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Ba_2AuTl_7: An Intermetallic Compound with a Novel Condensed Structure

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In this novel motif, thallium and gold atoms define a complex three-dimensional $[AuTl_7]$ polyanion in which the barium atoms fill pentagonal cages that are part of highly condensed infinite channels. Relativistic effects appear to be significant in the short Au–Tl and Tl–Tl distances and the bonding by the more electronegative gold.

Recent studies of compounds of the triels, especially indium and thallium, with active metals have generated considerable interest because of their many novel cluster and network structures.[2,3] Alkali metal systems with these two triels exhibit a considerable variety of discrete cluster anions, not just in binary compounds such as K_8In_{11}[4] and $K_{10}Tl_7$[5] but also in metal-centered clusters such as $K_8In_{10}Zn$[6] and $Na_3K_8Tl_{12}(Tl)$.[7] The same triels with the alkaline-earth metals form complex three-dimensional anionic triel networks instead in which about half as many cations are encapsulated within the polyanion net. The problems of filling space in an efficient and energetically favorable way in these are accordingly more complex than with isolated clusters, and more examples with deviations from ideal (closed band or otherwise optimized) electronic structures are found. However, only a limited number of binary and relatively few ternary triel examples are well studied in what appears to be a rich field of polar intermetallic chemistry.

In binary systems we have recently reported on the hypoelectronic compounds $SrIn_4$,[8] $BaTl_3$,[9] and Sr_3In_5[10] for which the Madelung energy and atom size matching in somewhat complex structures appear to be particularly important in structure determination and stability. (The only other structurally known triel-rich examples are $CaIn_2$ types for $SrIn_2$, $BaTl_2$, and $BaIn_2$.[8,9]) Some ternary alkaline-earth-metal−transition-metal−indium compounds with network structures, such as $CaNiIn_4$, Ca_2CuIn_3,[11] and $CaTnIn_2$ (Tn = Pd, Pt, Au),[12] have also been reported. We have recently found the first thallium members as $AeTnTl_2$, Ae = Sr, Ba, Tn = Pd, Pt[13] (orthorhombic $MgCuAl_2$ structure), as well as $BaAuTl_3$ with a $BaAl_4$-type structure.[14,15] We here report Ba_2AuTl_7 with a novel 3D structure type that contains condensed augmented pentagonal prisms in a pseudo-close-packed array. This compound was synthesized via a typical high-temperature reaction[16] and characterized by single-crystal X-ray diffraction methods in the orthorhombic space group $Pnma$ ($P\ 2_1/n\ 2_1/m\ 2_1/a$).[17]

A [010] projection of the Ba_2AuTl_7 structure along the short (5.19 Å) repeat is shown in Figure 1. The most obvious feature is the presence of two types of pentagonal prisms oriented along $\vec{b}$ and constructed of Tl and Au atoms that sandwich crystallographically different barium atoms. All atoms lie at $y = \pm^1/_4$ along the projection axis, and the two types of centering barium cations likewise alternate. Further inspection shows that all prisms are actually augmented on

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(16) Silvery Ba_2AuTl_7 was first encountered as a high-purity (>95%) single phase that resulted from a Ba:Au:Tl = 1:0.5:3.5 reaction stoichiometry run during an exploration for the correct stoichiometry of what turned out to be $BaAuTl_3$.[14] This had been reacted in a welded Nb tube jacketed in a fused silica container at 1050 °C for 5 h, quenched, reheated at 600 °C for 14 days, and finally cooled at 5 °C/h to room temperature.

(17) Single-crystal data were collected on a Bruker APEX SMART CCD-equipped X-ray diffractometer, from which space group *Pnma* (No. 62) was indicated. Absorption effects were corrected by SADABS.[18] Lattice parameters for Ba_2AuTl_7 were obtained by least squares refinements of the positions of 26 lines from Guinier film data: $a = 21.884(2)$ Å, $b = 5.1881(5)$ Å, $c = 10.462(1)$ Å, $V = 1187.8(3)$ Å^3. The structure was solved by direct methods and refined with SHELXTL.[19] The full-matrix least-squares refinement converged at R1 $[I > 2\sigma(I)] = 5.04\%$, wR2 = 13.23%, and GOF = 1.058 (see Supporting Information).

