

# Synthesis, Characterization, Electronic Structure, and Bonding of Heteroatomic Deltahedral Clusters: $\text{Na}_{49}\text{Cd}_{58.5}\text{Sn}_{37.5}$ , A Network Structure Containing the First Empty Icosahedron without a Group 13 Element and the Largest *closo*-Deltahedron

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**Abstract:** The intermetallic compound  $\text{Na}_{49}\text{Cd}_{58.5}\text{Sn}_{37.5}$  was obtained in nearly 100% yield after fusion of the elements in stoichiometric proportions in a Nb container and quenching of the mixture. The structure was determined by single-crystal X-ray diffraction (rhombohedral,  $R\bar{3}m$ ,  $Z = 3$ ,  $a = 16.034(1) \text{ \AA}$ ,  $c = 50.64(1) \text{ \AA}$ ;  $R, R_w(F) = 3.3\%, 4.2\%$ ). The covalently-bonded part of the structure is a network of cadmium and tin that contains the following: (a) the first empty icosahedra built without atoms of an element of group 13; (b) 12-bonded 18-atom *closo*-deltahedra, the largest *closo*-deltahedron ever made; (c) 20-atom spacers. The sodium cations are located between the clusters and also center the 18-atom cluster. Band calculations on the network and molecular orbital calculations on the 12-bonded 18-atom cluster show that the latter is *hyperelectronic* with  $2n + 4$  skeletal electrons, and also that its six lone-pair orbitals are not occupied. Magnetic measurements show small temperature-independent paramagnetism.

## Introduction

The fascination with the high symmetry of three-dimensional bodies is not new and dates back to the age of the five Platonic solids and even before that. Today, this fascination is still very much alive, and we find it in the shapes of the fullerenes, the “metcars” of  $\text{Ti}_8\text{C}_{12}$ , the octahedral transition metal clusters, etc. It is also in the high-symmetry Platonic and Platonic-like main-group deltahedral clusters found in intermetallic and Zintl solid-state compounds. These latter clusters come mainly from group 13, although there are also tetrahedral clusters of groups 14 and 15, and a recently synthesized monocapped square antiprism of germanium, the first larger cluster of this group in the solid state.<sup>1</sup> A variety of these deltahedral clusters of Ga, In, and Tl was synthesized and characterized in the last few years.<sup>2,3</sup> The most reoccurring shape among them is the icosahedron, and the pronounced tendency of the elements of this group to form icosahedra has led to suggestions for naming them “icosogens” (similarly to pnictogens, chalcogens, and halogens).<sup>4</sup> Furthermore, all known icosahedral species,  $\text{M}_{12}$ , contain one or more atoms of group 13, i.e., it seemed that the presence of an icosogen was crucial for the formation of icosahedra, the trademark of the boron group. Some examples of phases with homonuclear icosahedra are  $\beta$ -boron,  $\text{RbGa}_7$ ,<sup>2</sup>  $\text{Li}_2\text{Ga}_7$ ,<sup>5</sup>  $\text{Na}_3\text{K}_8\text{Tl}_{13}$ ,<sup>6</sup> and  $\text{Rb}_3\text{Na}_{26}\text{In}_{48}$ .<sup>7</sup> Compounds with heteroatomic icosahedra in the structures are, for example,  $\text{Mg}_{11}\text{Zn}_{11}\text{Al}_6$ ,<sup>8</sup>  $\text{Na}_{35}\text{Cd}_{24}\text{Ga}_{56}$ ,<sup>9</sup>  $\text{Na}_{23}\text{In}_{38.4}\text{Zn}_{4.6}$ ,  $\text{Na}_9\text{In}_{16.8}\text{Zn}_{2.3}$ ,

$\text{Na}_{49}\text{In}_{90-x}\text{Sn}_x$ ,  $\text{K}_{37}\text{In}_{69-x}\text{Cd}_x$ ,<sup>10</sup> etc. We have embarked on exploring the possibilities of building icosahedral and larger deltahedral clusters without the “help” of an icosogen.

Our approach in the search for such clusters is to use combinations of post-transition elements that will be isoelectronic with an icosogen, and study eventual Zintl (or Zintl-like) phases in the corresponding alkali metal-containing ternary systems. The Zintl phases form a large and important class in inorganic chemistry but only a very small part of their enormous combinatorial potential has been investigated to date. Usually the structures are very complex, difficult to understand, and have even more complex chemical bonding. Phases containing heteroatomic clusters of the kind mentioned above are expected to be even more complicated in that respect. In addition, a general observation can be made that the more “electron-poor” the elements in these heterometallic compounds (groups 11 and 12), the more unusual the structural motifs they create. This usually leads to novel bonding since the electronic requirements and the electronic structure as a whole will be quite different in these compounds.

We report here on the synthesis and structure of the first compound,  $\text{Na}_{49}\text{Cd}_{58.5}\text{Sn}_{37.5}$ , made by following the strategy of combinations of elements that are isoelectronic with an icosogen. This compound contains the first empty icosahedron made without group 13 elements. Also, an 18-atom *closo*-deltahedral cluster, the largest *closo*-deltahedron ever made, is present in the structure. In support of the elimination of the exclusive rights of the boron group to form icosahedra, we have also obtained a second compound,  $\text{Na}_{13}\text{Cd}_{20}\text{Pb}_7$ , with icosahedra of Cd and Pb only.<sup>11</sup> The 12-bonded 18-atom deltahedron has unusual electronic structure in what appears to be the first example of a *closo*-deltahedron with empty lone-pair orbitals. This apparently is due to the size of the cluster and the resulting curvature of its surface. Band calculations on the three-

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dimensional anionic network show a narrow band in the density of states that is low-lying above the Fermi level. The band is due to the same lone-pair orbitals and is empty. The cluster is also unusual in that it requires  $2n + 4$  electrons for bonding rather than the prescribed by the Wade's rules  $2n + 2$ .

### Experimental Section

**Synthesis.** Series of mixtures of Na (Alfa, 99.9%, sealed under Ar), Cd (Alfa, 99.999%), and Sn (Alfa, 99.9%) were prepared in a N<sub>2</sub>-filled glovebox (<1 ppm of moisture) after scraping off the surfaces of sodium and tin to remove the oxide films. The molar ratios varied from 3:1 to 1:2 for Na/(Cd–Sn) and from 2:3 to 3:2 for Cd/Sn. The mixtures were loaded in Nb tubes arc-welded at one end. The second end is then crimped, the tube is placed in the chamber of an air-tight arc-welder, the chamber is evacuated and filled with argon to about 0.8 atm, and the container is sealed by arc-welding. The tubes are then placed in fused-silica ampules sealed under vacuum. The ampules were heated at 650 °C for 2 days and then slowly cooled to 100 °C at a rate of 5 °C/h. (The highest melting points in the Na–Cd, Na–Sn, and Cd–Sn binary systems are 390, 580, and 320 °C, respectively.)

The tubes were opened in a glovebox, and finely ground samples were prepared for X-ray powder diffraction. In order to avoid contact with air during transfer, the samples were isolated between pieces of scotch tape. An Enraf–Nonius Guinier camera with vacuum chamber, Cu K $\alpha$  radiation ( $\lambda = 1.540562$  Å), and NBS (NIST) silicon as an internal standard were used for powder diffraction.

