Ba_2NiSi_3: A One-Dimensional Solid-State Metallocene Analog

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Received May 11, 2000

Polar intermetallics and Zintl phases of group 14 elements exhibit a rich variety of complex structures and chemical bonding.[1,2] In this regard, the Zintl concept provides a simple and useful way to rationalize relationships between stoichiometry, crystal structure, and chemical bonding along the border between metals and nonmetals.[2,3]

Investigations on polar intermetallic trielides and tetrelides pose intriguing questions about their ability to accommodate high negative charges, open-shell electronic structures, and multiple bonding.[4−7] Recent studies aim to understand structural, chemical, and electronic characteristics of "electron-deficient" Zintl phases that exhibit chemical bonding, wherein normal pictures of singly bonded anionic metalloids is insufficient, and hence implies the presence of multiple bonding. The complex Zintl phases, $SrCa_2In_2Ge$ and $Ca_5In_9Sn_6$, are illustrative examples.[5,6] Their electronic and crystal structure patterns emphasize the need to understand the stabilization of intermetallic π-systems.

A challenge in inorganic chemistry is the synthesis of main group compounds, other than carbon, that exhibit unsaturation or aromaticity.[7,8] Successful syntheses of molecular cyclogallene,[7] cyclotrigermenium,[7c] cyclotrisilene[8] provide the stimuli to prepare new inorganic unsaturated hydrocarbon analogues among polar intermetallics. It has been reported that aromatic Zintl anions isoelectronic to cyclopropenium, such as $[Sn_3]^{2-}$ and $[In_3]^{5-}$ were formulated to exist in the superconducting phase, $BaSn_3$, and the ternary, $Ca_5In_9Sn_6$.[6,9]

The title compound Ba_2NiSi_3 (**1**) was obtained in high yield by reacting stoichiometric amounts of the pure elements (with a slight excess of Ba) at high temperatures under argon using an arc furnace. The compound was initially obtained as a minor phase from our attempts to prepare "$BaNiSi_2$". Silver needle-like crystals of **1** obtained from the as-cast melt were found to be air-stable up to 1 day, but reacted strongly with moisture. Subsequently, the compound was prepared in high yield (>95%) from the reaction of stoichiometric amounts of Ba, NiSi, and Si within welded Ta tubes at 900 °C. The lack of an appreciable phase width in Ba_2NiSi_3 is indicated by the relatively invariant lattice parameter and unit cell volumes refined from patterns of a number of nominal compositions. The narrow homogeneity range and the refined chemical composition were confirmed by microprobe/wavelength dispersive (WDS) analysis of bulk and single crystal samples and the observation that single-phase samples were only obtained from reactions with nominal stoichiometry of Ba_2NiSi_3. As a general precaution, all manipulations were carried out under purified Ar-atmosphere in a glovebox with moisture levels <0.1 ppm.

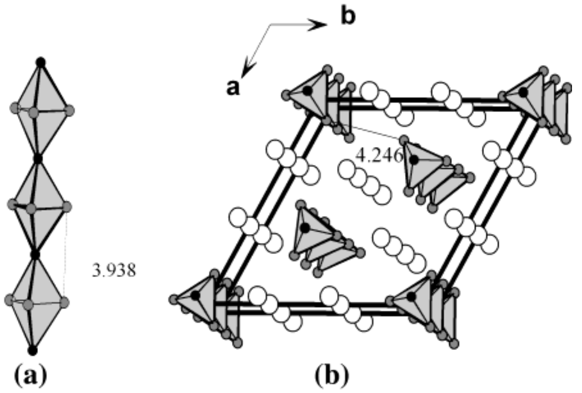

Figure 1. (a) A $[NiSi_3]^{4-}$ chain in Ba_2NiSi_3; (b) [001] view of the crystal structure of Ba_2NiSi_3. Atoms are represented as follows: Ba, large light spheres; Ni, small dark spheres; and Si, small gray spheres.

