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# Ca<sub>5</sub>In<sub>9</sub>Sn<sub>6</sub>: Interplay of Structural and Electronic Factors between Intermetallic and Zintl Phases

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Intermetallic phases formed between elements of groups 13 and 14 with one or more of the electropositive alkali or alkaline earth metals show a rich variety of very often complex structures.<sup>1</sup> More importantly, the smooth transition of electronic properties from semiconducting Zintl phases to normal intermetallic compounds along the Zintl border provides a fertile area to search for materials with novel electronic properties and offers unique opportunities in investigating relationships between crystal structure, chemical bonding, and physical properties. In this context, the Zintl concept provides an effective and useful way to rationalize chemical bonding and electronic properties of materials in the border between metals and nonmetals.<sup>2</sup> Our most recent results using the concept in rationalizing the synthesis and discovery of ternary and quaternary compounds successfully led to the synthesis and description of SrCa<sub>2</sub>In<sub>2</sub>Ge, which contains [In=In–Ge]<sup>–6</sup> chains, analogous and isoelectronic with the allyl anion chain [CH=CH–CH<sub>2</sub>]<sub>∞</sub>.<sup>3</sup>

Electron deficiency in compounds of group 13 (trilide) post-transition elements is usually demonstrated by the formation of 3-center 2-electron bonds that leads to the formation of cluster units. The tendency of polar intermetallic tritides to form borane-like clusters is illustrated by the extensive studies on a wide variety of novel trilide cluster compounds which can be rationalized in terms of Wade's rules as in the boranes.<sup>4,5</sup> Other reports on polar intermetallic tritides have resulted in intriguing questions concerning the ability of indium to accommodate high negative charges.<sup>6,7</sup>

One challenge in inorganic chemistry is the synthesis of main group compounds, other than carbon, that exhibit unsaturation and/or aromaticity.<sup>8–11</sup> Recently, it has been reported that Sn<sub>3</sub><sup>2–</sup> cyclopropenium-like trimers, were formulated to exist in the superconducting Zintl phase BaSn<sub>3</sub> (Ni<sub>3</sub>Sn structure type).<sup>12</sup> Our exploratory syntheses on “electron-deficient” Zintl phases among tritides and tetrelides have led to the discovery of a novel phase, Ca<sub>5</sub>In<sub>9</sub>Sn<sub>6</sub>, with an unprecedented intergrowth structure featuring anionic indium trimer fragments, [In<sub>3</sub>]<sup>5–</sup>, analogous and isoelectronic with cyclopropenium, C<sub>3</sub>H<sub>3</sub><sup>+</sup>. This compound exemplifies the combination of a normal intermetallic compound and a Zintl phase and addresses important issues concerning the bonding and properties of compounds containing post-transition metals along the Zintl border.

The title compound was synthesized through high-temperature reactions of stoichiometric amounts of the pure elements (distilled Ca metal from APL Engineering Labs; In shots, 99.9999%; Sn chunks, 99.9999%) in welded Ta tubing within an evacuated quartz jacket. To obtain single crystals suitable for X-ray structure analysis, a temperature of 1050 °C was held for 5 days followed by slow cooling to about 300 °C. These shiny silver crystals with gem-like morphologies were found to be air sensitive. Hence, all syntheses manipulations were done only in argon atmosphere, and single crystals were sealed within thin-walled glass capillaries.

Accurate lattice constants were refined from the indexed X-ray diffraction pattern measurements on a single phase sample by the least-squares method with NBS Si as an internal standard. Chemical compositions of a number of single crystals were analyzed by WDS (wavelength dispersive spectrometer). Results showed uniform composition corresponding to Ca<sub>5</sub>In<sub>9</sub>Sn<sub>6</sub>, and this stoichiometry was used in the starting model of the single-crystal structure refinement.<sup>13</sup>

Ca<sub>5</sub>In<sub>9</sub>Sn<sub>6</sub> crystallizes in a hexagonal structure in space group *P6<sub>3</sub>/mmc* with *a* = 6.7091(5) Å and *c* = 26.9485(9) Å, as shown in Figure 1. The structure can be derived from the intermetallic cubic AuCu<sub>3</sub> and hexagonal Ni<sub>3</sub>Sn structure types. The relationships between these structure types are based on their differences in the stacking order of closed packed layers of (MX)<sub>3</sub> metal atoms.<sup>14</sup> The AuCu<sub>3</sub>-type is cubic closed packed (*ccp*) with “abc”-stacking and Ni<sub>3</sub>Sn is hexagonal closed packed (*hcp*) with “ab”-stacking. The structure of Ca<sub>5</sub>In<sub>9</sub>Sn<sub>6</sub> is made up of two *hcp* and eight *ccp* layers of Ca(In/Sn)<sub>3</sub> stacked along the *c*-axis with “*abcbacbacb*” as the repeat stacking unit. The two *hcp* layers in the unit cell contain only In and Ca atoms while the *ccp* (AuCu<sub>3</sub>-type) layers consist of Ca, In, and Sn atoms. Within the *hcp* layers, indium atoms In(1) are displaced from ideal closed packed positions resulting in the formation of In trimers with In–In distances of 3.045(3) Å, a normal In–In bonding distance. The distances between trimers within this closed packed layer are much longer at 3.665(5) Å. In the *ccp* Ca(In,Sn)<sub>3</sub> layers, the distortions leading to In/Sn trimer formation are not observed. The distances among metalloid in the *ccp* layers (3.30–3.36 Å) are relatively longer than the bonding distances observed in the cluster compounds and Zintl phases containing In and Sn atoms,<sup>4–6,18</sup> and are consistent with those found in (non-Zintl)