The powder patterns were compared with calculated patterns of known binary compounds and the only known ternary compound, Na<sub>2</sub>–CdSn.<sup>12</sup> It was clear that a new compound was present in some of the samples. We also compared the observed powder patterns with calculated ones for the systems A–In–(M), where A = alkali metal and M = main-group element, since an equimolar mixture of Cd and Sn is isoelectronic with indium, and therefore possibilities for isostructural relations exist. The lines of the unknown compound were very closely related to that of Na<sub>49</sub>In<sub>90–x</sub>Sn<sub>x</sub><sup>10</sup> (structurally characterized but with unknown stoichiometry). After the structure of the cadmium–tin compound was determined from single-crystal X-ray diffraction, it was confirmed that the two are indeed isostructural. Our attempts to make isostructural compounds in the systems Na–Cd–Pb, K–Cd–Pb, and Na–Zn–Sn (in order to distinguish the post-transition elements by X-ray diffraction) were unsuccessful.

**Structure Determination.** Pieces from a crushed sample loaded as Na<sub>6</sub>Cd<sub>5</sub>Sn<sub>6</sub> (gray, metallic appearance, very brittle) were picked and sealed in glass capillaries. They were checked by oscillation and Weissenberg photographs for singularity and eventually cell parameters assignment. One of the parameters was determined to be around 16.06 Å, a value different from the lattice parameters of any known binary or ternary compound in the system. The corresponding crystal, 0.15 × 0.20 × 0.28 mm in size, was chosen, and X-ray data were collected on an Enraf–Nonius CAD4 single-crystal diffractometer with monochromated Mo K $\alpha$  radiation (2 octants,  $2\theta \leq 50^\circ$ , room temperature). The data were corrected for Lorentz and polarization effects and for absorption with the aid of the average of eight  $\psi$ -scans at different  $2\theta$  angles. The observed absence condition  $-h+k+l \neq 3n$  suggested a rhombohedral space group. The lattice parameters of the compound,  $a = 16.034(1)$  Å and  $c = 50.64(1)$  Å, were determined from the corresponding X-ray powder pattern by least-squares refinement of the measured  $2\theta$  values together with those of the internal standard. Details of the data collection and refinement are listed in Table 1.<sup>13</sup>

The atomic positions of Na<sub>49</sub>In<sub>90–x</sub>Sn<sub>x</sub> were used as starting positions for the refinement of the structure.<sup>10</sup> Initially it was assumed that only cadmium atoms occupy the anionic sites, and later the procedure was repeated using only tin instead. The two refinements showed no substantial differences, i.e., the positional and thermal parameters were well within  $1.5\sigma$  of each other. This result is expected since tin and cadmium differ by 2 electrons only, and moreover, these 2 electrons account for only 4% of the scattering power of either of the two elements. Random assignments of Sn or Cd for the 14 different anionic

**Table 1.** Crystallographic Data for Na<sub>49</sub>Cd<sub>58.34(3)</sub>Sn<sub>37.69(2)</sub>

empirical formula	Na <sub>49</sub> Cd <sub>58.34(3)</sub> Sn <sub>37.69(2)</sub>
formula weight	12157.75
unit cell parameters <sup>a</sup>	$a = 16.034(1)$ Å $c = 50.64(1)$ Å $V = 11275(2)$ Å <sup>3</sup>
Z	3
space group	$R\bar{3}m$ (No. 166)
$\mu$ (Mo K $\alpha$ )	143.2 cm <sup>-1</sup>
transmission range	0.3653–0.9985
$F(000)$	15 672
density (calculated)	5.372 g/cm <sup>3</sup>
R indices ( $I > 2\sigma_I$ )	$R_1^b = 3.29\%$ , $wR_2^c = 6.82\%$
R indices (all data)	$R_1^b = 4.23\%$ , $wR_2^c = 7.21\%$

<sup>a</sup> Room temperature Guinier data with Si as an internal standard ( $\lambda = 1.540562$  Å). <sup>b</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>c</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ ;  $w = 1/[\sigma^2 F_o^2 + (0.0875P)^2 + 4.7318P]$ ,  $P = (F_o^2 + 2F_c^2)/3$ .

sites did not bring recognizable differences either. Nevertheless, it was clear that two sites, M12 and M13 (M represents either Cd or Sn), were partially occupied. This was determined by varying the multiplicities of all anionic sites while keeping the sodium multiplicities fixed. All, except for M12 and M13, were within  $3.5\sigma$  of full occupancy, independent of whether Cd or Sn was placed at a particular position. Therefore, these sites were kept with full occupancies for the subsequent procedures. The occupancies of the sodium sites were varied next while keeping the occupancies of the anionic sites fixed. All were within  $3\sigma$  of full occupancy. For the final refinement all multiplicities except those of M12 and M13 were fixed.

The stoichiometry of the compound was determined by other means (see below). The formula was found to be exactly or very close to Na<sub>49</sub>Cd<sub>58</sub>Sn<sub>38</sub> based on the loaded stoichiometry of a reaction with 100% yield of the compound. Since the occupancies of the anionic sites by either Cd or Sn did not lead to significant differences in the final results, these sites were more or less arbitrarily assigned to the two elements but in such a way that (a) would reproduce most closely the determined stoichiometry and (b) would place the Sn atoms at sites with the smallest thermal parameters when the structure is refined with Cd only. Thus, there are six different Sn atoms (Sn3, 5, 8, 11, 12, 14) and eight different Cd atoms (Cd1, 2, 4, 6, 7, 9, 10, 13) in the structure. The partially occupied site M12 is Sn12 while M13 is Cd13. Of course, this assignment of different atoms for the different positions does not mean that some or all of the sites could not be with mixed Cd–Sn occupancies. The final refined formula is Na<sub>49</sub>Cd<sub>58.34(3)</sub>Sn<sub>37.69(2)</sub>.

**Stoichiometry.** The atomic ratio of the alkali metal to Cd–Sn was easily determined from the refinement as 49:96.03(3) but the Cd to Sn ratio was unclear. Since it is next to impossible to distinguishing Cd from Sn by X-rays, we looked for other ways to determine that ratio. We used molecular orbital and band calculations to estimate a meaningful value of  $x$  in Na<sub>49</sub>Cd<sub>58.34(3)</sub>Sn<sub>x</sub>. The result was rather a range of possible numbers,  $52.5 \leq x \leq 58.5$ , due to the presence of nonbonding states that could be either populated or empty (see below). Subsequently reactions with stoichiometries within this range were loaded in order to determine the correct stoichiometry. These were heated at 680 °C for 1 day and then quenched in cold water in order to avoid any possible peritectic disproportionation. This was followed by annealing at 350 °C for 2 weeks.

The X-ray powder patterns taken from the samples showed that all but the one with  $x = 58$  had another unknown phase in addition to the expected one. (Work is in progress to characterize this other unknown compound.) The powder pattern of the reaction loaded as Na<sub>49</sub>Cd<sub>58</sub>–Sn<sub>38</sub> showed only lines of the refined structure, and no lines of other phase could be seen. (For the Guinier camera, we expect ca. 3 wt % detection limit assuming similar scattering powers of the phases.<sup>14</sup>) The 100(±3)% yield defines the stoichiometry of the compound (the

(14) West, A. R. *Solid State Chemistry and its Applications*; Wiley: New York, 1987; p 50. (It is stated that “the lower limit of detection of impurity phases in routine work is usually in the range of 1–5 percent” but “under favorable conditions such as when looking for a specific impurity, the detection limit may be decreased considerably ... by increasing the time of exposure”. These limits are given for a maximum of 1 h exposure time, whereas we had 2 h of exposure for these particular samples.)