The crystal structure of **1** was determined by single crystal X-ray diffraction.[10] The crystal structure, as shown in Figure 1, features infinite chains of $^{1}_{\infty}[NiSi_3]$ separated by Ba atoms. The chains consist of equilateral Si_3 triangles stacked in an eclipsed manner, forming columns of face-shared Si_6 trigonal prisms. Ni and Ba atoms form nominal "Ba_2Ni" layers, with Ni located at the centers of the Si trigonal prisms. Ba atoms cap rectangular faces of the trigonal prisms formed by eclipsed Si_3 triangles, essentially isolating the $[NiSi_3]$ chains. There are two independent $[NiSi_3]^{4-}$ chains that run parallel to the *c*-axis. One chain passes through the origin with Si−Si and Ni−Si distances of 2.454(12) and 2.426(4) Å, respectively. A second chain lies along [$^1/_3$, $^1/_3$, *z*] with Si−Si and Ni−Si distances of 2.438(9) and 2.420(3) Å, respectively. The observed Ni−Si and Si−Si distances compare favorably to the Pauling single bond distances of (Ni−Si) 2.400 Å and (Si−Si) 2.354 Å and those found in planar cyclic Si π-systems.[11,14] The relatively longer Si−Si distances agree with the trend observed in the C−C bonds of η^3-cyclopropenyl−metal complexes.[15]

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[10] Crystal Structure data for **1**: $M_r = 417.66$, hexagonal, space group P-62m (no. 189), $a = 11.392(5)$, $c = 3.938(3)$ Å, $V = 442.6(4)$ Å^3, $Z = 3$, $\rho = 4.701$ g cm^{-3}, $\mu = 16.810$ mm^{-1}, $\lambda = 0.71073$ Å (Mo Kα), $2\theta_{max} = 56.54$; of 1261 total reflections, 411 were independent and 396 were observed ($I > 2\sigma(I)$); 23 total variables; final R indices R1 = 0.0502, wR2 = 0.1201, GOF = 1.13 ($I > 2\sigma(I)$) and R1 = 0.0522, wR2 = 0.1217, GOF = 1.12 (all data). The analysis, using a Siemens SMART diffractometer equipped with a CCD detector, was carried out at 25 °C. Empirical absorption correction was applied on a hemisphere of data, and redundant reflections were averaged. The structure was solved by direct methods and refined by full-matrix least-squares calculations. A final Fourier difference map was essentially featureless. All calculations were made with SHELXTL crystallographic software.

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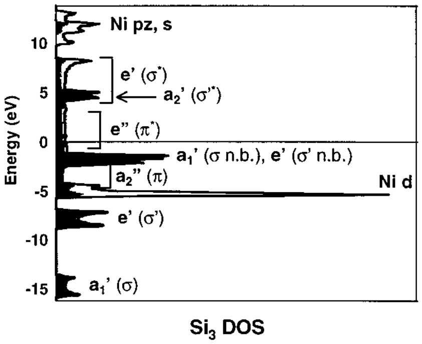


Figure 2. Total density of states of $[NiSi_3]^{4-}$ in Ba_2NiSi_3. The Si_3 projection is shaded black, and its bands are labeled accordingly. Ni p_x and p_y bands are not shown. The Fermi level (E_F) is set to 0 eV.

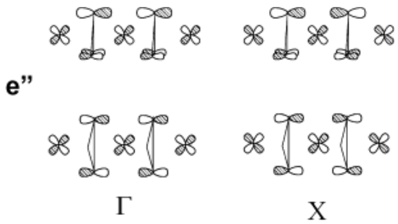
The Ni-centered trigonal prismatic silicide chains in the unique crystal structure of compound **1** are similar to chains found in $NbSe_3$ that reportedly exhibit novel charge density wave (CDW) behavior.[12] However, significant Se−Se bonding between Se atoms of neighboring chains was observed in $NbSe_3$. A closer structural relative of **1** is found in the oligomeric $[ZnGe_8]^{6-}$ cluster in Cs_6ZnGe_8, wherein Zn atoms occupy trigonal prismatic sites formed by the eclipsed condensation of two Ge_4 pyramidal clusters.[13]

The Si_3 rings are notable features of the crystal structure. There have been reports of solid-state ring structures for silicon that are mainly derived from six-member benzene-like units.[14] Detailed investigations of these electron-deficient silicides and germanides indicate the existence of cyclic tetrelide π-systems that were characterized as having partially filled π* states.[14,15] It is tempting to associate the structure to a Zintl electronic scheme as $(Ba^{2+})_2Ni^{2+}[Si_3]^{6-}$.[6] However, the identical electronegativities of Ni and Si dispute this simple assignment. It is more appropriate to depict the infinite chain as a one-dimensional $[NiSi_3]^{4-}$ anion. This leads us to liken it to an infinitely stacked face-to-face metallocene polymer.[16] Transition metal sandwich complexes with unsaturated cyclic P_3 and As_3 ligands are known and characterized as having metallocene-like interactions.[17] To our knowledge, metal complexes or polymers with cyclic η^3-Si_3 π-donor ligands have not yet been reported.

