Articles

Synthesis, Characterization, and Bonding of Heteroatomic Clusters: $Na_{13}Cd_{20}E_7$ (E = Pb, Sn), a Further Example of a Structure Containing Empty Icosahedra without an Element of Group 13

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The compounds $Na_{13}Cd_{20}E_7$ (E = Pb, Sn) were made in nearly 100% yield by quenching the melts of appropriate mixtures of elements sealed in niobium containers. They crystallize in the cubic space group $Im\bar{3}$, Z = 4, with a = 15.992(2) and 15.790(4) Å for E = Pb and Sn, respectively. The Cd/E part of the structure is a framework of heavily fused monocapped truncated trigonal prisms. Twelve-bonded icosahedra are nested in cavities of the framework. This is the second example of a structure containing empty icosahedra made without the participation of an element of the boron group. The sodium cations occupy the space between the clusters and inside the 13-atom polyhedra.

Introduction

One fascinating area in solid-state chemistry is the chemistry of post-transition "metallic" elements in negative oxidation states. This is especially true for the early post-transition groups where many clusters and networks of clusters have been discovered. Such networks are often quite complex due to the coexistence of delocalized bonding in the clusters and "normal" 2-center−2-electron bonding between them. The boron group, for example, provides some of the most complex and unusual networks of this type. Such are the complicated networks of icosahedra as in β-boron, Li_2Ga_7, $Rb_3Na_{26}In_{48}$, $Na_3K_8Tl_{13}$, etc.[1−4] Even more interesting behavior should be expected for more electron-poor elements, the group to the left of the boron group, i.e. Zn, Cd, and Hg. This has been recently confirmed by the structure of the compound $Na_{49}Cd_{58.5}Sn_{37.5}$ which contains the largest *closo*-deltahedra, 18-atom clusters, as well as the first empty icosahedra made without an element of the boron group.[5] Of further interest are the systems (Na or K)−Cd−(Pb or Sn). Here we report on two compounds found in these systems, $Na_{13}Cd_{20}Pb_7$ and the isostructural $Na_{13}Cd_{20}Sn_7$. They represent the second example of a structure with such icosahedra.

Experimental Section

Synthesis. Mixtures with different atomic ratios of Na (99.9%, an ingot sealed under Ar), Cd (99.999%, tear drops) and Pb (99.999%, a rod), all from Alfa-Aesar, were prepared in a N_2-filled glovebox (≈0.2 ppm moisture) after scraping off the surfaces of the sodium and lead to remove the oxide films. The mixtures were enclosed in welded niobium tubes, and the latter were jacketed in evacuated quartz ampules. They were then heated at 450 °C for 2 days and slowly cooled to room temperature at a rate of 5°/h. (The highest melting points in the Na−Cd, Na−Pb, and Cd−Pb systems are 390, 403, and 328 °C, respectively.[6]) X-ray diffraction patterns from powders of finely ground samples were obtained on an Enraf-Nonius Guinier camera with monochromated Cu Kα₁ radiation (λ = 1.540 562 Å) and NBS (NIST) silicon as an internal standard.[7] The patterns were compared with those calculated for the known binary and ternary compounds in the Na−Cd−Pb system: Na_2Cd_{11}, NaPb, $NaPb_3$, and Na_2CdPb.[8] It was clear that a new compound is present in several samples.

After the structure and therefore the stoichiometry of the new compound were determined, attempts to obtain it as a single phase were made. A reaction loaded with the stoichiometric composition was treated under the same thermal conditions as above. Nevertheless, most likely due to incongruent melting, the powder pattern of the product contained lines from $NaPb_3$ and Na_2Cd_{11} in addition to the lines of the new compound, the major phase. Another stoichiometric reaction was heated at 450 °C for a few hours and then quenched in liquid nitrogen. There remained a couple of lines that could not be assigned to $Na_{13}Cd_{20}Pb_7$. They most likely belong to $NaPb_3$ but slightly shifted toward lower angles possibly due to some cadmium mixed at the lead sites.

