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Synthesis, Structure, and Magnetic Properties of a New Ternary Zintl Phase: $Sr_{21}Mn_4Sb_{18}$

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We have made a new Mn-containing transition metal Zintl phase. It is the first example of a Mn_8Sb_{22} cluster which is composed of a dimer of dimers linked through an Sb_2 bond. It also exhibits highly unusual magnetic properties.

The investigations of Zintl phases of alkali and alkaline earth metal groups with elements of the groups 13−15 have shown various structural units of polyanion framework, such as a diamondlike Tl-net in NaTl,[1] a "butterfly" homonuclear anion $[Si_4]^{6-}$ in Ba_3Si_4,[2] and heteronuclear anions with tetrahedral units. Ternary Zintl compounds have been explored intensively because of their rich variety of solid structures formed from the different connection of the heteronuclear tetrahedral units. The ternary Zintl phases containing tetrahedral anions are generally divided into three groups, which contain isolated, oligomeric or polymeric, and highly condensed tetrahedral frameworks,[3] depending on the condensation of the tetrahedral unit. Recently, many interesting physical properties have been observed in these compounds by making isostructural transition metal analogues[4] of main group metal Zintl compounds and by synthesis of heavy element analogues[5] of the Zintl phases, and they illustrate the potential of this area.

$Sr_{21}Mn_4Sb_{18}$ is a new structure type and exhibits a new type of connection of the heteronuclear tetrahedral units. A total of eight $MnSb_4$ tetrahedral units are connected by sharing an edge and by sharing a corner to make one large cluster-anion unit. This is a unique structure compared to the previous three groups of tetrahedral framework compounds. It cannot be a member of the group of isolated[6] or oligomeric tetrahedral structures[7] because there are eight tetrahedral units connected together. It is also different from the polymeric[8,9] tetrahedral unit forming one-dimensional infinite chains or highly condensed tetrahedral networks,[10,11] containing highly coordinated pnictogen atoms since the anionic units in the title compound are linked to make an isolated cluster.

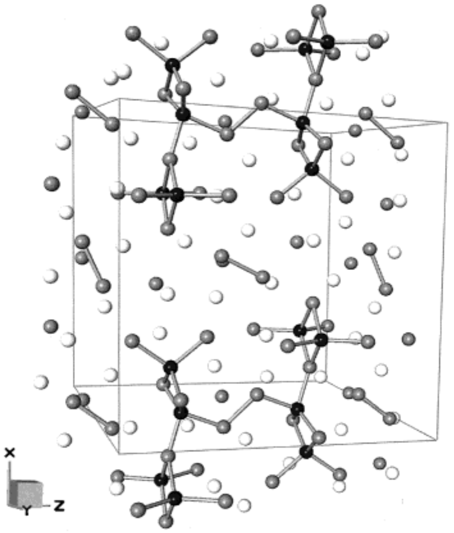

Figure 1. A view of a portion of the unit cell of $Sr_{21}Mn_4Sb_{11}$ showing the packing of the $[Mn_8Sb_{22}]^{48-}$ clusters, $[Sb_2]^{4-}$ dumbbells, Sb^{3-} atoms, and the Sr^{2+} atoms. Black circles: Mn; gray: Sb, white: Sr.

$Sr_{21}Mn_4Sb_{18}$ was synthesized from the elements Sn (99.99%, Alfa), Sr (99.95%, Alfa), Mn (99.98%, Alfa), Sb (99.995%, Cerac) using Sn flux method.[12] All preparations were performed in a nitrogen-filled drybox with water levels less than 1 ppm. The mixture of elements (Sr:Mn:Sb:Sn, 21:7:18:64) were placed in an alumina crucible, which is then sealed under 1:5 atm/Ar in a quartz tube. The mixture was heated to 950 °C at the rate of 3 °C/hr, held at 950 °C for 24 h, cooled to 800 °C at 3 °C/hr, and held at 800 °C for approximately 7 days. The reaction was removed from the box furnace at the final temperature of 800 °C, immediately inverted into a centrifuge and spun at 6500 rpm for 1 min to remove the liquid Sn flux from the crystals. Many large silver-colored crystals of the title compound were found upon examination. Single-crystal X-ray diffraction data of a crystal (0.02 × 0.03 × 0.13 mm) were collected using a Bruker SMART 1000 CCD diffractometer equipped with a CRYO COOLER low-temperature apparatus (CRYO INDUSTRIES of America, Inc.).[13]