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(13) The structure was refined with the SHELXTL-V5 package (SIEMENS, 1994).

**Table 2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters of  $\text{Na}_{49}\text{Cd}_{58.34(3)}\text{Sn}_{37.69(2)}$ 

atom	<i>N</i>	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}} (\text{\AA}^2)^a$
Cd1	18h	0.2718(1)	- <i>x</i>	0.9269(1)	0.017(1)
Cd2	18h	0.6050(1)	- <i>x</i>	0.9880(1)	0.021(1)
Sn3	18h	0.2268(1)	- <i>x</i>	0.9793(1)	0.021(1)
Cd4	18h	0.2711(1)	- <i>x</i>	0.7362(1)	0.019(1)
Sn5	18h	0.5399(1)	- <i>x</i>	0.9430(1)	0.019(1)
Cd6	18h	0.5615(1)	- <i>x</i>	0.0418(1)	0.023(1)
Cd7	36i	0.6674(1)	0.1479(1)	0.8935(1)	0.020(1)
Sn8	18h	0.2169(1)	- <i>x</i>	0.8807(1)	0.020(1)
Cd9	36i	0.6668(1)	0.9930(1)	0.8642(1)	0.017(1)
Cd10	18h	0.5602(1)	- <i>x</i>	0.2927(1)	0.020(1)
Sn11	18h	0.2182(1)	- <i>x</i>	0.7841(1)	0.019(1)
Sn12 <sup>b</sup>	6c	0	0	0.4713(1)	0.041(1)
Cd13 <sup>c</sup>	18h	0.1111(1)	- <i>x</i>	0.9828(1)	0.035(1)
Sn14	36i	0.4913(1)	0.3374(1)	0.1672(1)	0.018(1)
Na1	6c	0	0	0.4045(2)	0.029(2)
Na2	18h	0.5406(2)	- <i>x</i>	0.1072(1)	0.026(1)
Na3	18h	0.1270(2)	- <i>x</i>	0.1053(1)	0.029(1)
Na4	18h	0.2170(2)	- <i>x</i>	0.0478(1)	0.028(1)
Na5	18h	0.5404(2)	- <i>x</i>	0.8340(1)	0.033(1)
Na6	36i	0.2898(3)	0.3328(3)	0.9312(1)	0.032(1)
Na7	6c	0	0	0.2016(2)	0.023(2)
Na8	6c	0	0	0.1287(2)	0.023(2)
Na9	3a	0	0	0	0.044(4)
Na10	18f	0.3757(5)	0	0	0.051(2)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor. <sup>b</sup> Occupancy 84.6(8)%. <sup>c</sup> Occupancy 72.4(5)%.

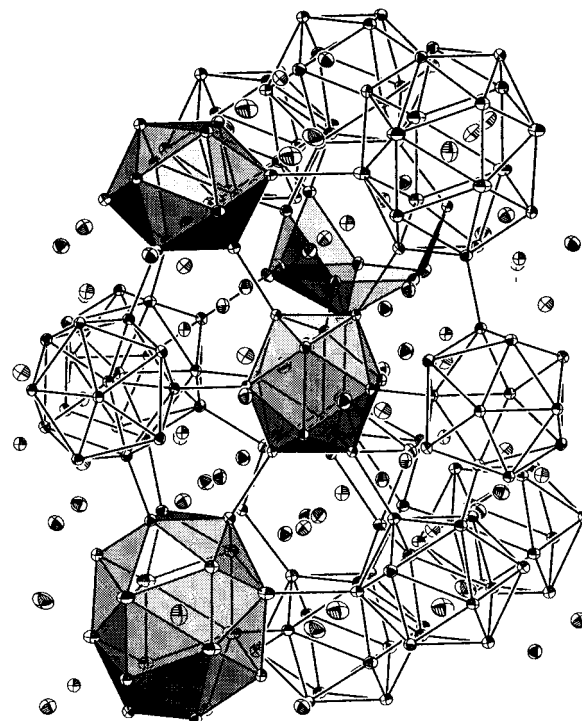
Cd to Sn ratio to be more specific). The 3% detection limit translates into the following uncertainties in the formula  $\text{Na}_{49}\text{Cd}_{58(2)}\text{Sn}_{96.03(5)-58(2)}$ . For the calculation, we used the two extreme cases of pure Sn or pure Cd as the second phase below the detection limit.

An X-ray powder diffraction pattern was calculated based on the refined structure, and the lines on the observed powder patterns were indexed. A least-squares refinement of their  $2\theta$  values together with those of the standard Si resulted in a small interval of fluctuation for the *a* parameter of the compound,  $a = 16.039(3)$  and  $16.068(2)$  Å (*ca.*  $7\sigma$  difference) for the end members with  $x = 58$  and  $43$ , respectively, but no change for the *c* parameter,  $c = 50.690(10)$  and  $50.680(8)$  Å for the same stoichiometries. Since Cd and Sn have very similar sizes, large changes are not expected even if compounds with different Cd–Sn ratios exist. On the other hand, different temperature treatments may result in differences in the lattice parameters. Thus, the parameters of the refined structure are somewhat closer to the parameters for composition with  $x = 58$ , although the loaded stoichiometry is closer to that of  $x = 43$  (the actual  $x$  is 43.6). The difference between these reactions is in the cooling rates.

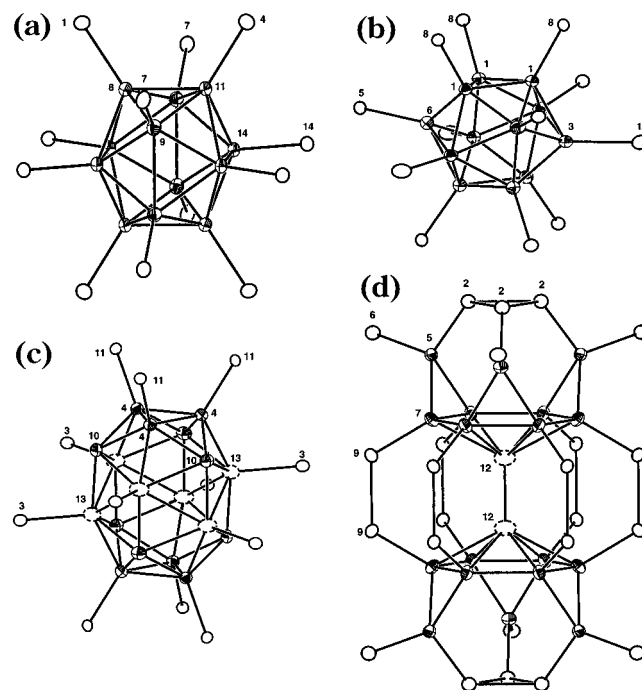
**Magnetic Susceptibility.** The magnetization of 25 mg of the sample with 100% yield (loaded as  $\text{Na}_{49}\text{Cd}_{58}\text{Sn}_{38}$ ) was measured at fields of 3 T and of 100 Oe over the ranges of 6–295 K and 2–10 K, respectively. Quantum Design MPMS SQUID magnetometer was used for that purpose. A sample holder made of  $3 \times 5 \times 160$  mm (i.d.  $\times$  o.d.  $\times$  length) tubing and two half-length pieces of tightly fitting rods, all made of fused-silica, was used. One piece of rod is inserted all the way into the tubing and the ends of tubing, and rod are sealed together. The sample is then loaded from the other end of the tube (inside the glovebox), the other piece of rod is inserted, and the second end is sealed as well. The raw data were corrected for the susceptibility of the container.

