Synthesis, Structure and Bonding of SrCa₂In₂Ge: A New Zintl Phase with an Unusual Inorganic π-System

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The Zintl concept provides an effective and useful way to describe the chemical bonding in a wide variety of main group intermetallic structures. The success of the concept in rationalizing the syntheses and discovery of complex Zintl phases has enhanced its validity as an effective approach in the search for new polar intermetallics and for rationalization of their chemical bonding.[1−5] In evaluating the limits of the Zintl concept, an empirical boundary between elements of groups 13 (trelides) and 14 (tetrelides) represents the violations for many group 13 polar intermetallics. This is illustrated by the unlikely situation that the elements of group 13 have enough effective core potential to accumulate a high number of electrons, up to 5 electrons, without significant mixing with the electronic states of the metal component. However, existence of normal trelide Zintl phases and the non-Zintl behavior of several tetrelides and pnictides certainly imply that the Zintl boundary is not exact. The novelty in the chemical bonding and crystal structure of polar main group intermetallics that lie near the Zintl border allows for the possibility of discovering unique electronic phenomena.

In recent years, Corbett and co-workers, as well as Belin and co-workers, have reported on many novel Ga, In, and Tl cluster compounds that follow Wade's rules as in the boranes.[7−9] Studies on trelides have been spurred by the novelty of their cluster chemistry. Other reports on polar intermetallics of trelides and mixed In−Ge anions have resulted in intriguing questions concerning the ability of In to accommodate high negative charges.[1,3,6−10] Recently, it was shown that La₃In₄Ge contains layers of indium with a delocalized open-shell band structure.[10] Also, recent work by von Schnering and co-workers on new silicides and germanides reveals the existence of Si and Ge arene-like systems in describing complex electron-deficient silicides and germanides.[11]

Our present studies on polar intermetallics involving trelide and tetrelide post-transition-metals focus on the structural, chemical, and physical characteristics of "electron-deficient" Zintl phases.[16] These phases represent a class of Zintl phases where the normal picture of covalent networks of singly bonded metalloids may not be sufficient to satisfy the valence requirements of the anionic substructures. Our exploratory syntheses along the Zintl border have led to the discovery of one such compound, SrCa₂In₂Ge. Its crystal structure and chemical bonding feature a novel $[In_2Ge]^{6-}$ chain analogous and isoelectronic with an allyl anion chain.

The air-sensitive title compound was synthesized through high-temperature reactions of nearly stoichiometric amounts of the pure elements (distilled Ca and Sr metals from APL Engineering Labs: in shots, 99.9999%; Ge pieces, 99.9999%) in welded Ta tubing within an evacuated quartz jacket. A slight
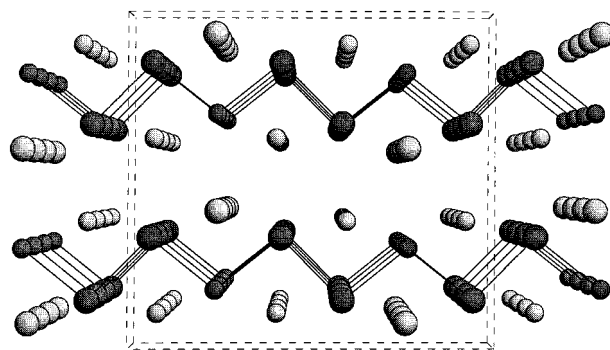

Figure 1. A [001] view of the crystal structure of SrCa₂In₂Ge. The atoms are represented by the following: large light spheres, Sr; small light spheres, Ca; large dark spheres, In; small dark spheres, Ge.

excess (∼10%) of indium and germanium were necessary to obtain high yields (>80%). The reactions were performed at 1050 °C over 5 days with prior heating under dynamic vacuum at 350−450 °C for 5−8 h. The reaction was terminated by rapid quenching to room temperature. All sample manipulations were done within a purified Argon atmosphere glovebox. The title compound, SrCa₂In₂Ge, forms as dark metallic rods and decomposes peritectically, which makes it difficult to obtain as pure phase product. Single crystals were obtained from reactions with large excess (>100%) of In and Ge. Dimensional analyses do not show any significant changes in the lattice parameters with variations in the loaded reaction stoichiometries. This is confirmed by chemical analysis on several single crystals which indicates a nearly constant stoichiometry corresponding to SrCa₂In₂Ge.

