distorted trigonal S coordination and sit in the boats defined by the buckling of the Au–S sheets. They are moved off the prism centers; as a result, there are short Tl–Tl contacts of 3.307(3) Å (*cf.* Tl metal where it is about 3.36 Å¹⁰). The presence of 16-membered rings in the structure is to be contrasted to previous A_{2-x}Au_xQ structures which have (so far) been reported as having 6 ($x = 1$),^{2a} 8 ($x = 1$),^{2b} 12 ($x = 3/2$),⁹ and 24 ($x = 6/5$)^{8b}-membered rings.

Fig. 2(a) and (b) display the decomposed LMTO densities of state (DOS) of the Tl₂Au₄S₃ near the Fermi energy. It is clear from Fig. 2(a) that there is strong mixing of the s, p and d states of gold. Interestingly, despite short Au–Au contacts, the states closest to *E_F* are actually derived from a mixing of Tl 6s and S 3p [Fig. 2(b)]. Thus Tl acts not only as an inert counteranion, in contrast to the other ternaries described earlier, where K⁺, Rb⁺, etc. serve only to balance charge. This is also seen from the COHP plots displayed in Fig. 2(c). Strong Au–Au interaction leads to bonding and antibonding states below *E_F*, with the bonding states being much greater in number. Above *E_F*, the COHP is flat but slightly bonding. This is because the Au 6s and 6p states are mixed in with the 5d states. This behaviour has been previously remarked in some silver oxides.¹¹ The principle Au–Au bonding interaction around 5 eV below *E_F* arise due to Au d states as seen from the DOS. The Au–S interactions lead to well separated bonding and antibonding states below and above the *E_F*. However, the occupied states closest to *E_F* are associated with the (shorter) Tl–S distance of 2.978(1) Å. The gap between filled and empty states in the LMTO DOS is in agreement with the measured optical band gap of 1.5 eV obtained from the diffuse-reflectance spectra [Fig. 2(d)]. From the preceding discussion, the transition that causes this direct band gap is from filled Tl 6s–6p to the empty, hybridised Tl 6p–S 3p states.

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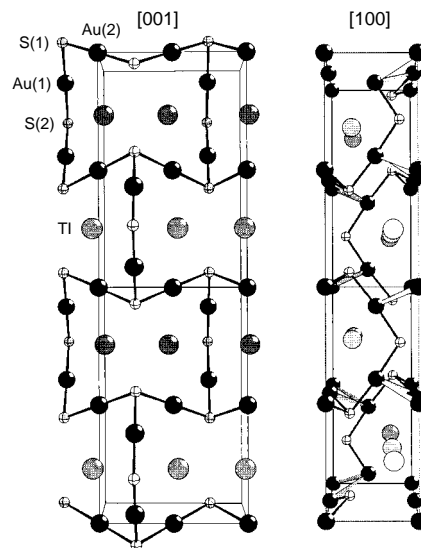


Fig. 1 [100] and [001] projection of the Tl₂Au₄S₃ structure (Tl, grey spheres; Au, black spheres; S, crossed spheres). Important bond distances and angles are given in the footnotes. Au(1)–S(2) 2.315(7), Au(1)–S(1) 2.320(9), Au(2)–S(1) 2.343(5) × 2, mean Au–S 2.330, Au(1)–Au(2) 3.0098(1) × 2, Au(1)–Au(2) 3.3502(1) × 2, Au(1)–Tl 3.152(2) × 2, Au(2)–Tl 3.2405(8) × 2, Tl–Tl 3.307(3), Tl–S(1) 3.563(8) × 2, Tl–S(1) 3.645(8) × 2, Tl–S(2) 2.978(1), Tl–S(2) 3.324(1), mean Tl–S 3.453; S(2)–Au(1)–S(1) 175.0(3), S(1)–Au(2)–S(1) 180.0, Au(1)–S(1)–Au(2) 91.8(3), Au(1)–S(2)–Au(1) 114.3(6), S(1)–Tl–S(2) 81.5(2), S(1)–Tl–S(1) 73.5(3), S(1)–Tl–S(1) 81.1(2), S(1)–Tl–S(2) 143.0(1), S(1)–Tl–S(1) 125.4(1).