## Results

**Structure Description.** The final positional and equivalent isotropic displacement parameters and the important distances ( $<4.0$  Å) for the refined composition  $\text{Na}_{49}\text{Cd}_{58.34(3)}\text{Sn}_{37.69(2)}$  are listed in Tables 2 and 3, respectively. A general view of (approximately) the primitive cell is shown on Figure 1. The three-dimensional structure is composed of four different building blocks: two types of icosahedra (labeled A and B), 18-atom *closo*-polyhedra and 20-atom spacers. The A-type icosahedra are arranged in Kagomé nets perpendicular to the



**Figure 1.** A general view of the structure of  $\text{Na}_{49}\text{Cd}_{58.5}\text{Sn}_{37.5}$ . Shown is about one-third of the hexagonal cell with the *c*-axis vertical. The thermal ellipsoids are drawn with 50% probability size. Lines are drawn for all (Cd/Sn)–(Cd/Sn) separations less than 4.0 Å. The two different icosahedra, the 18-atom *closo*-deltahedron and half of the 20-atom spacer are shaded.



**Figure 2.** Shown are the different building blocks of the structure of  $\text{Na}_{49}\text{Cd}_{58.5}\text{Sn}_{37.5}$ : (a) the 12-bonded A-type icosahedron ( $C_{2h}$ ); (b) the 12-bonded B-type icosahedron ( $C_{3v}$ ); (c) the 12-bonded 18-atom deltahedron ( $D_{3d}$ ); (d) the 20-atom spacer (all with 70% thermal ellipsoids). The thermal ellipsoids of the partially occupied sites are shown with broken line (positions 12 and 13 are 84.6(8) and 72.4(5)% occupied, respectively). The *exo*-atoms are shown with empty ellipsoids.

*c*-axis, and the nets alternate with puckered close-packed layers of B-type icosahedra together with 18-atom deltahedra.

The two types of icosahedra, A and B, are both 12-bonded (Figures 2a and 2b). The A-type (Cd9; Sn8, 11, 14) is with

**Table 3.** Selected Distances ( $d \leq 4.0$  Å) in  $\text{Na}_{49}\text{Cd}_{58.34(3)}\text{Sn}_{37.69(2)}$ 

Cd1—2 Cd1	2.961(2)	Cd9— Cd7	2.8891(9)	Na3—2 Cd4	3.552(5)
Sn3	2.931(2)	Sn8	3.0338(8)	2 Cd7	3.479(5)
2 Cd6	2.995(1)	Cd9	3.129(2)	2 Cd9	3.290(3)
Sn8	2.792(1)	Sn11	3.0750(8)	Cd10	3.324(6)
2 Na2	3.490(5)	Sn14	2.8908(9)	2 Sn11	3.429(4)
2 Na6	3.539(4)	Sn14	2.921(1)	2 Sn14	3.529(6)
Na7	3.429(9)	Na2	3.257(3)	Na4	3.837(8)
Cd2— Cd2	2.967(2)	Na3	3.290(3)	2 Na6	3.571(5)
2 Sn3	3.060(1)	Na5	3.359(4)	Na8	3.719(7)
Sn5	2.909(1)	Na5	3.388(4)	Na4—2 Cd2	3.337(5)
Cd6	2.979(2)	Na6	3.442(5)	Sn3	3.481(6)
Na1	3.45(1)	Cd10—2 Cd4	2.959(1)	2 Sn5	3.417(3)
2 Na4	3.337(5)	Cd13	2.934(2)	2 Cd7	3.381(6)
2 Na10	3.583(5)	2 Cd13	3.247(1)	Cd10	3.090(6)
Sn3— Cd1	2.931(2)	Na3	3.324(6)	Na1	3.442(7)
2 Cd2	3.060(1)	Na4	3.090(6)	Na3	3.837(8)
2 Cd6	3.1275(8)	2 Na6	3.500(4)	2 Na6	3.770(5)
Cd13	3.218(2)	Na9	3.603(1)	2 Na10	3.949(4)
Na4	3.481(6)	Sn11— Cd4	2.838(1)	Na5—2 Cd7	3.493(6)
2 Na6	3.558(4)	Sn8	2.828(1)	2 Cd7	3.542(6)
2 Na10	3.368(2)	2 Cd9	3.0750(8)	2 Cd9	3.359(4)
Cd4—2 Cd4	2.993(2)	2 Sn14	2.973(1)	2 Cd9	3.388(4)
2 Cd10	2.959(1)	2 Na3	3.429(4)	Sn12	3.783(6)
Sn11	2.838(1)	2 Na6	3.466(4)	Sn12	3.809(6)
Cd13	2.973(2)	Na8	3.248(2)	2 Sn14	3.536(6)
2 Na3	3.552(5)	Sn12—6 Cd7	3.379(1)	Na2	3.732(9)
2 Na6	3.505(4)	Sn12	2.906(5)	2 Na5	3.508(6)
Na8	3.461(9)	Na1	3.38(1)	Na6— Cd1	3.539(4)
Na9	3.921(1)	3 Na5	3.783(6)	Sn3	3.558(4)
Sn5— Cd2	2.909(1)	3 Na5	3.809(6)	Cd4	3.505(4)
Cd6	2.920(1)	Cd13— Sn3	3.218(2)	Sn5	3.524(4)
2 Cd7	3.068(1)	Cd4	2.973(2)	Cd6	3.501(4)
Na1	3.593(2)	Cd10	2.934(2)	Cd7	3.606(4)
Na2	3.387(6)	2 Cd10	3.247(1)	Sn8	3.524(4)
2 Na4	3.417(3)	2 Cd13	3.547(2)	Cd9	3.442(5)
2 Na6	3.524(4)	2 Na6	3.617(5)	Cd10	3.500(4)
2 Na10	3.678(5)	Na9	3.206(2)	Sn11	3.466(4)
Cd6—2 Cd1	2.995(1)	2 Na10	3.793(7)	Cd13	3.617(5)
Cd2	2.979(2)	Sn14— Sn8	2.948(1)	Na2	3.637(5)
2 Sn3	3.1275(8)	Cd9	2.8908(9)	Na3	3.571(5)
Sn5	2.290(1)	Cd9	2.921(1)	Na4	3.770(5)
Na2	3.364(6)	Sn11	2.973(1)	Na10	3.682(5)
2 Na6	3.501(4)	Sn14	2.746(1)	Na7—3 Cd1	3.429(9)
2 Na10	3.372(5)	Sn14	2.943(1)	3 Sn8	3.295(2)
Cd7— Sn5	3.068(1)	Na2	3.481(6)	6 Sn14	3.363(5)
Cd7	2.962(1)	Na3	3.529(6)	3 Na2	3.714(7)
Cd7	2.995(1)	Na5	3.536(6)	Na8	3.69(2)
Cd9	2.8891(9)	Na7	3.363(5)	Na8—3 Cd4	3.461(9)
Sn12	3.379(1)	Na8	3.420(6)	3 Sn11	3.248(2)
Na1	3.473(6)	Na1—3 Cd2	3.45(1)	6 Sn14	3.420(6)
Na2	3.517(5)	3 Sn5	3.593(2)	3 Na3	3.719(7)
Na3	3.479(5)	5 Cd7	3.473(6)	Na7	3.69(2)
Na4	3.381(6)	Sn12	3.38(1)	Na9—6 Cd4	3.921(1)
Na5	3.493(6)	3 Na4	3.442(7)	6 Cd10	3.603(1)
Na5	3.542(6)	Na2— Cd1	3.490(5)	6 Cd13	3.206(2)
Na6	3.606(4)	Sn5	3.387(6)	Na10— Cd2	3.583(4)
Sn8— Cd1	2.792(1)	Cd6	3.364(6)	Sn3	3.368(2)
2 Cd9	3.0338(8)	2 Cd7	3.517(5)	Sn5	3.678(5)
Sn11	2.828(1)	2 Sn8	3.429(3)	Cd6	3.372(5)
2 Sn14	2.948(1)	2 Cd9	3.257(3)	Cd13	3.793(7)
2 Na2	3.429(3)	2 Sn14	3.481(6)	Na4	3.949(4)
2 Na6	3.524(4)	Na5	3.732(9)	Na10	3.98(2)
Na7	3.295(2)	2 Na6	3.637(5)	2 Na6	3.682(5)
Na7	3.714(7)				