Crystal structure investigations were performed on powder and single crystals by X-ray diffraction. SrCa₂In₂Ge crystallizes in the orthorhombic space group *Pnna* with four formula units in the unit cell.[17] The crystal structure of SrCa₂In₂Ge, an ordered derivative of the CrB-type, is shown in Figure 1. The crystal structure can be described as an ordered-derivative of CrB structure type.[18,19] This structure type is characterized by trigonal prisms of the metal atoms (Cr) centered by nonmetal atoms (B). The nonmetal atom arrangement results in parallel zigzag chains along the *c*-axis. Most alkaline-earth- and rare-earth-metal monosilicides and monogermanides crystallize in

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the CrB-type or in the related FeB-type structure.[19] The main structural feature of the alkaline-earth- and rare-earth-metal monotetrelides are the parallel zigzag chains of 2-bonded tetrelide atoms making the alkaline-earth tetrelides normal Zintl phases and the rare-earth tetrelides metallic phases. These observations result in a Zintl picture of their chemical bonding: $[(M^{2+}) + (2\text{-bonded})Ge^{2-}]$ in the alkaline-earth-metal analogs; $[(R^{3+}) + (2\text{-bonded})Ge^{2-} + 1e^-]$ in the rare-earth-metal compounds.

In $SrCa_2In_2Ge$, the chain axis of the quaternary compound is about 3 times longer than that of the parent binary compound CaGe (CrB-type): $3c_{CaGe} \simeq b_{SrCa2In2Ge}$. The repeat unit in the nonmetal atom chain, $[In_2Ge]^{6-}$, is [-In-In-Ge-In-In-Ge-], and the shortest distance between neighboring parallel chains is 4.6582(4) Å. The cations, Ca and Sr, are ordered in that only Ca atoms lie on the shared face between two In-centered trigonal prisms and Sr and Ca atoms lie on the shared face between Ge-centered and In-centered trigonal prisms. On the basis of the crystal structure refinement, there are no significant mixed occupancies or vacancies in the Sr, Ca, In, and Ge atomic positions. The observed metal−nonmetal distances in the crystal structure which range from 3.1 to 3.4 Å (Ca−In, Ca−Ge, Sr−Ge, and Sr−In) are comparable to those found in related polar intermetallic compounds.[19,20] However, the ensuing cation arrangement and nonmetal ordering result in short distances between adjacent In atoms ($d = 2.772(2)$ Å), which are very short compared to those observed in the metal ($d = 3.2-3.4$ Å), and other anionic In clusters and networks ($d = 2.86-3.3$ Å).[9,21] The short In−In interatomic distances are comparable to those observed in cationic In fragments such as In_3^{5+}, In_5^{7+}, and In_6^{8+} ($d_{In-In} = 2.62-2.78$ Å) and in molecular In complexes ($d = 2.81-2.93$ Å).[21,22] The calculated Pauling bond order (PBO) is about 1.54.[23] The observed Ge−In distances ($d_{In-Ge} = 2.629(3)$ Å) are also comparably smaller than the sum of the single bond radii of In and Ge ($d1_{In-Ge} = 2.665$ Å), PBO = 1.15.[23] In the spirit of the Zintl concept, the corresponding 6 electrons per formula unit associated with the charge transfer from the cations does not satisfy the valence electronic requirement of ($[In_2Ge]^{8-}$) if the 2-bonded nonmetal atoms along the chain are all singly bonded. Hence, it is tempting to attribute the short In−In and In−Ge interatomic distances to the presence of multiple bonds such as in [-In=In-Ge-]$^{6-}$, thereby explaining the perceived electron deficiency.