The isostructural compound in the Na−Cd−Sn system was made from the corresponding stoichiometric mixture (Sn rods, 99.9%, Alfa-Aesar, surface was scraped off before use) by heating it at 650 °C for 2 days and then cooling it at a rate of 5°/h. (The highest melting points in the Na−Sn and Cd−Sn binary systems are 580 and 320 °C, respectively.[6]) Besides the major phase, $Na_{13}Cd_{20}Sn_7$ (>95%), the Guinier powder pattern of this reaction also shows a few weak lines from an unknown phase(s).

Structure Determination. Irregularly shaped pieces from the crushed product of a reaction loaded as $Na_{10}Cd_6Pb_7$ were picked. They were sealed in glass capillaries, and a quality check and a cell parameter estimation were done by the oscillation X-ray technique. An axial length of around 16.1 Å was observed for some crystallites, and this does not match a parameter of any of the known compounds in the system. Consequently one of these single crystals (0.10 × 0.06 × 0.06

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Table 1. Selected Data Collection and Refinement Parameters for Na$_{13}$Cd$_{20.1(1)}$Pb$_{6.9}$

chem formula	Na$_{13}$Cd$_{20.1(1)}$Pb$_{6.9}$
fw	3988.67
unit cell params[a]	$a = 15.992(2)$ Å
	$V = 4089.9(8)$ Å^3
space group, Z	$Im\bar{3}$ (No. 204), 4
radiation, λ	Mo Kα, 0.710 73 Å
μ	386.42 cm^{-1}
temp	293 K
d(calcd)	6.478 g·cm^{-3}
R indices $(I > 2\sigma_I)$[b]	$R1 = 3.15\%$, w$R2 = 4.79\%$
R indices (all data)[b]	$R1 = 6.34\%$, w$R2 = 5.88\%$

[a] Room temperature Guinier data with Si as an internal standard ($\lambda = 1.540\,562$ Å). [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R2 = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[s^2F_o^2 + (0.0086P)^2]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Positional and Isotropic Equivalent Displacement Parameters for Na$_{13}$Cd$_{20.1(1)}$Pb$_{6.9}$

atom	N	x	y	z	U_{eq}[a] (Å^2)	occ, % Cd	occ, % Pb
M(1)	24g	0.09475(7)	0.15425(7)	0	0.0209(4)	68.1(9)	31.9
M(2)	48h	0.19046(5)	0.40521(5)	0.15793(5)	0.0242(3)	72.2(9)	27.8
M(3)	12e	0.09412(8)	0.5000	0	0.0277(5)	44(1)	56
M(4)	24g	0.17707(9)	0.3113(1)	0	0.0319(6)	100	
Na(1)	16f	0.1876(3)	x	x	0.032(2)		
Na(2)	12e	-0.3016(7)	−0.5000	0	0.030(3)		
Na(3)	24g	0.3046(5)	0.1169(5)	0	0.032(2)		

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

mm) was mounted on a CAD4 single-crystal diffractometer and the 25 reflections found from random search were indexed with a body-centered cubic cell. Data were collected at room temperature with monochromated Mo Kα radiation (one octant, $2\theta \leq 50°$) and corrected for Lorentz and polarization effects and for absorption with the aid of the average of four ψ-scans at different θ-angles. The structure was solved by direct methods and successfully refined by the SHELXTL-V5.0 software package in the cubic $Im\bar{3}$ space group. The direct methods provided 4 positions with distances suitable for Cd and/or Pb. Two of them were heavier and were assigned to Pb while Cd atoms were refined initially at the other two. A few least-squares cycles followed by a difference Fourier map revealed three lighter positions with distances appropriate for sodium. They were so assigned, and after a few more cycles it was clear that the lead was too heavy for its positions while one of the Cd positions needed some more electron density. Thus cadmium was "mixed" at the lead positions and lead was "mixed" at one of the cadmium positions for the consequent refinements. (The lead content in the cadmium-only position was zero within 1σ when refined.) The final refinement was done with anisotropic thermal parameters for all atoms. Some details of the data collection and refinement are listed in Table 1. The refined stoichiometry, Na$_{13}$Cd$_{20.1(1)}$Pb$_{6.9}$, means 161.6(4) electrons per primitive cell. This is somewhat lower than expected according to the corresponding position of the Fermi level in the calculated density of states (see below). In order to clarify this we collected X-ray data from another single crystal of the same sample and refined the structure again. The refined stoichiometry was *exactly* the same but with slightly larger errors, Na$_{13}$Cd$_{20.1(2)}$Pb$_{6.9}$.