$C_{2h}$  symmetry and is centered on the 9d ( $2/m$ ) position. It is *exo*-bonded to four A-type icosahedra (Sn14—Sn14, 2.746(1) Å, the shortest bond in the structure), two B-type icosahedra (Sn8—Cd1, 2.792(1) Å), two 18-atom clusters (Sn11—Cd4, 2.838(1) Å), and two 20-atom spacers (two Cd9—Cd7 bonds to each, 2.889(1) Å). The B-type icosahedra (Cd1, 6; Sn3) are centered on the 6c ( $3m$ ) positions and have  $C_{3v}$  symmetry. Each is bonded to three A-type icosahedra (Cd1—Sn8), three 18-atom clusters (Sn3—Cd13, 3.218(2) Å), and four 20-atom spacers

(three Cd2—Sn5 bonds to one, 2.909(1) Å, three Cd6—Sn5 bonds to three others, 2.920(1) Å). As expected, the intercluster bonds are in general shorter than the intracluster ones (see Table 3).

The 18-vertex cluster (Cd4, 10, 13) is with very high symmetry of  $D_{3d}$  (Figure 2c). It is centered on the 3a ( $\bar{3}m$ ) position and is 12-bonded to six A-type icosahedra (Cd4—Sn11, 2.838 Å), and six B-type icosahedra (Cd13—Sn3, 3.218 Å). The remaining six atoms, Cd10, are not *exo*-bonded. They are the

only atoms in the structure that do not have *exo*-bonds. All faces of the cluster are triangular, and therefore the cluster is a *closo*-deltahedron. Cd4 and Cd10 are 5-bonded within the cluster while Cd13 has six such bonds. When combined with the *exo*-bonds, the total number of bonds becomes 6, 5, and 7 for Cd4, Cd10, and Cd13, respectively. Usually atoms that are 6-bonded within a cluster and are also *exo*-bonded, such as Cd13 in this case, have longer distances and often their occupancy is less than full. The *exo*-distance and the average of the *endo*-distances around Cd13 are 3.218(2) and 3.249(4) Å, respectively. For comparison, these numbers are 2.838(1) and 2.976(4) Å for Cd4 and 3.069(3) Å for Cd10 (*endo*-bonded only). Cd13 is also one of the two atoms with partial occupancies. The structure refinement indicated 72.4(5)% occupancy for this position.

The 20-atom spacer (Figure 2d) is centered on the 3b ( $\bar{3}m$ ) position and consists of Sn5, Cd7, and Sn12. These atoms are 4-, 5-, and 7-bonded, respectively. Similarly to Cd13, the 7-bonded atom Sn12 is partially occupied (84.6(8)% occupancy), and the distances to the seven neighboring atoms are relatively long (3.312(6) Å average). The spacer as a whole is connected to six A-type (twelve Cd7–Cd9 bonds) and eight B-type icosahedra (six Sn5–Cd2 and six Sn5–Cd6 bonds).

All sodium atoms except Na9 are positioned between the building blocks of the structure and cap their triangular faces. Na9 is at the center of the 18-atom cluster.

**Properties.** The magnetic measurements at 3 T gave temperature-independent susceptibilities of  $-(3.34-3.44) \times 10^{-3}$  emu/mol over the range of 50–295 K. A “tail” toward higher susceptibilities is observed below 50 K ( $-1.0 \times 10^{-3}$  emu/mol at 6 K). It is most likely due to extremely small amounts of adventitious para- or ferromagnetic impurities. Two types of diamagnetic corrections were applied to the experimental numbers. One is for the ion cores of Na<sup>+</sup>, Cd<sup>2+</sup>, and Sn<sup>4+</sup> and amounts to  $-2.13 \times 10^{-3}$  emu/mol.<sup>15</sup> The second correction is for the Larmor precession of the delocalized electron pairs on cluster orbitals. This number,  $\chi_L$ , is estimated from  $\chi_L = -0.79Z(r/a_0)^2 \times 10^{-6}$  emu/mol per cluster where  $Z$  is the number of delocalized cluster electrons,  $r$  is the average radius of the cluster (center-to-edge), and  $a_0 = 0.529$  Å.<sup>16</sup> We calculated  $r$  values of 2.82, 2.87, and 3.58 Å for the A- and B-icosahedra and for the 18-atom cluster, respectively. These, together with the fact that there are three A-type and two B-type icosahedra and one 18-atom cluster per cell and that the numbers of delocalized electrons are 26 per icosahedron and 40 per 18-atom cluster (see below), result in a total of  $-4.40 \times 10^{-3}$  emu/mol for that correction. The sum of the two corrections becomes  $-6.53 \times 10^{-3}$  emu/mol, and when applied, the corrected susceptibilities become  $+(3.09-3.19) \times 10^{-3}$  emu/mol. This indicates that the sample is Pauli-paramagnetic (metallic paramagnetism) in agreement with the electronic structure and the possibility of having small electron population of low-lying nonbonding states. The close-shell formula derived from band calculations is Na<sub>49</sub>Cd<sub>58.5</sub>Sn<sub>37.5</sub> (see below), and therefore, the measured sample of Na<sub>49</sub>Cd<sub>58</sub>Sn<sub>38</sub> (assuming the formula of the single-phase product is the same as the loaded stoichiometry) would have one electron in the narrow conduction band that has a capacity for 12 electrons.