The structure can be described in the framework of the Zintl concept. The contents of the unit cell are 84 Sr^{2+} cations, 16 Sb^{3-} anions, 6 $[Sb_2]^{4-}$ dumbbells, and 2 $[Mn_8Sb_{22}]^{48-}$ heteroanion clusters. Figure 1 shows a portion of the unit cell of $Sr_{21}Mn_4Sb_{18}$ (The clusters residing at $y = 0$ and 1 have been removed for clarity.) In one formula unit, a total of 42 electrons from the electron-donating alkaline earth metal, Sr, is transferred to the three different anionic subunits. The basic scheme of this new structure is similar to the previously reported ternary Zintl phase, $Ca_{11}InSb_9$[15] and $Ca_{14}AlSb_{11}$.[15] $Ca_{11}InSb_9$ contains an isolated tetrahedral anion, $[InSb_4]$,$^{9-}$ and shows the same dumbbell $[Sb_2]^{4-}$ unit and isolated pnictogen anions, Sb^{3-}. $Ca_{14}AlSb_{11}$ is another interesting example in which total 28 positive formal charges from the electron reservoir of 14 Ca^{2+} are equalized by the isosteric ortho-anion, $[AlSb_4]^{9-}$ and a pnictogen linear unit, $[Sb_3]^{7-}$ with four isolated pnictogen anions, Sb^{3-}.

However, the uniqueness of the structure of the title compound originates from the heteronuclear tetrahedral cluster shown in Figure 2. To our knowledge, this is the largest isolated unit among the heteronuclear tetrahedral anions of Zintl phases excluding the

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[13] X-ray diffraction data ($2\theta_{\max} = 63°$) was collected at 90 K with Mo Kα radiation. Crystal data: monoclinic, $C2/m$, $Z = 4$, $a = 18.1981(6)$ Å, $b = 17.3589(6)$ Å, $c = 17.8391(6)$ Å, $\beta = 91.957(1)°$, V = 5632.1(3) Å^3, $\mu = 29.01$ mm^{-1}, $\rho_{calc} = 5.014$ g/cm^3, $R_1/wR_2 = 3.30/6.68\%$ for the observed 7042 reflections ($I > 2\sigma(I)$) and 215 parameters. The SMART software was used for data collection and SAINT for data integration. The absorption correction was performed using SADABS. The structure was solved by direct methods, refined using SHELXL-97.

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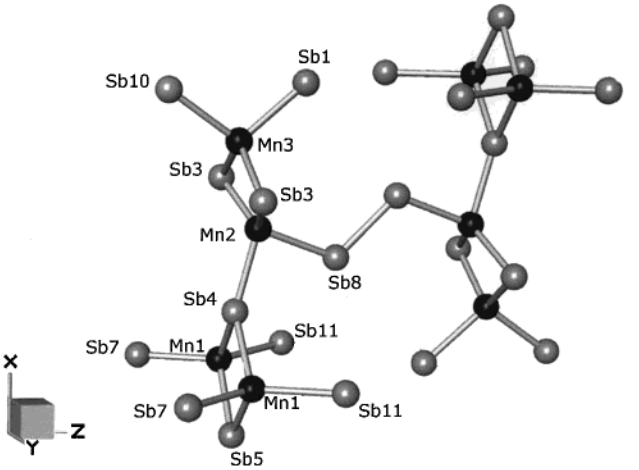

Figure 2. A perspective view of the $[Mn_8Sb_{22}]^{48-}$ cluster. Black circles: Mn; gray: Sb.

infinite chains or networks. The two edge-sharing tetrahedra are connected to the other two edge-sharing tetrahedra by corner-sharing, and again a total of four tetrahedra subunits are connected to each other via a dumbbell anion−anion bonding to make a heteronuclear anionic tetrahedral structure. As a result, there is surprisingly a total of six different types of pnictogen anions in the cluster, indicating the versatility of the pnictogen element for making bonds to follow the generalized (8-N) rule in the Zintl phase.