(13) Single-crystal X-ray analysis was carried out with an Enraf-Nonius four circle CAD4 diffractometer on a crystal with dimensions ca. 0.05 × 0.05 × 0.1 mm. Monochromated Mo Kα radiation was used and the intensities of monitored standard reflections showed no significant changes. Lorentz and polarization corrections and absorption corrections based on six  $\psi$ -scans were applied. The phase problem was solved by direct methods. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters, secondary extinction coefficient, and atomic occupancies refined. All calculations were made with NRCVAX crystallographic software. Microprobe analyses on several single crystals resulted in a uniform chemical composition of Ca<sub>5.0(1)</sub>In<sub>9.01(4)</sub>Sn<sub>5.99(4)</sub> and were used in the structural refinement. Although distinguishing between Sn and In by X-ray diffraction is difficult, complete disorder of Sn and In, with a 2:3 ratio, over all metalloid sites resulted in unsatisfactory refinement results (*R* = 0.062; *R<sub>w</sub>* = 0.078). Constrained refinement of the metalloid site occupancies resulted with In only in the *hcp* slab and a random 1:1 distribution of In and Sn in the *ccp* slabs. This resulted in the best reliability factors, *R* = 0.042 and *R<sub>w</sub>* = 0.039, and the resulting stoichiometry Ca<sub>5</sub>In<sub>9</sub>(In<sub>6</sub>Sn<sub>6</sub>) is consistent with the results of chemical analysis. A final Fourier difference map was essentially featureless.

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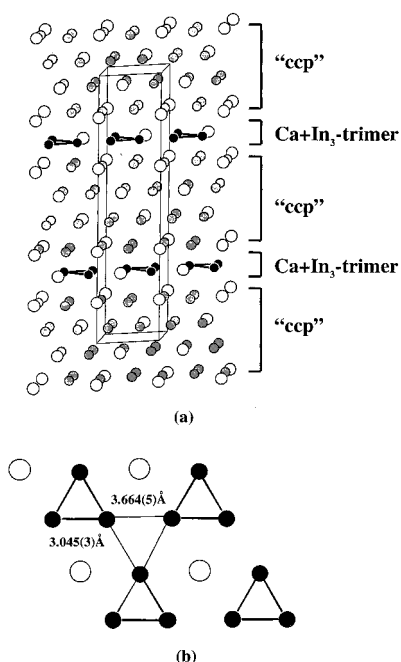
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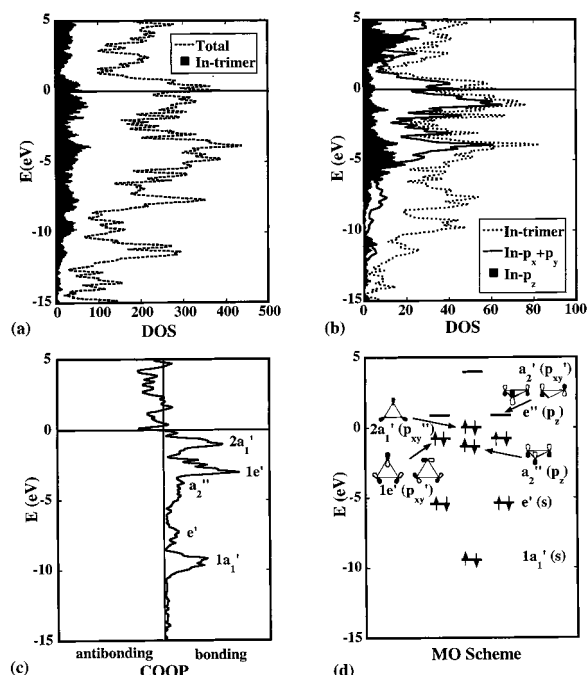
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**Figure 1.** (a) A [010] view of the crystal structure of  $\text{Ca}_5\text{In}_9\text{Sn}_6$ ; (b) a [001] view of the  $\text{CaIn}_3$  (*hcp*) layer which contains the  $\text{In}_3$  trimers. The atoms are represented as follows: Ca, large light spheres; In/Sn, small gray spheres; and In, small solid spheres.

intermetallic compounds such as  $\text{CaSn}_3$  and  $\text{LaIn}_3$ .<sup>14,15</sup> Careful examination of the Fourier difference maps does not show any significant electron density at the center of the In trimers nor at any of the interstitial sites.