## Discussion

**Structural Features.** Two features in the structure make it particularly exciting and unique. One of them is that this is

the first compound with icosahedra that are built without a single atom of an element of group 13. The two types of icosahedra, A and B, contain atoms of Cd and Sn only. Although the structure was refined with Sn and Cd at particular sites, it is more likely that all anionic sites have some average mixed Cd–Sn occupancies. Since cadmium is the major component in the structure (Cd–Sn  $\approx$  3:2) and the compound is Zintl-like, we can consider that the so-called Zintl border (between elements that are known to form Zintl phases and those that are not yet known to form such phases) has been moved to include yet another element, cadmium. Compounds near borders are often particularly interesting due to the possibility of having properties from both sides of the border or exhibiting interesting transitions across the border. Compounds near the Zintl border may display metal–insulator transitions or may have very specific electronic structures that deviate from the structures of either side of the border. Na<sub>49</sub>Cd<sub>58.5</sub>Sn<sub>37.5</sub> is near the Zintl border and has quite unusual electronic structure.

The second unique feature in the structure is the presence of the largest *closo*-deltahedron ever made, a cluster of 18 atoms. It has 32 triangular faces and can be named trianta(30)-dio(2)-hedron,<sup>17</sup> since deltahedra are named according to the number of the faces. The previous “record-holder” was a 16-atom cluster of indium with the geometry of a tetracapped truncated tetrahedron.<sup>18</sup> The triantadiohedron is with the highest possible symmetry for species with 18 vertices,  $D_{3d}$ . Lipscomb et al. on the other hand, have recommended  $D_3$  as the more likely geometry for a cluster of that size.<sup>19</sup> The only difference between the two geometries is the incomplete twist of the two halves of the cluster with respect to each other in  $D_3$ , and it is not clear why those authors preferred the lower symmetry.

The 18-atom cluster can be described in several ways. One way is to look at it as composed of two *hypho*-icosahedra (icosahedron with missing three atoms) twisted at 60° with respect to each other and joined together at their open sides via the Cd13–Cd10 bonds of 2.935(2) Å. (There are also Cd13–Cd13 bonds between the two halves but they are too long, 3.547(2) Å, to be considered the primary interaction.) The dividing plane is horizontal on Figure 2c, and the two *hypho*-species are the northern and southern hemispheres of the cluster. Another way of describing the cluster is of being a hexacapped (Cd13) truncated trigonal antiprism (Sn4, Cd10), but this is somewhat more difficult to see.

Another important feature of the cluster is that it is oblong-like rather than spherical. This has very important implications on the number of delocalized electrons required for bonding and therefore on the electronic structure of the whole compound.

The 20-atom spacer can be looked on as composed of two monocapped (Sn12) triply-bridged (Sn5) hexagons (Cd7). These two parts are connected through the capping Sn12 atoms. In borane terminology, they can be called triply-bridged *nido*-octanes, where the *closo*-octane would have a hexagonal bipyramidal geometry. These bridges are quite common in the boranes where the bridging atoms are hydrogens. Furthermore, the hydrogens are often “substituted” by other groups such as BH<sub>2</sub> or similar. In our case, the atoms Sn5 play the role of the BH<sub>2</sub> groups since they are bridging (two bonds to Cd7) and are additionally 2-bonded to Cd2 and Cd6. The word “spacer” is used for this formation to indicate a group of atoms that does not have delocalized bonding electrons and differs in that respect from being a cluster.

**Electronic Structure.** Perhaps the most interesting aspect of Na<sub>49</sub>Cd<sub>58.5</sub>Sn<sub>37.5</sub> is its electronic structure, and more notably

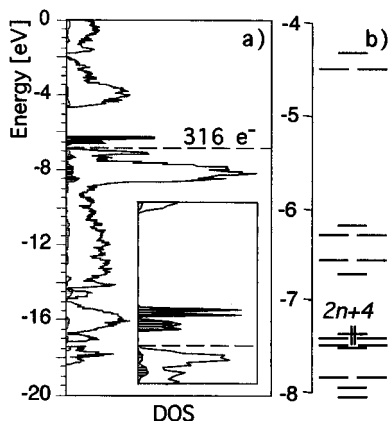
(15) Selwood, P. W. *Magnetochemistry*, 2nd ed.; Interscience Publishers: New York, 1956; p 70.

(16) Ashcroft, N. W.; Mermin, D. N. *Solid State Physics*; Holt, Reinhart, and Wilson: Philadelphia, Pa, 1976; p 649.

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(19) Brown, L. D.; Lipscomb, W. N. *Inorg. Chem.* **1977**, *16*, 2989.



**Figure 3.** Plots of (a) density of states for  $\text{Na}_{49}\text{Cd}_{58.5}\text{Sn}_{37.5}$  and (b) part of the molecular orbital diagram for the 12-bonded 18-atom deltahedron near the HOMO–LUMO gap. The Fermi level for 316 electrons is indicated by a dashed line. The partial DOS for the atoms without *exo*-bonds are shown striped. The insert shows closer view of the area near the Fermi level and spans from  $-7.5$  to  $-4.5$  eV.

the electronic structure of the 18-atom *closo*-triantadiohedron. This cluster is a violation of the well-known Wade's rules by being *hyperelectronic*, and it is also the first cluster beyond a critical size for which the lone-pair orbitals become empty.

Extended-Hückel band calculations on the Cd–Sn part of the structure and molecular orbital calculations on the triantadiohedron were performed, and the results are shown on Figures 3a and 3b, respectively. The calculations were carried out with “average” parameters for the two elements. We used the  $\xi$  and  $H_{ij}$  parameters for the element that is in between cadmium and tin, i.e., indium (5s 1.9 and  $-12.6$ ; 5p 1.68 and  $-6.19$ ). (Calculations with Cd only or Sn only as well as with different combinations of arbitrarily distributed Cd and Sn gave very similar results. For simplicity only the results from the calculations with average parameters are presented.) Dummy atoms with s orbitals only were used to model the *exo*-atoms to the  $M_{18}$  cluster (Figure 2c) in the molecular orbital calculations. For the  $\xi$  and  $H_{ij}$  parameters of these s orbitals, we used the corresponding parameters of the p orbitals of indium, 1.68 and  $-6.19$ , respectively. This allows for good overlap with the radial p orbital on the corresponding cluster atom and for a normal 2-center 2-electron *exo*-bond, a model which is in accord with the observed short *exo*-bonds.

The density of states (DOS) clearly shows the distinctively wide s band of states between *ca.*  $-18$  and  $-8$  eV, and the much narrower p band in the  $-9$  to  $-5$  eV region (Figure 3a). A large band gap between *ca.*  $-6.25$  and  $-4.75$  eV is also clearly noticeable. The states above that gap are strictly antibonding. The gap in the DOS corresponds to the gap between *ca.*  $-6.2$  and  $-4.5$  eV on the molecular orbital (MO) diagram of the  $M_{18}$  cluster (Figure 3b). Initially it was assumed that the states (or orbitals) below that gap would be filled in order to have a relatively stable compound. The number of electrons needed to do that is 328 per formula unit. This number of electrons defines the formula of the compound as  $\text{Na}_{49}\text{Cd}_{52.5}\text{Sn}_{43.5}$ , since the only unknown from the structure refinement is the Cd to Sn ratio. (It is clear that the sum of the Cd and Sn atoms is 96.) This theory-suggested formula narrowed substantially the region of possible stoichiometries, as discussed in the Experimental Section. Since the only way to confirm the formula of the compound in our case (and perhaps the best way for any case) was to make it in a 100% yield, we ran the series of reactions with stoichiometries near the suggested one. It was clear that it is unlikely to have more than 328 electrons, since that would have meant occupation of strongly antibonding states

above a gap of about 1.5 eV. Nevertheless, the loaded reactions covered the region below and above that number. The result from these reactions was somewhat surprising to us since the reaction with the closest stoichiometry to that of the theory was a mixture of phases. All other reactions, except one loaded for 317 electrons per formula unit, had the same outcome. The exception was  $\text{Na}_{49}\text{Cd}_{58}\text{Sn}_{38}$  which produced the compound as a single phase. This was somewhat puzzling, the explanation was not an obvious one, and therefore a more careful look at the results from our calculations was in order.