The lattice parameters of Na$_{13}$Cd$_{20}$E$_7$, a = 15.992(2) and 15.790(4) Å for E = Pb and Sn, respectively, were determined from the corresponding X-ray powder patterns by least-squares refinement of the measured 2θ values of the lines of the compounds and those of the silicon internal standard. Since the compounds are also found as products of reactions loaded with different stoichiometries, determinations of the cell parameters were performed for all of them. The parameters range between 15.976(2) and 15.992(2) Å or within 5σ of each other for Na$_{13}$Cd$_{20}$Pb$_7$, while the range is from 15.777(2) to 15.790(4) or within 3σ of each other for Na$_{13}$Cd$_{20}$Sn$_7$. These narrow ranges suggest line phases, i.e. fixed Na:Cd:E ratios.

Magnetic Measurements. The magnetization of 25-mg sample of Na$_{13}$Cd$_{20}$Pb$_7$ from the quenched stoichiometric rection was measured

Table 3. M−M Distances of Nearest Neighbors ($d \leq 3.5$ Å) about Each Atom in Na$_{13}$Cd$_{20.1(1)}$Pb$_{6.9}$

M	M	dist	M	M	dist
M1	M1	3.031(2)	M4	M1	2.835(2)
	M1 (4×)	3.047(1)		M2 (2×)	2.946(1)
	M4	2.835(2)		M2 (2×)	3.043(2)
	Na1 (2×)	3.390(8)		M3	3.297(2)
	Na3 (2×)	3.401(7)		Na3	3.395(4)
	Na3	3.408(8)	Na1	M1 (3×)	3.390(8)
M2	M2	3.032(2)		M2 (3×)	3.479(4)
	M2 (2×)	3.0396(9)		Na1	3.46(2)
	M3	3.324(1)	Na2	M2 (4×)	3.440(6)
	M4	2.946(1)		M2 (4×)	3.463(2)
	M4	3.043(2)		M3	3.32(1)
	Na1	3.479(4)		Na3 (2×)	3.387(8)
	Na2	3.440(6)	Na3	M1	3.401(7)
	Na2	3.463(2)		M1	3.408(8)
	Na3	3.486(7)		M2 (2×)	3.486(7)
M3	M2 (4×)	3.324(1)		M4 (2×)	3.395(4)
	M3	3.010(3)		Na2	3.387(8)
	M4 (2×)	3.297(2)			
	Na2 (2×)	3.32(1)			
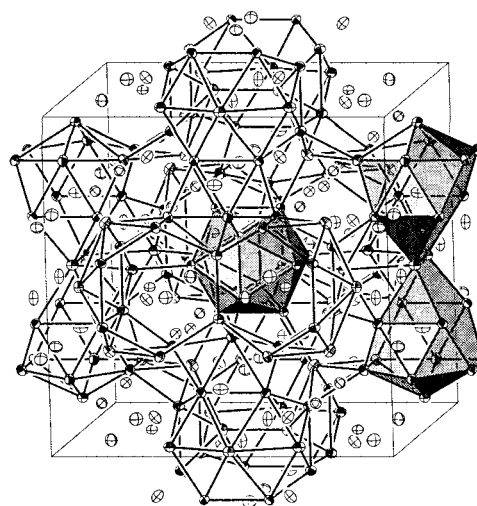
Figure 1. General view of the structure of Na$_{13}$Cd$_{20}$E$_7$. The thermal ellipsoids are drawn with 50% probability size. The icosahedron and two of the monocapped truncated trigonal prisms are shaded.

at a filed of 3 T over a temperature range of 50 to 295 K on a Quantum Design MPMS SQUID magnetometer.[7]

