Inorg. Chem. **2007**, *46*, 1036–1038

Inorganic Chemistry
Communication

$[Ni_5Sb_{17}]^{4-}$ Transition-Metal Zintl Ion Complex: Crossing the Zintl Border in Molecular Intermetalloid Clusters

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Received August 31, 2006

K_3Sb_7 and $Ni(COD)_2$ react in the presence of 2,2,2-cryptand in ethylenediamine solutions (∼1:8 Ni/Sb molar ratio) to give dark-brown crystals of the paramagnetic cluster anion $[Ni_5Sb_{17}]^{4-}$ as the $[K(2,2,2\text{-crypt})]^+$ salt. The cluster has a Ni(*cyclo*-Ni_4Sb_4) ring unit that sits inside a Sb_{13} bowl. The structure is similar to that of the previously reported $[Pd_7As_{16}]^{4-}$ ion containing a Pd(*cyclo*-Pd_4As_4) ring unit that sits inside a Pd_2As_{12} bowl. Density functional theory and bond valence analyses suggest delocalized charge distributions and intermetallic-like properties.

Recent advances in inorganic cluster science have led to the development of extremely large metallic and binary clusters that have blurred the lines between nanomaterials and cluster chemistry.[1] Structural analysis of very large metallic clusters[2−4] show that their cores are discrete pieces of bulk metallic lattices stabilized by organometallic ligands on the periphery. Large binary transition-metal chalcogenide clusters[5−7] sometimes contain cores that mimic the structures of solid-state binary phases but can also show structures that are unique and "molecular" in nature. The transition from molecular to solid-state structures seems to depend upon the binary elements involved and the supporting ligands of the cluster.[5,8] The ability to traverse the line between molecular and solid-state structures provides new opportunities to evaluate structure−property relationships in nanoscale architectures.

Large binary transition-metal pnictide clusters are less studied than the chalcogenide systems, and the regimes for the molecular to solid-state structural transitions have yet to be established. Transition-metal derivatives of the E_7^{3-} Zintl anions have generally fallen into the molecular regime in which their molecular and electronic structures are adequately described by traditional bonding schemes (e.g., the Zintl concept). Generally, these complexes have isoelectronic organometallic molecular analogues, and most have two-center two-electron bonds. The $[As@Ni_{12}@As_{20}]^{3-}$ ion[9] is unusual in its architecture, but it too has subunits reminiscent of other known clusters. In contrast, the recently reported $[Pd_7As_{16}]^{4-}$ and the $[Zn_9Bi_{11}]^{5-}$ ions[10,11] are examples of ligand-free clusters that differ from both the known molecular structures and the solid-state intermetallic phases. We report here the new binary cluster anion, $[Ni_5Sb_{17}]^{4-}$, that joins this emerging class of intermetalloid clusters. These complexes have unique structures and do not easily lend themselves to traditional bonding schemes.

Ethylenediamine (en) solutions of $Ni(COD)_2$ and K_3Sb_7 (0.5:8 to 1:8 Ni/Sb molar ratio) react in the presence of 2,2,2-crypt to give dark-brown crystals of $[K(2,2,2\text{-crypt})]_4[Ni_5Sb_{17}]$·en intermixed with crystals of $[K(2,2,2\text{-crypt})]_4[(Sb_7)_2Ni_x(Ni_2Sb_2)]$·2en in low yields after 48 h. The latter crystals contain the $[Ni_x(Sb_7)_2(Ni_2Sb_2)]^{4-}$ ion, **1**, which has a partially occupied Ni interstitial of variable occupancy. Resolution of this complicated synthetic and crystallographic problem is ongoing and will be described in a subsequent publication. The two crystalline solids are similar in color and shape (small dark-black blocks) but can be differentiated by semiquantitative energy-dispersive X-ray analysis (EDX) and single-crystal X-ray diffraction (XRD). The $[K(2,2,2\text{-crypt})]_4[Ni_5Sb_{17}]$·en salt contains the title $[Ni_5Sb_{17}]^{4-}$ ion, **2**, which has been characterized by single-crystal XRD, EDX, and density functional theory (DFT) analysis. The ion is a 139-valence-electron paramagnetic cluster, but electron paramagnetic resonance (EPR) experiments have not revealed an EPR