It was realized that the narrow bands around  $-6.4$  eV in the DOS (Figure 3a and the insert) are almost 100% of Cd10 character, the atom without *exo*-bonds in the  $M_{18}$  cluster. Similarly, the six molecular orbitals between  $-6.2$  and  $-6.7$  eV in the MO diagram (Figure 3b) are orbitals located on the six Cd10 atoms. Upon closer investigation, it was revealed that these are the lone-pair orbitals on these atoms, which explained why the band is so narrow on the DOS and also why they are with such high energy in the MO diagram. These orbitals are strictly nonbonding when they have only p character. This is the case when the corresponding atom is in the plane of the nearest atoms that surround it. However, the same orbitals become somewhat bonding and occupied when mixing with s orbitals and therefore stabilization is allowed due to the “pyramidal” geometry of cluster atoms. The degree of mixing depends on the deviation from planar coordination, i.e., the curvature of the cluster at the particular atom.

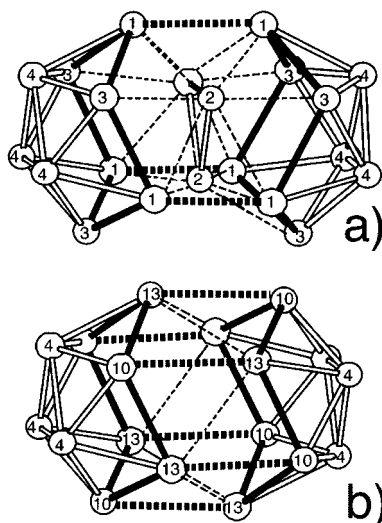
The energy of these lone-pair orbitals, essentially  $\pi$ -type p-orbitals, will also depend on whether similar  $\pi$ -orbitals exist on the nearest atoms and whether they are empty or filled. Thus, filled orbitals will destabilize the lone-pair orbitals while empty ones will stabilize them.

The third factor that will affect the relative energy position of the lone-pair orbitals with respect to the bonding ones is the degree of discrepancy in the  $H_{ij}$  values of the central atom and those of the atoms bonded to it. Larger differences will cause larger separation (destabilization) of the lone-pair orbitals. This discrepancy may come from two sources: chemically different central atom and some of the atoms surrounding it, i.e., heteroatomic cluster, and different charge accumulation. If a site in a cluster needs to carry four electrons, for example, this will mean a charge of  $-2$  for an element from group 12, a charge of  $-1$  for an element from group 13, and a charge of 0 for group 14. These different charges will “lift” the ionization potentials of the orbitals of these elements to different extent, with the largest charge causing the greatest destabilization.

All of the factors described above will guide the destabilization or stabilization of the lone-pair orbitals by one or another mechanism. The simple rules that can be derived are that flatter coordination, ligands with filled  $\pi$ -type orbitals, presence of more electronegative heteroatoms, and high negative charges will all work toward destabilization of a lone-pair orbital.

Burdett and Canadell have shown how lone-pair orbitals in borane clusters are strongly affected by the curvature (the flatness) of the cluster, the lack or the presence of neighboring *exo*-bonds or lone-pairs, and by the presence of heteroatoms.<sup>20</sup> Those authors compared the energy of a lone-pair orbital on boron atom in a flat hexagonal net of B–H groups and in a formation of two fused borane icosahedra similar to the one shown on Figure 4a. (The two icosahedra are fused through the triangular face made of atoms number 2. The bonds to the triangle are shown with thin broken lines.) Empty lone-pair orbitals were predicted for the flat net as well as for atoms number 1 in the fused icosahedra. On the other hand, the lone-

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**Figure 4.** Shown is how two hemispheres of *hypho*-icosahedra can form: (a) two fused icosahedra or (b) 18-atom deltahedron (shown with the 3-fold axis horizontal), depending upon the rotation with respect to each other.

pair orbitals of atoms 3 and 4 in the latter are calculated to be occupied. The difference is that the geometry around 3 and 4 is not affected by the oligomerization, while that around 1 has become closer to planar and atoms 1 have become relatively close to each other (shown by thick broken lines). This allows for stronger  $\pi$ -antibonding interactions with the surrounding pairs of electrons on *exo*-bonds. Stressing on the primary importance of the curvature the authors conclude: "A simple prediction is that as the nuclearity, and hence the radius of the curvature of the cluster, increases, we expect to reach a particular point where occupation of the lone-pair orbitals might be questionable. It is interesting to inquire at which critical cluster size might the lone-pair orbital become vacant".<sup>20</sup>

We think that the 18-atom triantadiohedron is such a cluster beyond or with a critical size. Figure 4b clearly shows the similarity between the triantadiohedron, shown artificially slightly more elongated, and the fused icosahedra (Figure 4a). It was already pointed out that the cluster can be "assembled" from two *hypho*-icosahedra (the two parts are shown on Figure 4b). The "open" side of this species is in the form of a cyclohexane with the shape of a chair, outlined with thick solid lines on Figure 4b (atoms 10 and 13). The cluster is formed with two chairs in parallel formation with respect to each other, and bonds are formed between them (thick broken lines between 10 and 13). The same representation can be used to describe the fused icosahedra but with the two chairs (atoms 1 and 3) in oblique formation and bonded via atoms 1 (the triangle of atoms 2 can be disregarded). The *hypho*-species on Figures 4a and 4b are exactly the same, the only difference is that they are rotated at different angles with respect to each other. The coordination and the curvature at atom 1 in Figure 4a are virtually the same as those at atom 10 in Figure 4b. Also, the atoms around 10 are *exo*-bonded just like the discussed case for atoms 1 in the fused icosahedra. Therefore, we can expect similarly that the lone-pair orbital on 10 will be with high energy and empty.

In addition, our compound contains heteroatoms that have different ionization potentials. Moreover, these atoms are from different groups in the periodic table and therefore will accumulate different negative charges when the same or similar numbers of electrons are at their sites. Cadmium will become more negative than tin, and as a result, its orbitals will be even higher in energy. This is particularly true for lone-pair orbitals

since they mix much less with orbitals of other atoms. These lone pairs may become destabilized so much that they may remain unoccupied. Different atoms and different charges will translate into shifting the band of the lone-pair orbitals on Figure 4a toward higher energies and opening a larger gap below it that may become even larger than the one above it. Therefore, a compound where this band is empty may be more stable than where it is filled.