Extended-Hückel Calculations. Extended-Hückel band calculation were carried out on the "anionic" part of the structure, i.e. without the sodium atoms. For ionization potentials of the sites with mixed Cd/Pb occupancies we calculated average values after weighting the H_{ii} values for Pb and Cd according to their fractions at each site. Thus for the s-orbitals of M1, M2, and M3 we obtained (and used) −13.49, −13.43, and −14.15 eV, respectively. The corresponding numbers for the p-orbitals were −7.03, −7.01, and −7.32 eV. We used cadmium exponents (2.3 and 2.1 for the 5s and 5p orbitals, respectively) for all atoms since cadmium is the major component in the compound and the values do not differ substantially from those of lead. Calculations performed with Cd-only, Pb-only, or different combinations of Cd and Pb gave qualitatively the same results.

Results and Discussion

Structure Description. The final positional and equivalent isotropic displacement parameters and the important distances for Na$_{13}$Cd$_{20}$Pb$_7$ are listed in Tables 2 and 3, respectively. The general view of the unit cell in Figure 1 outlines all M−M separations (M denotes Cd/Pb from hereafter) that are less than 3.5 Å. The structure is a three-dimensional network of two types of M polyhedra with the Na cations nested between or within them. The polyhedra are monocapped truncated trigonal
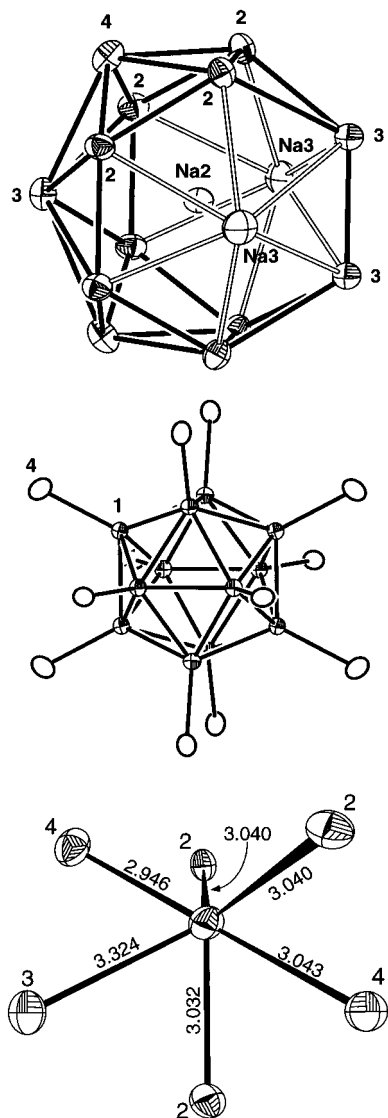
Figure 2. (a) Top: Monocapped truncated trigonal prism (C_{2v}) shown with the capping and centering sodium atoms (the pseudo-3-fold axis of the prism is vertical through Na2 and the midpoints of the triangles of atoms 2, 2, and 4). (b) Middle: 12-bonded icosahedron (T_h). (c) Bottom: Coordination around atoms M2. The thermal ellipsoids are drawn with 70% probability size.

prisms of 13 atoms (Figure 2a) and icosahedra (Figure 2b). The prisms are heavily fused with each other through triangular faces (M2−M2−M3) and edges (M3−M3). Each prism is fused with 5 other prisms, and the so-formed network has voids where the 12-bonded icosahedra are nested.

The 13-vertex polyhedra (atoms M2, 3, 4) are with C_{2v} symmetry and have two hexagonal and fourteen triangular faces. The cadmium-only atoms, M4, are exo-bonded to the icosahedra in the cavities. Na3 atoms cap the two hexagonal faces. If the latter are considered as members of the cluster it becomes a *closo*-15-vertex deltahedron, a tricapped truncated trigonal prism, as shown on Figure 2a. However, since these two Na atoms are not a part of the cluster it is rather an *arachno*-species.