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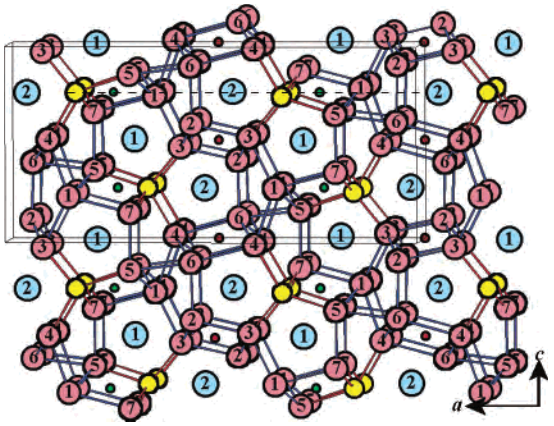

Figure 1. ~[010] view of the structure of Ba_2AuTl_7. Single cages are shown around the two Ba, which differ by b/2. The Ba, Tl, and Au atoms are blue, red-brown, and yellow, respectively.

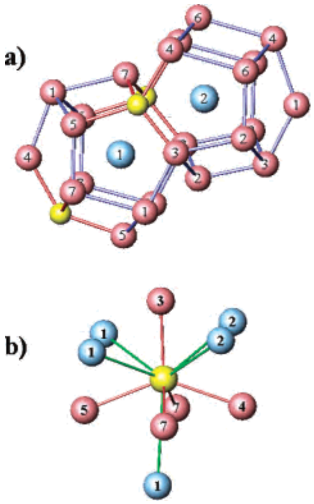

Figure 2. (a) The polyanion atoms around each type of barium atom and the common face unique to one of their interconnections. Other polyhedral pairs involve internal displacements of b/2 (see text). (b) The environment of gold in Ba_2AuTl_7, five Tl atoms and the staggered inverse arrangement of cations.

the outside by an additional ring of five more atoms that are coplanar with the central Ba, giving the cages a "fat tire" impression. (Similar augmented pentagonal prisms are also found in $SrIn_4$,[10] but their interconnections are different.) Most pairs of adjoining pentagonal prisms are correspondingly staggered in the [010] view, but one pair are coplanar and share a common plane of atoms, Tl2−Tl3(×2)−Au(×2)−Tl7. This is illustrated in Figure 2a, in which the augmentation can now be easily seen as well. The prismatic units are of course also infinitely condensed along $\vec{b}$ via four Tl atoms and one Au atom in the pentagons, the result giving a pseudo-close-packed array of chains. For all other condensation modes normal to $\vec{b}$, the outer ring atoms in one cage are inner atoms in an adjoining pentagonal prism displaced by b/2 and thus part of the condensation (see Figure 2a). Figure 1 is drawn so as to show only single pentagonal prisms and their shared atoms, around each Ba, avoiding the b-axis repeats that would generate a distracting third atom in an adjoining unit. This appears to be a unique condensation mode in triel solids, only the shared Au−Tl3 bonds paralleling types in most other networks.[10,13,14]

The detailed connections between pentagonal columns generate laddering sequences along $\vec{b}$ wherever the adjoining chains lie at different levels. These components can be seen surrounding centers of symmetry at 0, 0, 0, etc. (red dots in Figure 1) in separate Tl4, Tl6 and Tl2, Tl3 rectangles as well as those containing pairs of gold and thallium atoms (green dots). The latter lie on horizontal screw axes along x, $^{1}/_{4}$, $^{1}/_{4}$, etc. (dashed line). A perhaps easier way to follow the stacking of columns is via vertical screw axes at $^{1}/_{4}$, 0, z and so on. Among the five outer thallium atoms in cage 2 (Figure 2a), four pair (6−4, 1−3, 3−2) are also members of inner pentagonal rings in adjoined chains, whereas one gold and four thallium atoms of the outer ring in cage 1 likewise consist of inner bonds in adjoining pentagonal rings (5−Au, Au−4, and 1−7). Again, all such sharing involves cages that differ by b/2. Short bond distances are the rule in this polyanion.

