Yb₉Zn₄Bi₉: Extension of the Zintl Concept to the Mixed-Valent Spectator Cations[†]

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Zintl phases are compounds typically formed between very electropositive metals and more electronegative main group metals.[1] Complete electron transfer is assumed to take place, and once reduced, the electronegative elements form polyanionic substructures whose bonding and architecture are understood in terms of the (8-N) rule. The Zintl substructures build valence-precise semiconducting zero-, one-, two-, or three-dimensional polyanionic frameworks. These phases are especially interesting because of their extraordinary structural variety. Generally the electropositive metal cations play a charge-balancing "spectator" role. Although up until recently almost all Zintl phases contained alkali metal or alkaline earth metals as the charge-balancing cations, the use of certain lanthanide ions (e.g., Eu, Yb) raises the prospect of *mixed* valency and the observation of unusual electronic phenomena associated with it.[2] This changes the focus from the semiconducting polyanionic frameworks to the so-called "spectator" cations. In addition because the charge transfer from electropositive metals to the framework is considered complete (e.g., one or two electrons), the type and amount of such metals in the compound directly determines the structure and bonding of the anionic framework. Therefore, metals that can transfer formally fractional charge may stabilize novel anions and stoichiometries not possible with stable-valent metals. After many years of research activity in this area this possibility has not been given significant attention.

Recently, a mixed valent compound Yb₁₄ZnSb₁₁[3] was described as a member of the so-called "14-1-11" family of Zintl compounds.[4] This compound was rationally designed from the valence-precise semiconducting Yb₁₄AlSb₁₁ analogue and features 13 Yb²⁺ and one Yb³⁺ atom. Here we report the discovery of Yb₉Zn₄Bi₉,[5] a new Zintl compound with clearly observed *mixed valency* in the electropositive part (i.e., Yb) of the structure. This compound features [Zn₄Bi₉]¹⁹⁻ ribbons running along the *c*-axis found previously in Ca₉Zn₄Bi₉.[6,7] The infinite chains have a ribbonlike character that results from four condensed ZnBi₄ tetrahedra sharing Bi corners. Yb atoms reside between the chains as shown in Figure 1. The projection along the *c*-axis illustrates that half of the chains are related to the other half by *b*-glide and
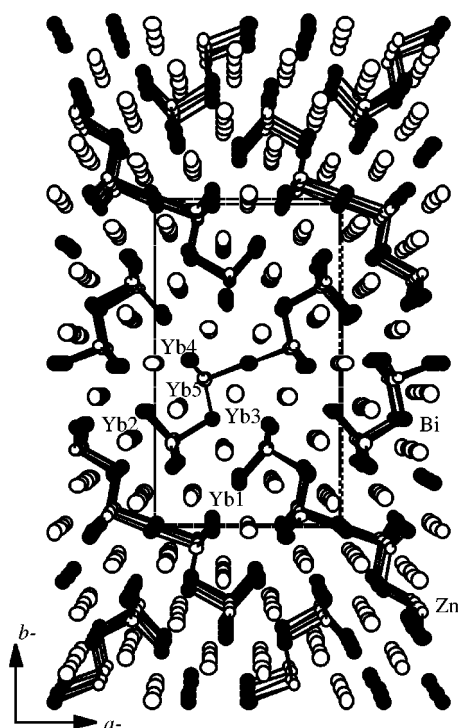
Figure 1. (a) A [001] view of the orthorhombic unit cell of Yb₉Zn₄Bi₉. The Yb, Zn, and Bi atoms are indicated as large open, small open, and small filled circles, respectively.

a-glide symmetry. The Bi(4) atom is situated on a *2/m* symmetry site in the center of the infinite [Zn₄Bi₉]¹⁹⁻ ribbons.

Figure 2 shows a ribbon fragment with atom labels and bond distances. There are five crystallographically different Bi atoms coordinated to two nonequivalent Zn atoms. Bi(1), Bi(2), and Bi(3) are shared by Zn(1)- and Zn(2)-centered tetrahedra forming a double chain. The Bi(5) atom acts as a terminal anionic ligand of the Zn(2) tetrahedron. The Bi(4) atom is exceptional, using its linear two-fold coordination to join the double chains into quadruple chains (Zn(1)−Bi(4)−Zn(1) angle of 180°). The Zn−Bi bond distances, except for Zn(1)−Bi(4), are in the range of 2.771(1) to 2.833(3) Å, and they compare well to the 2.770(5)− 2.929(8) Å found in Ca₉Zn₄Bi₉. The Zn(1)−Bi(4) bond is significantly longer at 3.085(3) Å. Linear coordination geometry around pnicogen atoms is rare, with the Pn₃⁷⁻ units of Yb₁₄MnBi₁₁ being another example.[2b] The angles around Zn(1) and Zn(2) atoms are slightly distorted from the ideal tetrahedral bond angle