The polyhedron is centered by a sodium atom, Na2. Similar centering is observed for many large clusters (larger than an icosahedron). For example, Na-centered *closo*-clusters are the In_{15} in $Na_{23}In_{38.4}Zn_{4.6}$ and $Na_{23}In_{39.8}Au_{3.4}$,[9] the In_{16} in $Na_7In_{11.8}$ and $Na_{15}In_{27.4}$,[10,11] and the $(Cd/Sn)_{18}$ in $Na_{49}Cd_{58.5}Sn_{37.5}$.[5]

Sodium and potassium atoms can also center large "spacers" (non-deltahedral open formations) such as In_{15} in $K_{22}In_{39}$ and $(Cd/Sn)_{13}$ in $Na_{49}Cd_{58.5}Sn_{37.5}$.[5,9]

The icosahedra in this structure are built of only one type atoms, M1, and have the rare T_h point group symmetry. There are very few other examples of icosahedra with such symmetry: $(Al, Zn)_{12}$ in $Mg_{11}Zn_{11}Al_6$,[12] zinc-centered Zn_{12} in Mg_2-Zn_{11} and $NaZn_{13}$,[13,14] $Al_{12}(W)$ in WAl_{12},[15] Ga_{12} in $Li_{13}Cu_6Ga_{21}$,[16] and In_{12} in $A_3Na_{26}In_{48}$ (A = K, Rb, Cs).[3] Due to this symmetry 3 pairs of opposite parallel edges are of one length, 3.031(2) Å, while the remaining 24 are of another, 3.047(1) Å. Thus the cluster has 8 equilateral and 12 isosceles triangular faces. It is 12-bonded to 12 M4 atoms, the Cd-only position. These intercluster bonds are the shortest M−M distances in the structure, 2.835(2) Å. It is very common for structures of interconnected clusters to have very short intercluster bonds since bonding within clusters is usually delocalized and fewer electrons are available per each M−M contact while bonding between clusters is via conventional 2-center−2-electron bonds. Na1 and Na3 cap all 20 faces of the cluster.

Another interesting feature in the structure of $Na_{13}Cd_{20}E_7$ is that it is the second example of a structure with icosahedra that are built without a single atom of group 13. The first such example was recently found in $Na_{49}Cd_{58.5}Sn_{37.5}$,[5] a three-dimensional network also built of "mixed" Cd/Sn atoms. The Cd:E ratio in the present compounds is higher, almost 3:1 and indicates that networks of clusters can be built even from such extremely electron-poor "mean" atoms. Notice that the average number of electrons per M atom is 2.5 in the compound (not counting electrons from the alkali metal), i.e. fewer than that in the boron group. This suggests that the icosahedron is perhaps the preferred geometry not only for the boron group but for even electron-poorer atoms. In addition to this, as expected for electron poor systems, fusion of clusters occurs. This trend is carried further in $K_{0.8}Cd_{3.75}Sn_{0.25}$, more electron-poor with 2.13 electrons/atom, where the degree of fusion approaches that of a metal or an alloy. However, since the cations need some space too, the result is a novel intermetallic zeolite-like structure.[17]

The coordination around M1 and M4 is very common for the elements of the boron group and has been observed in numerous compounds.[18,19] It is the typical inverted umbrella with five spokes, bonds within a cluster (the five bonds within the icosahedron for M1 and the prism for M4; see Figure 2), and a handle, an intercluster bond (M1−M4 in our case). The geometry around M3 is also common although not found as frequently. It is also an inverted umbrella but with six spokes, the six bonds of M3 within the prism, and the handle is the M3−M3 bond. Usually the six bonds within the cluster are longer than the five bonds of five-bonded atoms. M3 is no exception since 3.297(2) and 3.324(1) Å are the longest M−M distances in the structure.