All three factors, i.e., curvature, environment, and heteroatoms, work toward destabilization of the lone pairs in  $\text{Na}_{49}\text{Cd}_{58.5}\text{Sn}_{37.5}$ . In reality, of course, it is possible to have some partial occupation of the nonbonding band and this will make the compound somewhat metallic. This may explain the small Pauli-paramagnetism measured for the slightly Sn-rich  $\text{Na}_{49}\text{Cd}_{58}\text{Sn}_{38}$ . Although the band is narrow, it apparently is wide enough and contains enough contribution from other atoms in order to be somewhat conducting, i.e., with delocalized rather than localized electrons.

The number of electrons needed to fill the bonding states (Figure 3a) is 316. This gives a formula of  $\text{Na}_{49}\text{Cd}_{58.5}\text{Sn}_{37.5}$ . The formula from the refined structure is  $\text{Na}_{49}\text{Cd}_{58.34(3)}\text{Sn}_{37.69(2)}$  which is equivalent to 316.4(1) electrons.

Another unique feature in this compound is in the number of electrons required for bonding in the triantadiohedron. Deltahedral clusters normally follow the rules established for electron counting in boranes, the Wade's rules.<sup>21</sup> According to them, a *closo*-species has one radial and  $n$  tangential bonding orbitals and therefore requires  $2n + 2$  bonding electrons. The rules have been tested and work satisfactory for borane-like deltahedra of up to 12 atoms, but it is not clear whether they will hold for larger sizes as well. There are a few exceptions known for deltahedral clusters of 10 and 11 atoms where a lower number of bonding electrons is required due to a geometry different from that of the corresponding boranes. These hypoelectronic species are the compressed pentacapped trigonal prism of  $\text{In}_{11}$ ,<sup>22</sup> the compressed tetracapped trigonal prism of  $\text{In}_{10}(\text{Ni})$ ,<sup>23</sup> and the compressed bicapped square antiprism of  $\text{In}_{10}(\text{Zn})$ .<sup>24</sup> A higher number of bonding electrons is observed for the larger size cluster of  $\text{In}_{16}$  with the shape of a tetracapped truncated tetrahedron.<sup>18</sup> Nevertheless, in this particular case, the violation is not due to the size of the cluster but is rather intrinsic for the  $T_d$  point groups due to orbital degeneracies. (Similarly the simple tetrahedron has *closo*-shape but has  $2n + 4$  electrons and is therefore considered *nido*-species.) Our MO calculations show that the triantadiohedron requires  $2n + 4$  bonding electrons. Figure 3b shows the HOMO at *ca.*  $-7.4$  eV corresponding to that number of electrons. The deviation in this case is clearly not due to particular symmetry but rather to the size of the cluster. It is the first such *hyperelectronic* species where the size leads to an additional bonding orbital.

This "additional" orbital exists in smaller clusters as well but is of antibonding character. It becomes bonding in  $M_{18}$  due to the oblong-like shape of the cluster and its size. The orbital is bonding within each of the hemispheres of the cluster but is  $\pi$ -antibonding between the two. Naturally, since the cluster is quite elongated, the bonding interactions predominate over the antibonding ones, and the end result is a bonding orbital. In smaller or spherical clusters the orbital has a net antibonding character since the two "hemispheres" are too small in small clusters (and therefore the bonding interactions are smaller) or are not separated enough in spherical clusters (and therefore the antibonding interactions are not that small).

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The fact that the lone-pair orbitals are empty in the triantadiohedron also means that the cluster will have smaller negative charge as a whole. Large negative charges are usually not tolerated. For the boranes, the problem is solved by the hydrogen ligands which bring one additional electron each. For deltahedral clusters without ligands (unlike the boranes), the charge problem has to be solved in a different manner. Such clusters have "found" different creative ways to do this, such as (a) forming relatively small clusters that will naturally require smaller charges; (b) forming clusters with geometries that require fewer than  $2n + 2$  electrons; (c) forming centered clusters where the central atoms bring additional electrons; (d) forming clusters with *exo*-bonds since each *exo*-bond reduces the charge by one; and (e) forming clusters where some of the atoms are electron-rich.<sup>2,3</sup> Therefore, forming large enough clusters where the lone-pair orbitals remain empty is yet another way of reducing the charge on the cluster. This may involve a requirement for more skeletal bonding electrons as in our case,  $2n + 4$  vs  $2n + 2$ , and the need for increased charge as a result, but the net effect is reduced charge since the 12 electrons that would have filled the lone-pair orbitals are not required.

**Electron Count.** It is possible to rationalize the bonding in this structure also by simply counting the number of electrons needed for bonding in the different segments of the structure and the number of electrons provided by the stoichiometry. The segments are icosahedra, triantadiohedra, and 20-atom spacers. As yet we have not discussed the electronic requirements for bonding in the latter. Extended-Hückel MO calculations were performed for that purpose. They clearly showed that (a) the Sn12–Sn12 bond connecting the two halves of the spacer (Figure 3d) is simply a 2-center–2-electron bond; (b) all 4 bonds around Sn5 are also 2-center–2-electron bonds; and (c) the triangles Cd7–Cd7–Sn12 that share edges with two triangles of Cd7–Cd7–Sn12 and one of Cd7–Cd7–Sn5 are bonded by 3-center 2-electron bonds (every other triangle in the capped hexagon of Cd7). This means that all atoms in the spacer satisfy the simple octet rule: the Sn5-atoms are 4-bonded, the Cd7-atoms have three "normal" bonds and one 3-center–2-electron bond or total of 4 electron pairs, and the Sn12-atoms have three 3-center–2-electron bonds and one "normal" bond or total of 4 electron pairs as well. Thus, the 20-atom spacer will require

$20 \times 4$  (if all bonds were 2-center 2-electron) – 6 (for the six 3-center–2-electron bonds) = 74 electrons for bonding.

There are 5 icosahedra (three of A-type and two of B-type), 1 triantadiohedron, and 1 spacer per formula unit. The electron requirements for each of them are as follows: (a)  $2n + 2 = 2 \times 12 + 2 = 26$  skeletal and  $12 \times 1$  *exo*-bonding electrons per icosahedron or a total of 38; (b)  $2n + 4 = 2 \times 18 + 4 = 40$  skeletal and  $12 \times 1$  *exo*-bonding electrons per triantadiohedron or a total of 52; (c) 74 electrons per spacer. This yields  $5 \times 38$  (for the icosahedra) +  $1 \times 52$  (for the triantadiohedra) +  $1 \times 74$  (for the spacer) = 316 electrons needed for bonding, i.e., the same number that was derived from the band calculations.

The partial occupation of Sn12 and Cd13 will not affect the electron count. When an atom is missing then the pair of electrons of the corresponding *exo*-bond is simply replaced by a lone pair on the *exo*-atom. It is well known that *closo*- and *nido*-species have the same number of bonding electrons, and therefore, the number of skeletal electrons for the triantadiohedron will not change either if an atom of Cd13 is missing. The same is true for the spacer where a missing Sn12 simply converts the 3-center–2-electron bonds to 2-center–2-electron ones, and the number of electrons needed for the bonding remains the same.

In conclusion, it is clear that this compound provides many first-of-a-kind structural and electronic features, and their understanding outlines directions for further exploration. One of these paths clearly suggests that cluster phases may exist in previously unsuspected regions of the periodic table. Some of them may be unique structurally as well as property-wise, and their characterization and understanding is of great importance.

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**Supporting Information Available:** Tables of data collection and refinement details, and of anisotropic thermal parameters (2 pages). See any current masthead page for ordering and Internet access instructions.

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