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[†] This paper is dedicated to the victims of the WTC September 11, 2001.
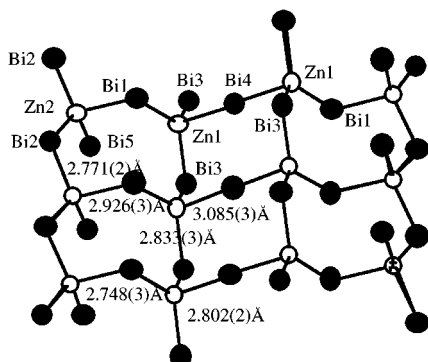[‡] Department of Chemistry.
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(5) Synthesis of Yb₉Zn₄Bi₉: The crystal used in the structure determination resulted from the reaction of a mixture of the three elements in the molar ratio of 1 (0.1730 g): 2 (0.1308 g) : 2 (0.4180 g). The mixture was placed in a graphite tube and sealed in an evacuated silica tube and heated slowly up to 950 °C for 2 days. It was kept at that temperature for 1 day, and subsequently cooled to room temperature over 1 day. The reaction led to rod-shaped black crystals along with gray featureless pieces. Once the stoichiometry was determined from the X-ray single-crystal structure analysis, Yb₉Zn₄Bi₉ was prepared as a single phase, starting from the exact stoichiometric ratio. The X-ray diffraction pattern of bulk samples agreed well with that calculated from single-crystal data. Energy dispersive analysis using a scanning electron microscope on many single crystals gave Yb₉.₀₂(₂)Zn₄.₀(₂)Bi₈.₈(₂). Yb₉Zn₄Bi₉ is air stable and melts congruently at 653 °C.
(6) Brechtel E.; Cordier G.; Schafer H. *Z Naturforsch B* **1979**, *34*, 1229.
(7) A Bruker SMART Platform CCD diffractometer was used to collect intensity data using graphite monochromatized Mo Kα radiation. The SMART software was used for data acquisition and SAINT for data extraction and reduction. The absorption correction was performed empirically using SAD-ABS and the structure was refined by full-matrix least-squares techniques with the SHELXTL package of programs. (a) Yb₉Zn₄Bi₉: orthorhombic space group *Pbam*, a = 12.5705(13) Å, b = 22.028(2) Å, c = 4.6401(5) Å, T=298 K, Z=2, V=3699.66 Å³, final R indices R1 [F_o² > 2σ(F_o²)] = 3.78%, wR2 [(F_o² > 0)] = 13.64%.

Figure 2. A short fragment of the $[Zn_4Bi_9]^{19-}$ ribbon with labeling.

of 109.5° and range between 102.44(10)−114.49(7) and 99.72(9)−119.26(7)°, respectively. According to the Zintl concept, the formal charge of two-bonded Bi atoms can be assigned as Bi^{1-} and that of single-bonded Bi atoms can be assigned as Bi^{2-}. Therefore, the compound must be described as $(Yb^{3+})(Yb^{2+})_8$-$(Zn^{2-})_4(Bi^{2-})_2(Bi^{1-})_7$. This requires mixed valency in Yb; however, it is not clear which if any Yb sites involve Yb^{3+} ions. All five nonequivalent Yb atoms have six nearest neighbors. The shortest average Yb−Bi bond distances are found in Yb(2) at 3.279(1) Å, whereas the remaining Yb−Bi bond distances range between 3.306(1) and 3.343(1) Å. Bond valence sum[8] calculations indicate greater positive charges of 2.61 and 2.48 on Yb(2) and Yb(3) and lower charges of 2.10, 2.26, and 2.25 on Yb(1), Yb(4), and Yb(5), respectively, suggesting that Yb(2) and Yb(3) are more likely to be in +3 state.[9]

Temperature-dependent magnetic susceptibility data for samples of $Yb_9Zn_4Bi_9$ show that the inverse susceptibility above 100 K obeys Curie−Weiss law with Weiss temperature of −23.5 K.[10] The effective moment is $4.04(2)\mu_B$ per unit of $Yb_9Zn_4Bi_9$, and provides strong evidence of an intermediate Yb^{3+}/Yb^{2+} oxidation state. On the basis of the expected moment of a free Yb^{3+} ion, $4.50\mu_B$,[11] it corresponds to 0.9 Yb^{3+} ions per unit of $Yb_9Zn_4Bi_9$ and is very close to the expected value.