Quite unusual and somewhat difficult to describe is the coordination around the M2 atoms (Figure 2c). The site is a

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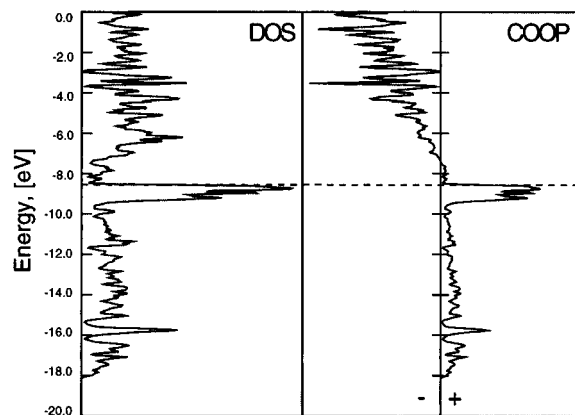(11) Sevov, S. C.; Corbett, J. D. *J. Solid State Chem.* **1993**, *103*, 114.
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Figure 3. (a) Density of states for Na$_{13}$Cd$_{20}$Pb$_7$. (b) Total COOP curve for all M−M bonds less than 3.5 Å. The Fermi level at 162 electrons per primitive unit cell is shown with a dashed line.

general position, and therefore no symmetry element passes through it. One way to look at the geometry is as yet another inverted umbrella but this time with only three spokes. These are the bonds of 3.040 Å to two other M2 atoms and of 2.946 Å to one M4 atom. The handle is the M2−M2 distance of 3.032 Å. The remaining two bonds, M2−M3 of 3.324 Å and M2−M4 of 3.043 Å, are almost in one plane with the handle. It is this strange coordination that seems to have the largest implication on the number of electrons per cell in this compound; i.e. it determines the stoichiometry (see below).

Properties. The magnetic measurements at 3 T show temperature-independent susceptibilities of $-(7.40-7.83) \times 10^{-4}$ emu/mol over the range 50−250 K. Two types of diamagnetic corrections were applied to the experimental values. One of them, -6.87×10^{-4} emu/mol, is for the ion cores of Na$^+$, Cd^{2+} and Pb^{4+}.[20] The other is Larmor precession correction for the delocalized electron pairs on cluster orbitals. Its value is given as $\chi_L = -0.79Z(r/a_0)^2 \times 10^{-6}$ emu/(mol·cluster), where Z is the number of delocalized cluster electrons, r is the average radius of the cluster (center-to-edge, Å), and $a_0 = 0.529$ Å.[21] This correction, $\chi_L = -6.55 \times 10^{-4}$ emu/mol for one icosahedron per unit cell, was calculated for the icosahedra only since it is not possible to apply to the heavily fused truncated prisms. The sum of the two corrections is -13.42×10^{-4} emu/mol and when applied the susceptibilities become $+(5.58-6.02) \times 10^{-4}$ emu/mol. This is consistent with small metallic (Pauli) paramagnetism and is in agreement with the results from the electronic structure calculations (below).

Electronic Structure. The density of states (DOS) and a total crystal orbital overlap population (COOP) curve for all M−M bonds with $d \leq 3.5$ Å are shown on Figure 3. As can be seen (and expected for a structure with fused deltahedra) there is no band gap in the DOS at the Fermi level which is shown for 162 electrons per unit cell (primitive). (The exact number of electrons defined by the formula is 161.6(4).) The Fermi level cuts slightly through the shoulder of the large peak, the p-band, of the DOS curve. For *ca.* 164 electrons, which is within 6σ, this band is completely filled and the corresponding Fermi level lies in the "valley" right above the peak. This is a more reasonable position according also to the COOP curve since at this place the character of the states changes from strongly bonding to almost nonbonding. The somewhat large difference between the two numbers of electrons, 6σ, was of