The coordination polyhedra about the two Ba atoms contain 13 or 14 atoms in the polyanion over a range of 3.57−3.84 Å, two of the outer type Tl at >4.05 Å thus being excluded (Supporting Information). The Tl1 and Tl7 in the shared faces between cages, Figure 2a, are within reasonable distances of both barium atoms. There are five Tl neighbors about Au at 2.80−3.01 Å, plus five Ba neighbors in a staggered inverted figure as well, Figure 2b. Similar Au−Tl distances occur in the novel Tl_9Au_2 anion (D_{3h}) in $K_{18}Tl_{20}Au_3$ with 4-bonded Au (2.87−3.02 Å)[20] and in chains in Au_2TlP_2 (2.89−3.25 Å).[21] Even the slightly zigzag −Au−Tl− backbone chain that is phosphine-sheathed in $AuTe[Ph_2P(CH_2)S]_2$ has Tl−Au distances of 2.96 and 3.00 Å.[22] The sum of the single bond metallic radii is 2.78 Å,[23] substantially the same as the shortest observed here (2.80 Å). All thallium atoms have either 4 or 5 Tl and Au bonded neighbors. The former group, with Tl−Tl distances of 3.03−3.51 Å, is characteristic of four-bonded Tl^- in what could be a normal-valent situation, as in $SrTl_2$[24] and $SrPdTl_2$.[13] A shorter and simpler Tl−Tl σ bond, 2.95 Å, occurs in chains in Na_6TlSb_4,[25] in which the cation interactions appear important as well (the single bond metallic diameter is 2.87 Å). However, Tl1, Tl3, Tl5, and Tl6 have five Tl, Au neighbors, over which the bonding must be more delocalized in character, and these Tl−Tl distances are 3.05 to 3.51, mostly ≤3.28. Further neighbors at 3.65−3.76 Å have relatively small Mulliken overlap populations (MOP) (see discussion below).[26] The shorter Au−Tl and Tl−Tl contacts within the

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(26) The MOP values for the shorter independent Tl−Tl distances (Å) in Ba_2AuTl_7 are as follows: 3.030 (×2), 0.66 av; 3.046, 0.57; 3.086 (×2), 0.66; 3.094, 0.58; 3.10−3.20 (×3), 0.45 (av); 3.373, 0.38; 3.514, 0.33; 3.65−3.67 (×2), 0.13; 3.75, 0.08. The Tl5−Tl6 distance of 3.282 Å, with a comparatively low OP of 0.28, is not associated with the cocondensed cages (Figure 1). The Tl−Au distances are shorter by 0.2 Å or greater, appropriate to the metallic radii.

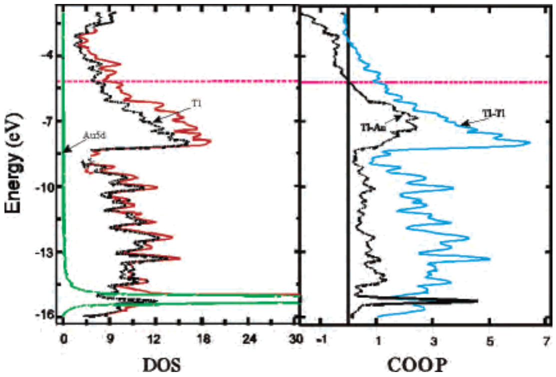

Figure 3. Densities-of-states (DOS) and the crystal orbital overlap populations (COOP) plots for Ba_2AuTl_7 (EHTB). Left: the red, black, and green lines refer to total DOS and the PDOS of Tl and of Au 5d, respectively. Right: The blue and black COOP lines mark data for all Tl−Tl bonds within 3.76 and Tl−Au contacts within 3.1, respectively.