To assess the chemical bonding of the In trimers and to correlate crystal structure, stoichiometry, and physical properties, band structure calculations were performed on  $\text{Ca}_5\text{In}_9\text{Sn}_6$ . Full three-dimensional band structures were calculated by using the extended-Hückel formalism.<sup>1,16,17</sup> Densities of states (DOS) and overlap populations (COOP) were calculated on the basis of 60 k-points and results are shown in Figure 2. The calculated density of states (DOS) shows that the compound is essentially metallic with no observable band gap around the Fermi level, and that the contributions of the In trimers to the total density of states are small. The important question about the bonding within the In trimer layer is analyzed by using orbital projected DOS and COOP plots which show that all bonding states and fragment molecular orbitals associated with the In trimer are occupied and that the Fermi energy ( $E_F$ ) corresponding to the observed stoichiometry lies between bonding and antibonding levels of the In trimer. To further elucidate the nature of the bonding states, molecular orbital calculations were performed on an isostructural  $\text{In}_3$  unit and the results are shown in Figure 2d. The calculated molecular orbitals of the  $\text{In}_3$  trimer correlate well with the orbital projection analysis of the bands below the Fermi level from corresponding projected DOS and COOP curve of the solid-state calculations. The resulting correlation shows that the "electron-filling" of the  $\text{In}_3$ -derived bands in  $\text{Ca}_5\text{In}_9\text{Sn}_6$  results in a 14-electron count for the In trimer wherein all bonding states are occupied. This leads to the unusual formulation of the In trimer as  $[\text{In}_3]^{5-}$ . This electronic scheme for  $\text{In}_3$  trimers is different from those found in the cluster network compound  $\text{Na}_{28}\text{In}_{14}\text{Sn}_{15}$  wherein the In and Sn triangles are formally analogous with their arachno- $\text{B}_3\text{H}_9$  derivatives.<sup>18</sup> The band structure calculations also indicate that the remaining occupied states in the DOS corresponding to  $[\text{In}_6\text{Sn}_6]^{5-}$  are the delocalized states within the *ccp* intermetallic slabs. Physical property measurements on powder samples of  $\text{Ca}_5\text{In}_9\text{Sn}_6$ , between 4 and 300 K, show it to be a typical



**Figure 2.** COOP and DOS curves for  $\text{Ca}_5\text{In}_9\text{Sn}_6$ : (a) DOS curves, the dotted line is the total DOS and the solid line represents the states associated with the  $\text{In}_3$  (*hcp*) layer; (b) projected DOS of  $\text{In}_3$ -derived orbitals, the dotted line is the total  $\text{In}_3$  contribution to the DOS, the solid lines are the  $p_{x-y}$  contributions and the shaded areas, are  $p_z$  contributions. (c) A plot of the COOP (crystal orbital overlap population) of the In–In interactions within the  $\text{In}_3$  (*hcp*) layer. (d) Molecular orbital diagram of  $[\text{In}_3]^{5-}$ .

intermetallic that is very conducting and Pauli-paramagnetic.<sup>19</sup> No superconducting transitions were observed above 4 K.

The  $[\text{In}_3]^{5-}$  trimers in  $\text{Ca}_5\text{In}_9\text{Sn}_6$  are isoelectronic and analogous with cyclopropenium,  $\text{C}_3\text{H}_3^+$ , the simplest aromatic hydrocarbon. Similar organometallic cyclotrigermenium and the Zintl ion  $\text{Sn}_3^{2-}$  analogues have been reported, and  $[\text{In}_3]^{5-}$  in  $\text{Ca}_5\text{In}_9\text{Sn}_6$  can be considered as the intermetallic indium analogue.<sup>14</sup> The high formal charge on  $[\text{In}_3]^{5-}$ , indicated by the calculations, has been reported in other In/Ge compounds.<sup>9,10</sup>

The phase  $\text{Ca}_5\text{In}_9\text{Sn}_6$  resides well at the Zintl border. Its crystal and electronic structures can be described as consisting of two components, namely, the "normal intermetallic" slab and a "molecular or Zintl" layer. This picture agrees well with the crystal structure description, property measurements, and band structure calculations which indicate that the intermetallic (*ccp*) slabs dominate the electronic structure (DOS) as well as the electronic properties of the compound. Submerged underneath the sea of conduction (delocalized) electrons due to the intermetallic slabs lie the valence or localized states of the  $[\text{In}_3]^{5-}$  trimers in the (*hcp*) layers. Hence, for compounds that lie on the Zintl border the interplay between the structural factors of delocalized (intermetallic) and localized (Zintl) constituents and the nature of the interactions between them mainly determine their electronic structures and properties.

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**Supporting Information Available:** Complete list of observed and calculated structure factors, crystallographic data, atomic coordinates and anisotropic thermal parameters, and relevant bond distances and angles for  $\text{Ca}_5\text{In}_9\text{Sn}_6$  (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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