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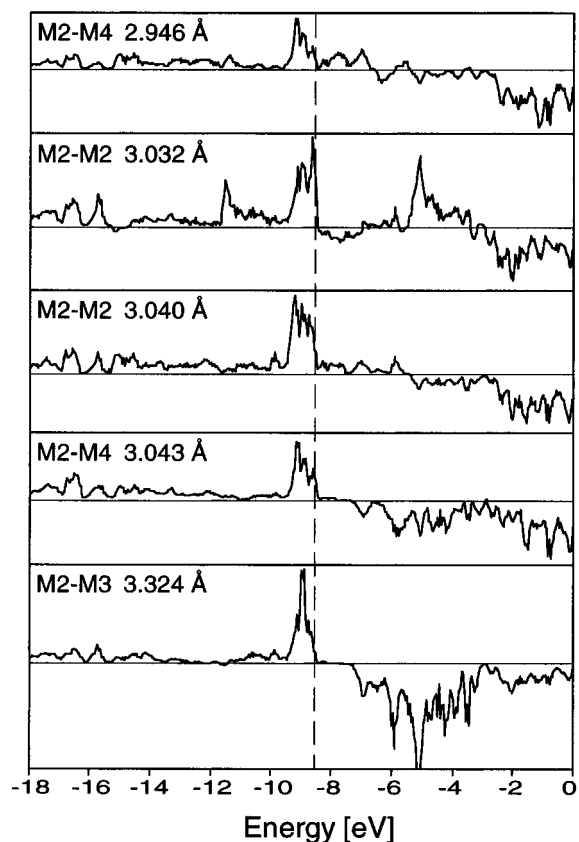
Figure 4. COOP curves (equal vertical scaling) for the five different interactions around M2. See also Figure 2c and Table 3.

concern, and led to the collection of a second X-ray data set from another crystal (see Experimental Section). Nevertheless, as mentioned above, the second crystal refined with *exactly* the same stoichiometry, i.e. with the same number of electrons per cell although with higher standard deviation, 161.6(8).

Figure 4 shows the COOP curves for all six bonds around M2. It is quite clear that the M2−M3 and one M2−M4 ($d = 3.043$ Å, Figure 2c) bonds are insensitive to additional electrons (by increasing the Pb:Cd ratio). The COOP curves for these bonds are virtually flat for more than 1 eV above the Fermi level. The rest of the interactions around M2 show quite different behavior. The M2−M2 interactions of 3.040 Å (two bonds) and the M2−M4 interaction of 2.946 Å (see Table 3 and Figures 2c and 4) are still bonding above the Fermi level. The M2−M2 interaction with $d = 3.032$ Å, on the other hand, shows antibonding character at these energies. This combined with the particular positioning of these four bonds around M2 could be the determining factor for the maximum number of electrons in this compound, or in other words, this defines the stoichiometry. As shown on Figure 2c the three bonds that are bonding above the Fermi level are the spokes of the inverted umbrella and are positioned exactly opposite to the bond with antibonding character, the handle of the umbrella. The bonds with nonbonding character above the Fermi level, M2−M3 and M2−M4, are the ones in the plane of the handle. Adding electrons above the present Fermi level will have the effect of shortening the spokes and elongating the handle. This would also lead to further elongation of the already too long M3−M2 bond of 3.324 Å making it practically nonbonding. This in turn will leave M3 as a three-coordinate atom in a flat triangle which is a very unlikely situation. Such possible effects of unusual coordination are likely to set the upper limit of the number of electrons to around 162−164. The lower limit is defined by the very strongly bonding p-band below the Fermi level. The

lack of substantial change in the lattice parameters of the compound made as a product of reactions loaded at different Cd:Pb ratios, above and below the refined 20:7, clearly indicates that the structure is stable either at only one number of electrons or within a very narrow range.

The two compounds described here and the recently reported $Na_{49}Cd_{58.5}Sn_{37.5}$[5] show that by combining elements from the left and right of the boron group it is possible to "mimic" that group and the structural features that are typical for it, i.e. deltahedral clusters. Moreover, these structural features seem to be preferred even when the post-transition "mean" atom has fewer than 3 electrons/atom as in $Na_{13}Cd_{20}E_7$ and $Na_{49}Cd_{58.5}$-$Sn_{37.5}$, where the numbers are 2.52 and 2.78, respectively. The possibility for drastic change in this number by very small changes in the ratio between the elements of the two groups could open doors to unique structures and properties.

Supporting Information Available: Plots of molar magnetic susceptibility vs temperature and of COOP curves for all 10 M−M bonds with $d \leq 3.5$ Å (2 pages). An X-ray crystallographic file, in CIF format is available. Ordering and access information is given on any current masthead page.