complex $[AuTl_7]$ polyanion and, in a roughly inverse parallel, the larger overlap populations are indicative of strong (covalent) bonding interactions. Similar results pertain to $SrPdTl_2$[13] and $BaAuTl_3$.[14]

Extended Hückel tight-binding (EHTB) band calculations[27] for Ba_2AuTl_7 yield the densities-of-states (DOS) and the crystal orbital overlap populations (COOP) shown in Figure 3. A total of 144 electrons per cell fill the states up to a Fermi energy of −5.14 eV, which cuts through the broad thallium-based valence band, whereas the Tl−Au bonding is optimized (COOP curve). Narrow low-lying d bands on Au around −15 eV are core-like. Not all of the Tl−Tl bonding levels are occupied according to the COOP curve, so the phase can be considered electron-poor and metallic, quite in accord with our experience with Sr_3In_5[8] and $SrPdTl_2$.[13]

Assuming a rigid band model, two extra electrons might accordingly be bound in the valence band, and we considered whether another Tl might be substituted for the Au atom to give Ba_2Tl_8 ($BaTl_4$) in this structure. However, the X-ray powder pattern of this composition is of an unknown structure and not like that of Ba_2AuTl_7. The effective charge (Mulliken approximation) for Tl ranges between −0.07 for Tl1 and Tl4 and −0.35 for Tl3, whereas that for Au is −2.76. These are in accord with the idea that smaller Au has the larger electronegativity, 5.78 eV for Au vs 3.2 eV for Tl according to the appropriate Mulliken scale for the *neutral* atoms.[28] In effect this means that Tl 6p is partially oxidized by Au $6s^1$, although Ba is really the source of the reduction electrons, and the principal bonding is Au p−Tl p. (The Au s and Au p projections in the DOS are consistent with this, spreading over −10.0 to −14.6 and −8.3 to −3.5 eV, respectively.) The bond lengths and overlap populations all suggest that the Au−Tl and Tl−Tl interactions are strong. Moreover, the unusual cage structure gives each barium atom a substantial number of Tl and Au neighbors (13 or 14 at 3.57−3.84 Å), reflecting the importance of both the Madelung energy and atom size matching with those in the polyanion, factors that are clearly more important with dipositive cations.[8−10] As expected, Ba_2AuTl_7 is metallic, showing Pauli-like paramagnetic susceptibilities above 120 K and $\chi_{298} = 9.9 \times 10^{-5}$ emu/mol.[29] The resistivities of Ba_2AuTl_7 increase linearly with temperature, with an isotropic room temperature value of 37.4 $\mu\Omega\cdot$cm and a mean temperature dependence of 0.13% K^{-1}.[30]

Thus Ba_2AuTl_7 certainly represents a novel and remarkable structure type among polar ternary intermetallic compounds that is not formed by its congener In. Some of this novelty must certainly arise from relativistic effects.[31] Gold is famous for this,[32] showing the greatest decrease of the 6s orbital energy among the 6th period elements, but thallium shows significant contractions of the 6s and 6p orbitals as well. These energy effects are clearly reflected in the Mulliken electronegativities quoted earlier for these two elements.

Supporting Information Available: Tables of data collection and refinement parameters, positional and anisotropic displacement parameters, and distances. Plots of magnetic susceptibility and resistivity data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Electrical resistivities were measured at 34 MHz over 110−251 K by the electrodeless "Q" method on 89.0 mg of a powdered sample with grain diameters between 150 and 250 μm that was dispersed with chromatographic alumina. Data are given in the Supporting Information.

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