On the basis of the above, it is evident that $Yb_9Zn_4Bi_9$ is a Zintl compound, and this fact raises questions as to the nature of $Ca_9Zn_4Bi_9$,[6] which contains the same $[Zn_4Bi_9]^{19-}$ ribbons and only nine divalent Ca^{2+} ions and thus is one-electron deficient. If the $[Zn_4Bi_9]^{x-}$ ribbons in the Ca^{2+} compound are in reality oxidized and x is 18, this is not discernible from the published metric data for this structure (albeit with high R values)[6] which are virtually identical to those of the Yb phase. Therefore, the origin of the stability of $Ca_9Zn_4Bi_9$ is an outstanding issue and raises the specter of nonstoichiometry.

To understand the bonding in $Yb_9Zn_4Bi_9$, we performed band structure calculations in the density functional theory (DFT) formalism.[12] The density of states (DOS) plot in Figure 3 shows that the Fermi level falls on nonzero density of states region, giving a metallic system. The bands near the Fermi level (E_F) are mainly composed of f orbital bands of Yb and p orbital bands
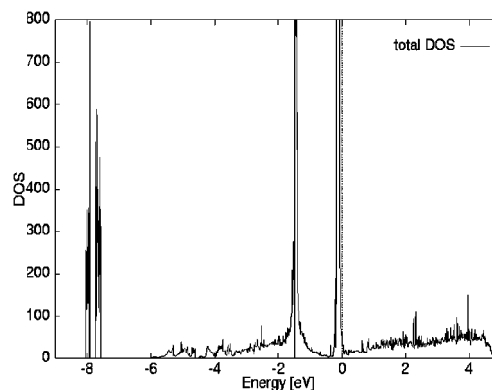
Figure 3. Total DOS curves for $Yb_9Zn_4Bi_9$,. E_F is set to 0 eV. The two sharp spikes at ∼−0.04 eV and ∼−1.7 eV (reaching off scale) are f orbital levels. The sharp spikes at ∼−8 eV are Zn d-orbital levels.

of Zn and Bi, and there is a significant amount of mixing between Yb and Bi states, indicating some covalent character in the Yb−Bi interactions.[13] The Yb f levels are energetically split in two groups through strong spin−orbit interactions. The major group, located very near E_F, is responsible for the good electron-donating ability of Yb^{2+} to the polyanionic framework and generation of mixed valency. Therefore, these calculations strongly suggest the presence of mixed-valent $Yb^{2+/3+}$ ions in $Yb_9Zn_4Bi_9$ and also the mixing of Yb states with those of the anionic framework. However, due to the inadequacy of treating strong Coulombic repulsion between f electrons within DFT, the degree of mixed valency cannot be obtained quantitatively.

The electrical conductivity and thermoelectric power of ingots of $Yb_9Zn_4Bi_9$ were measured as a function of temperature. The conductivity at 300 K is ∼180 S/cm, and it increases slowly with falling temperature, consistent with weakly metallic behavior. The thermopower of $Yb_9Zn_4Bi_9$ varied from ∼+4 to +15 μV/K between 300 and 400 K, indicating holes as the charge carriers; however, on cooling the sign changed from positive to negative at ∼225 K, which indicates a change in carrier type from p-type to n-type at low temperatures.

In conclusion, the discovery of $Yb_9Zn_4Bi_9$, a proper Zintl phase, heightens the notion that mixed valency among the electropositive cations can be a basis for the design of new phases. This insight broadens the scope of Zintl phase exploration and points to new avenues of synthetic experimentation. These results also call for a reexamination of the composition, crystal structure, and electronic properties of the corresponding electron-deficient Ca and Sr systems.

Supporting Information Available: X-ray crystallographic details (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

(8) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* B **1985**, *41*, 244.

(9) In bond valence sum calculations, we used a B value (ref 8) of 0.32 optimized using the Yb^{2+} compound $Yb_5In_2Sb_6$ as the standard.

(10) Magnetic susceptibility data were obtained with Quantum Design SQUID magnetometer at temperatures between 2 and 300K. Field-dependent magnetization data were taken at 5K with the field swept from +6 T to −6T. The samples were either polycrystalline powders or sintered pellets (heated at 500 °C for 2 h). Field dependence of magnetic moment does not saturate up to 6 T and magnetization at 5K is approximately linear with no measurable hysteresis.

(11) "*Magnetochemistry*", Selwood, P. E. 2nd Ed. Interscience Publisher: New York, 1956; pp276.

(12) The electronic structure calculations for these compounds were performed within density functional theory (DFT) using the full potential linearized augmented plane wave (LAPW) method implemented in WIEN 97 code. Blaha, P.; Schwarz, K.; Luitz, J. *WIEN 97*: A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties, Vienna University of Technology, Getreidemarkt 9/158, A-1060 Vienna, Austria. Spin−orbit interactions were included.

(13) A band structure calculation for only the anionic $[Zn_4Bi_9]^{19-}$ framework yields results that are significantly different from those including the Yb cations, where the Fermi level lies at the top of the valence band just below a large semiconducting band gap.