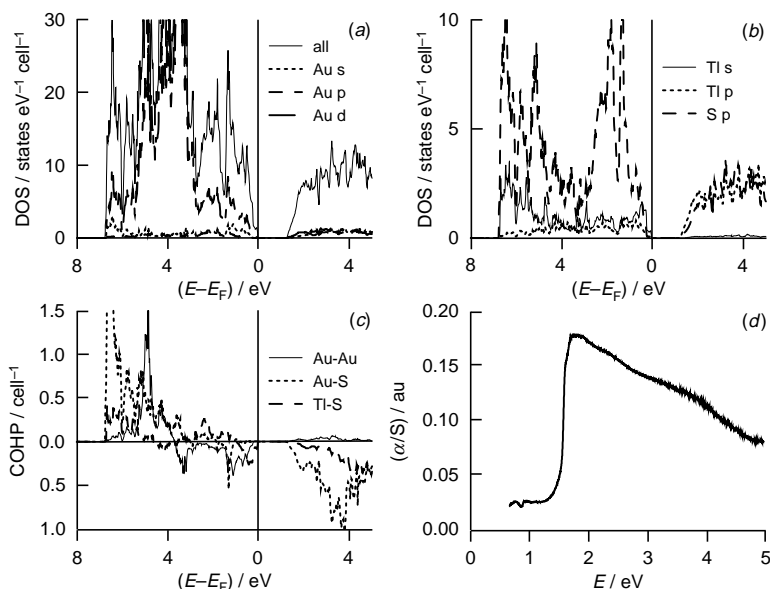


Fig. 2 Densities of states of $\text{Tl}_2\text{Au}_4\text{S}_3$ showing the Au (a) and Tl (b) contributions. (c) Crystal orbital hamiltonian populations for Au–Au, Au–S and Tl–S interactions (positive values are bonding, negative values antibonding). (d) Diffuse reflectance UV–VIS spectrum of $\text{Tl}_2\text{Au}_4\text{S}_3$ after transformation by the Kubelka–Munk function.

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Notes and References

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‡ $\text{Tl}_2\text{Au}_4\text{S}_3$ was prepared by combining 0.315 g (1.6 mmol) of Au powder, 0.176 g (0.4 mmol) Tl_2S and 0.026 g (0.8 mmol) S in a vacuum-sealed quartz tube. It was heated to 650 °C and kept at this temperature for 4 days and then cooled to room temperature at 4 °C h^{-1} . X-Ray powder patterns of the sample are single phase. IR data (KBr pellet): 1358w, 1059s, 668m, 590s, 467w, 296s cm^{-1} . Differential thermal analysis shows a congruent melting point endotherm at 436 °C and a crystallization point exotherm at 548 °C. UV–VIS–NIR spectra were acquired on a spectrometer equipped with a diffuse reflectance integrating sphere, with the sample diluted in BaSO_4 .

§ *Crystal data* for $\text{Tl}_2\text{Au}_4\text{S}_3$ at 25 °C: orthorhombic, space group $Pnmm$ (no. 59), $a = 7.507(2)$, $b = 11.919(2)$, $c = 4.688(1)$ Å, $U = 419.5(2)$ Å³, $Z = 2$, $\lambda = 0.71073$ Å, $M_R = 1292.79$, $D_c = 10.236$ g cm^{-3} , $\mu = 108.61$ mm^{-1} , platelike crystal, dark red, dimensions $0.4 \times 0.16 \times 0.14$ mm, $2\theta_{\text{max}} = 54^\circ$, data collected at 25 °C on a Nicolet P2₁ four circle diffractometer, θ – 2θ scan, absorption correction (ψ -scan), transmission factors 0.719–0.461, 975 reflections collected, 512 independent reflections, 436 reflections with $I > 2\sigma(I)$, 30 parameters. The structure was solved by direct methods (SHELXL-86). Full-matrix least-squares refinement of this model against F_o^2 (SHELXL-93) converged to final residual indices $R(R_w) = 0.055(0.112)$. CCDC 182/888.

¶ *Band structure calculations*: tight-binding linearised muffin-tin orbital (TB-LMTO)¹² calculations were carried out using version 47c of the program kindly provided by Professor O. K. Andersen. 315 irreducible k -points were used in the calculations.

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