To understand the bonding in the $[NiSi_3]^{4-}$ chain, one-dimensional band structure calculations were performed using extended-Hückel theory.[18] The calculated density of states (DOS), as shown in Figure 2, shows that there are no gaps near the Fermi level (E_F). The Ni-d bands lie above the Si s-bands and below E_F. The relevant d-bands, a_1' (d_{z^2}) and e'' (d_{xz} and d_{yz}), represent “molecular” bonding combinations between Ni and the Si_3 ligands. The occupied Si_3−derived p-bands (a_2'', e', a_1', e'') lie above the Ni d-bands, with $a_2''(\pi)$, $e''(\pi^*)$, exhibiting large bandwidths of 3 and 4.5 eV, respectively. The rest of the Si_3 occupied p-bands exhibit weak dispersions.

The most significant Ni−Si_3 interactions are manifested in the $a_2''(\pi)$ and $e''(\pi^*)$ bands. At $k = 0$ (Γ), $a_2''(\pi)$ is nonbonding between Ni p_z orbital and the π-states of Si_3, and transforms to a bonding combination at $k = \pi/2a$ (X) leading to the observed dispersion. The HOMO, $e''(\pi^*)$, exhibits significant mixing between the Ni (d_{xz} and d_{yz}) and Si_3 p_z orbitals. Antibonding interactions in $e''(\pi^*)$ at $k = 0$ (Γ), as shown in Scheme 1, become significantly bonding at $k = \pi/2a$ (X). The dispersion of the $a_2''(\pi)$ and $e''(\pi^*)$ bands provides an electronic rationale for the observed stability of the chain structure.[18] The $e''(\pi^*)$ bands are partially filled only up to where the metal−ligand states are bonding. Fragment MO analyses at $k = 0$ (Γ) indicate the charge assignment as $[Ni^0Si_3{}^{4-}]$. However, Mulliken population analyses indicate charges are $[Ni^{1-}(Si_3)^{3-}]$ that suggests significant hybridization of Ni and Si_3 due to the extended nature of the chain. Possible “back-bonding” from the “electron-rich” $Si_3{}^{4-}$ moiety to the metal is indicated by the significant mixing of empty Ni p_z states with filled Si_3 $a_2''(\pi)$ states. The average overlap populations for the Ni−Si and Si−Si bonds are 0.225 and 0.636, respectively. The overlap population between Si atoms of face-to-face Si_3 triangles is negligible. Hence, the interaction of the $[Si_3]$ trimer with Ni may be considered analogous to that observed in η^3-cyclopropenyl-metal complexes, and that the $[NiSi_3]^{4-}$ chains are solid-state analogues of an eclipsed (η^3-Si_3)Ni polymer.[19] A significant implication of the existence of **1** is the promise of stabilizing new main-group solid-state cyclic π-systems, as in inorganic metallocene analogues.[16,19]

Scheme 1



Magnetic and resistivity measurements on pressed pellets indicate **1** to be Pauli paramagnetic and metallic over the range 10−300 K ($\rho_{298K} = 7 \times 10^{-5}$ Ω/cm). A report on the isostructural nickel germanide will be published in a forthcoming report.[20]

Acknowledgment. We thank Professor Thomas Albright for his help with theoretical calculations. Support from the NSF (CAREER, DMR-9733587), Welch Foundation, and the PRF are acknowledged. This work made use of MRSEC/TCSUH Shared Experimental Facilities supported by the NSF (DMR-9632667) and the State of Texas through the TCSUH.

Supporting Information Available: Complete list of crystallographic data, atomic parameters, thermal parameters, relevant bond distances and angles, and band structure results for Ba_2NiSi_3 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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