To assess the chemical bonding, band structure calculations were performed on the anionic $[In_2Ge]^{6-}$ chain. One-dimensional band structures were calculated using the extended-Hückel formalism,[24] with atomic orbital and energy parameters employed as before.[25] Densities of states (DOS) and overlap populations (COOP) were calculated based on 50 k-points, and the results are shown in Figure 2. The calculations show that all states below E_f are In−In and In−Ge bonding or nonbonding, with some In−Ge antibonding states just below E_f. The observed In−In−Ge and In−Ge−In bond angles are 96.17(4)° and 103.06(6)°, respectively, and these indicate reduced sp hybridization as expected in heavier post-transition-metals. Hence, the lone pairs in In are mainly 5p orbitals. This is confirmed by the calculations wherein the projected DOS show that the states near E_f are mainly In-5p and Ge-4p states with the nonbonding lone pairs (In-5p$_y$) lying just below E_f. The In−In
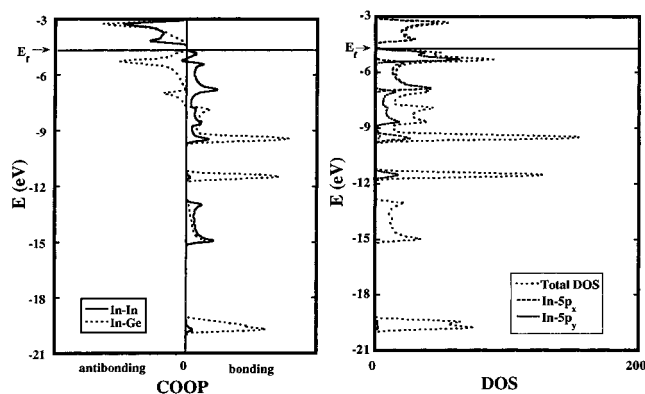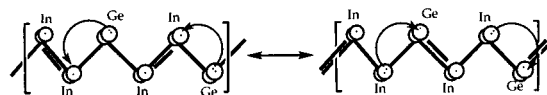

Figure 2. COOP and DOS curves for $SrCa_2In_2Ge$: (a) COOP curves of the In−In (solid line) and In−Ge (dashed line) interactions; (b) DOS curves, the dotted line is total DOS; the solid line, In5p$_y$ (lone pair); dashed line, In5p$_x$ (π-states).

Scheme 1

π-interactions, represented by the In-5p$_x$ and some of the In-Ge π^*-states (Ge-4p$_x$), lie just below the In-5p$_y$ states ranging from −9.0 to −5.2 eV. The In−In π^* antibonding π-states lie just above E_f with a small calculated band gap of ∼0.4 eV. Hence, the electronic structure and bonding in the compound can be represented by a conjugated $[In_2Ge]^{6-}$ π-system, as illustrated in Scheme 1, with the first resonance structure as the more dominant one. The calculated electron densities of 4.8 and 6.4 for In and Ge, respectively, are in agreement with the first resonance structure. The observed torsional angles around the In−In and In−Ge bonds are 178.34(6)° and 176.66(4)°, respectively. These reveal a slight nonplanarity of the atoms in the chain which could be attributed to the packing effects of the differently sized cations. This results in a small decrease in the overlap of the π-orbitals but stabilizes the resonance structure which features In double bonds. Hence, the observed characteristics of the calculated band structure that features a conjugated π-system explain the short In−In and In−Ge interatomic distances observed in $SrCa_2In_2Ge$. Furthermore, the electronic structure of the monomer $[In_2Ge]^{6-}$ is reminiscent of the allyl anion. Magnetic susceptibility measurements indicate the compound is diamagnetic, and this is consistent with being a semiconducting Zintl phase.[22] The electronic effects of the cation orbitals were neglected in our calculations and we believe that these effects can be considered as perturbations mainly on the orbitals directed at the cations, the In and Ge p$_y$-orbitals. However, the overall bonding picture is retained and the Zintl concept is validated.

Efforts are now underway to fully characterize the electronic properties of the undoped and doped phases of $SrCa_2In_2Ge$ and to search for related inorganic π-bonded systems. These studies are part of our continuing efforts to narrow the disparity between the synthesis of new materials and their physical characterization and to provide an improved understanding of structure, property, and bonding relationships in intermetallics in the region between metals and nonmetals.

Supporting Information Available: Crystallographic data, atomic coordinates and anisotropic thermal parameters, and relevant bond distances and angles for $SrCa_2In_2Ge$ (3 pages). See current masthead page for ordering and Internet instructions.

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