The Mn−Sb distances in this cluster range from 2.763 to 3.007 Å, which are similar to the previously reported ternary manganese antimonides, such as 2.736 Å in $Zn_{0.94}Mn_{0.89}Sb$,[16] 2.758 Å in $EuMn_2Sb_2$,[17] 2.804 Å in $BaMnSb_2$,[18] and 2.838 Å in $Sr_{14}MnSb_{11}$.[19] The bond angles of Sb−Mn−Sb in the tetrahedra show slight deviations from the ideal angle (109.5°) of tetrahedron with the exception of three bond angles. The relatively small angle (94.6°) of Sb(4)−Mn(1)−Sb(5) is attributed to the repulsion between Mn(1) and Mn′(1). The largest deviation (120.9°) is found in Sb(7)−Mn(1)−Sb(11), which is similar to the angle (120°) in a trigonal planar structure. The smallest angle (83.3°) is found in Sb(4)−Mn(2)−Sb(8). The four heteronuclear tetrahedral subunits, which are connected via a dumbbell Sb_2, are brought close to each other to make a more condensed structure. The Mn(2)−Mn(3) distance is relatively short at 2.932 Å, but larger than elemental Mn−Mn bond distance at 2.54 Å. The Sb−Sb distances range from 2.844 Å in the dumbbell to 2.865 Å in the pair bridging the Mn dimers. These values are consistent with the single-bond lengths.[14,20]

Another importance of the cluster structure is found in its unusual connection of isolated heteronuclear anionic tetrahedra. So far, there have been several examples of the dimerization of two tetrahedra via a common edge shown in Na_5HfAs_3 and Na_5SnSb_3.[21] In the case of the trigonal planar pnictido groups, the dimers or trimers of the heteroanionic unit were reported in Cs_3InP_2[22] and $K_{10}Ga_3Sb_{6.33}$.[23] However, these examples were limited to the connection of a small number of heteronuclear units making an isolated structure. One can now expect another possible heteranionic structure in the ternary Zintl phases triggered by the discovery of this new cluster-type structure.

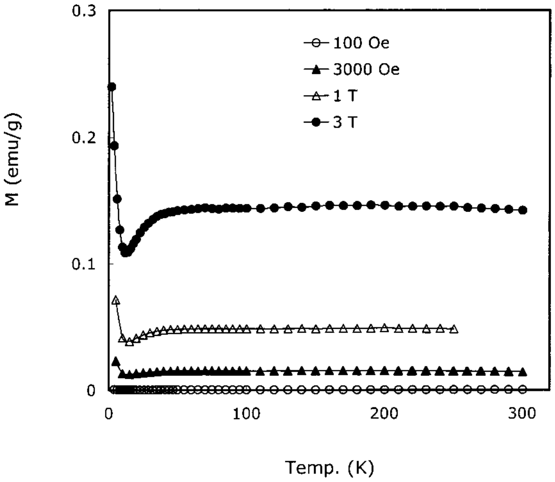

Figure 3. Temperature-dependent magnetization of a single crystal of $Sr_{21}Mn_4Sb_{18}$.

The temperature-dependent magnetization of a single crystal (∼0.0041 g) of the title compound was measured from 2 to 300 K using a SQUID magnetometer. In the high-temperature region, above 80 K, all of the different field data present very weak temperature dependence ($M_{300K}/M_{80K} = 0.95-1.02$) as shown in Figure 3. This is similar to the free-electron Pauli paramagnetic susceptibility[24] occurring in metals. However, there is some field dependence to the susceptibility so that the data are best shown here as magnetization.

There is a sharp increase of the magnetization that occurs at lower temperatures, below 12 K. This anomaly is field-dependent and is reminiscent of the magnetic tails found in spin-fluctuated systems.[25] The magnetic susceptibility at high fields (>3 kOe) is field independent, However, at lower fields (<3 kOe), the susceptibility is field-dependent. The magnetic data are not easily interpreted, and further electronic and magnetotransport characterization are underway to gain insight into the unusual magnetism.

Further studies are in progress in our group to explore different types of ternary Zintl phases, and the other alkaline earth analogues or rare earth analogues of the title compound are under investigation.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond distances, and aniostropic displacement parameters (PDF). X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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