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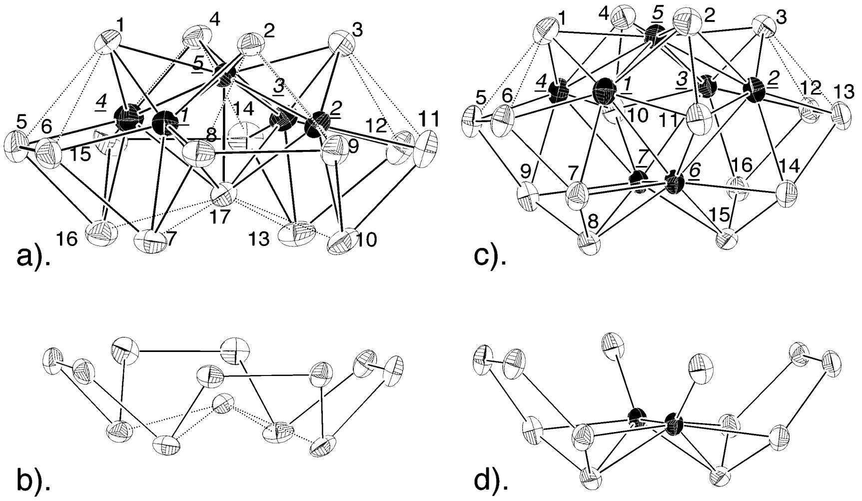

Figure 1. (a) ORTEP drawing of $[Ni_5Sb_{17}]^{4-}$, **2**. (b) ORTEP drawing of the Sb_{13} bowl of the $[Ni_5Sb_{17}]^{-4}$ structure. (c) ORTEP drawing of $[Pd_7As_{16}]^{4-}$, **4**. (d) ORTEP drawing of the Pd_2As_{12} bowl of $[Pd_7As_{16}]^{4-}$. Black atoms represent transition-metal atoms, and white atoms represent main-group atoms. Dotted lines indicate partial or secondary bonds. Data for **4** were from ref 11.

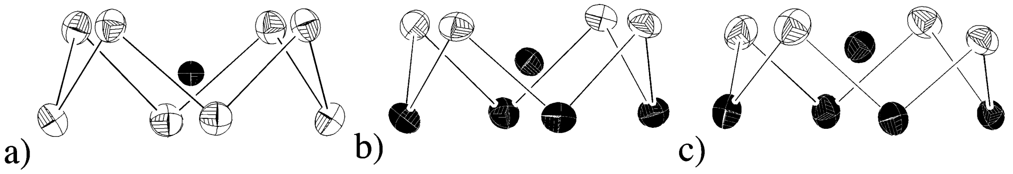

Figure 2. (a) ORTEP drawing of a ME_8^{n-} ion, $[CrAs_8]^{2-}$. (b) Ni(*cyclo*-Ni_4Sb_4) cap of $[Ni_5Sb_{17}]^{4-}$. (c) Pd(*cyclo*-Pd_4As_4) cap of $[Pd_7As_{16}]^{4-}$. Black atoms represent transition-metal atoms, and white atoms represent main-group atoms. Bonds from the centered atoms to the eight-membered rings have been omitted for clarity.

signal to date. The structure of **2** is reminiscent of the $[Pd_7As_{16}]^{4-}$ ion, **3**, which has been previously communicated.[11]

The $[K(2,2,2\text{-crypt})]_4[Ni_5Sb_{17}]\cdot$en salt has triclinic crystal symmetry and space group $P\bar{1}$ and contains four cations, the anion, and an en solvate molecule in the asymmetric unit. The structure of the $[Ni_5Sb_{17}]^{4-}$ anion, **2**, has rotational disorder with two different orientations in a 0.81:0.19 ratio. Full crystallographic data and a listing of distances and angles are given in the Supporting Information. The $[Ni_5Sb_{17}]^{4-}$ anion, **2** (Figure 1a), has virtual C_{4v} point symmetry and can be viewed as an Sb_{13} bowl (Figure 1b) with a [Ni(*cyclo*-Ni_4Sb_4)] cap (see Figure 2b).

The apical Ni5 atom is in an Sb_5 square-pyramidal environment with symmetrical Ni−Sb bond distances of 2.593(3) Å (av). The four other Ni atoms are in distorted 5 + 1 trigonal-prismatic environments with five Ni−Sb bonds in the range of 2.496(3)−2.590(2) Å and one longer contact in the range of 2.783(2)−2.845(2) Å. The four Ni−Ni contacts to Ni5 are *seemingly* indicative of metal−metal bonding [2.540(2)−2.590(2) Å]. However, DFT analysis and general electron counting indicate that there is little (if any) direct Ni−Ni bonding. The bonding analysis is discussed below.

Complex **2** has 12 Sb−Sb bonds [2.816(4)−2.928(4) Å] that are similar to those reported for other metalated polyantimonides, such as $[(CO)_3Ni_3Sb_7]^{3-}$ (2.842−2.977 Å).[12] These contacts are longer than those in the metal-free Zintl ions (i.e., Sb_7^{3-}, Sb_{11}^{3-})[13,14] and are more akin to typical organostibnides, such as $R_2Sb-SbR_2$ and $[(t\text{-Bu})_3(cyclo\text{-}Sb_4)]_2$ [2.826(4)−2.866(1) and 2.841(6)−2.866(6) Å, respectively].[15,16] There are 12 additional Sb−Sb contacts in the range of 3.095(2)−3.176(2) Å, which are indicative of fractional or secondary[17] Sb−Sb bonding.

The $[Ni_5Sb_{17}]^{4-}$ cluster has 139 total valence electrons, giving rise to a paramagnetic complex. DFT calculations were attempted with both $S = {}^1/_2$ and ${}^3/_2$ ground states, but, interestingly, only the latter converged. This result suggests an $S = {}^3/_2$ ground state, which may explain why the complex does not give a room-temperature EPR signal.

The $[Ni_5Sb_{17}]^{4-}$ cluster **2** has some important similarities to the previously reported $[Pd_7As_{16}]^{4-}$ complex[11] **4** (Figure 1c,d) and the M(*cyclo*-E_8)$^{n-}$ series of compounds where M = Mo, Nb, Cr, E = As, Sb, and $n = 2$ and 3 (Figure 2).[18−20] For example, **4** has a [M(*cyclo*-M_4E_4)] cap (Figure 2c) that is very similar to that of **2** (Figure 2b), but the corresponding bowl has a formula of Pd_2As_{12} (Figure 1d). In the M(*cyclo*-E_8)$^{n-}$ series of compounds, all atoms in the E_8 ring are equidistant from the centered transition metal inside the

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ring.[18−20] The centered Ni5 atom in the [Ni(*cyclo*-Ni_4Sb_4)] unit of $[Ni_5Sb_{17}]^{4-}$ is also in the geometrical center of the ring with statistically equivalent Ni5−Ni [2.56(2) Å (av)] and Ni5−Sb [2.59(3) Å (av)] contacts. In the (*cyclo*-Ni_4-Sb_4) ring, the Ni−Sb−Ni and Sb−Ni−Sb bond angles are 83(1)° (av) and 90(1)° (av), respectively. In contrast, the centered Pd5 atom in the [Pd(*cyclo*-Pd_4As_4)] unit is shifted significantly from the middle of the ring with shorter contacts to the As atoms [2.57(5) Å (av)] relative to the ring Pd atoms [2.85(3) Å (av)]. In addition, the bond angles in the corresponding (*cyclo*-Pd_4As_4) ring of $[Pd_7As_{16}]^{4-}$ are expanded [93(1)° and 94(1)° for Pd−As−Pd and As−Pd−As, respectively] relative to **2** to accommodate the larger transition metal, Pd.

In all of these cyclic units, the E atoms are assumed to be two-electron donors. Assuming that the Pd5 atom in **4** is a d^8 Pd^{II} center, it attains a 16-valence-electron configuration through bonds to the four As ring atoms. Therefore, Pd5 is not electronically saturated and is capable of forming Pd−Pd bonds. DFT calculations[21,22] show a significant degree of metal−metal bonding despite the rather long ∼2.8 Å separations. In contrast, the Ni5 atom centered in the *cyclo*-Ni_4Sb_4 ring of **2** is ligated by five Sb atoms in total (square-pyramidal coordination; Figure 1a), which presumably gives an electronically saturated 18-electron center. As such, there should not be significant Ni−Ni bonding to Ni5 despite the short ∼2.5 Å separations. Indeed, the DFT calculations show negligible metal−metal bonding to Ni5.

Bond orders derived from DFT calculations and a Jeitschko-like bond valence (BV) analysis[23,24] support similar degrees of partial bonding and overall bond orders within the cluster. Attempts to extend the valence bond descriptions, charge analysis, and subsequent oxidation-state determinations are quite tenuous with $[Ni_5Sb_{17}]^{4-}$. The total charge for the Sb_{17} cluster calculated by the BV analysis is −19.7 (i.e., $Sb_{17}^{-19.7}$), which suggests that the five Ni atoms carry a 15.7+ charge after the 4− charge on the total anion is taken into account. One scenario is that all five Ni atoms are formally 3+ or, alternatively, the square-pyramidal environment of Ni5 suggests that it is in a formal 2+ oxidation state, with the remaining four Ni atoms being 3+. We note that these oxidation states are strictly formalisms and are only used as a mechanism for electron accounting. Actual charges on the metal atoms are clearly negative in most cases. The mixed valencies, partial bonding, and lack of molecular analogues make it difficult to describe these intermetalloid clusters in a simple valence bond or Zintl−Klemm framework. Further analysis of **1** and the synthesis of new members of this class are in progress.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant 0401850. We are extremely grateful to Prof. Andrei Vedernikov for extensive help with the DFT calculations.

Supporting Information Available: Full crystallographic data and a CIF file for **2**, DFT and BV analysis for **2** and **4**, and experimental details for the synthesis of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0616535

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