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$Na_8K_{23}Cd_{12}In_{48}$: A Zintl Phase Containing Icosahedral and Triangular Indium Units and Displaying a Remarkable Condensed Metal Fullerane Stuffed with a Tubular Cluster. Synthesis and Crystal and Electronic Structures

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Abstract: The quaternary intermetallic compound $Na_8K_{23}Cd_{12}In_{48}$ was obtained in high yield after fusion of the elements in stoichiometric proportions in a Nb container followed by slow cooling. The structure was established by means of single-crystal X-ray diffraction techniques ($P6/mmm$, $Z = 1$, $a = 17.114(3)$ Å, $c = 10.442(2)$ Å; $R(F)$, $Rw(F) = 2.74\%$, 3.34% for 532 independent reflections and 55 parameters varied). It is composed of indium icosahedra, indium triangular clusters, and the novel $Cd_{12}In_6$ tubular cluster. The latter, which contains two sodium cations, stuffs a 96-atom polyhedron (fullerane) and is sheathed by 32 alkali cations ($20K^+$ and $12Na^+$). The clusters are linked together through two-center two-electron bonds within a 3-D anionic network. The poor metal-like resistivity of the compound ($\rho_{293K} = 5 \times 10^{-4}$ Ω cm) is consistent with the open shell band structure determined by extended Hückel methods. The shortage in electrons of the structure, mainly due to the cation packing limitation, is almost solely borne by the hypoelectronic $Cd_{12}In_6$ cluster which has a valence electron count of 61 (including the −19 ionic charge).

Introduction

Within the last ten years, a remarkable variety of clusters or cluster frameworks has been discovered in intermetallic compounds containing electron-poor group 13 (triels Ga, In, and Tl) elements and electropositive alkali or alkaline earth metals. In these systems, triels are reduced by the electropositive elements and are able to adapt their coordination and bonding, often in some very unusual networks, to fit an actual electron count.

Although a few naked clusters have been found,[1−6] gallium and indium show a general trend of forming extended cluster frameworks.[7,8] On the other hand, the intermetallic chemistry of thallium has been shown to be very rich in discrete clusters. Size or electron content tuning was formerly used for modeling the extended icosahedral structures of gallium systems.[7,9−12] Since then, it has also proved very efficient in synthesizing numerous indium and thallium ternary phases containing novel anionic clusters or original cluster frameworks.[8,13] Size tuning has been well exemplified in the icosahedron-based 3-D structures of the $Na_{17}Ga_{29}In_{12}$ compound[14,15] and of some ternary Na−K−In phases.[16−18] It is worth noting that in some intermetallic phases containing two types of alkali metals, cluster electron deficiency (with regard to Wade's electron counts) may result from cation packing limitations as recently demonstrated for thallium.[19,20]

Alkali metal−triel−heteroelement ternary systems also have been investigated, resulting in the discovery of heterometal-centered clusters of indium and thallium.[5,6,8,21] Tuning of both size and electron content has provided some interesting phases in quaternary systems containing gallium; these phases display very interesting networks, but their complexity often obscures the understanding of the electronic and bonding requisite. Quaternary systems including In or Tl have barely been investigated, with the structures of the few phases already known becoming more clear as recently found for $K_6(NaCd)_2Tl_{12}Cd$ which contains a Cd-centered thallium icosahedron embedded in a Na, K, Cd network.[22]

With the aim of modeling the structure of the original compound $K_6(NaCd)_2Tl_{12}Cd$,[22] we have prepared alloys in the quaternary Na−K−Cd−In system. In this work, we describe the preparation and crystal structure of the compound $Na_8K_{23}Cd_{12}In_{48}$ which contains In_{12} icosahedral units, In_3 triangular fragments, and the novel $Cd_{12}In_6$ tubular cluster.

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(1) Sevov, S. C.; Corbett, J. D. *J. Solid State Chem.* **1993**, *103*, 114.
(2) Corbett, J. D.; Zhao, J. T. *Inorg. Chem.* **1995**, *34*, 378.
(3) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1991**, *30*, 4875.
(4) Blase, W.; Cordier, G.; Somer, M. *Z. Krist.* **1991**, *194*, 150.
(5) Sevov, S. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 9089.
(6) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1993**, *32*, 1059.
(7) Belin, C.; Tillard-Charbonnel, M. *Prog. Solid State Chem.* **1993**, *22*, 59 and references therein.
(8) Corbett, J. D. In *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich, S., Ed.; VCH Publishers, in press.
(9) Tillard-Charbonnel, M.; Chahine, A.; Belin, C. *Mater. Res. Bull.* **1993**, *28(12)*, 1285.
(10) Tillard-Charbonnel, M.; Chahine, A.; Belin, C. *Z. Krist.* **1993**, *208*, 372.
(11) Chahine, A.; Tillard-Charbonnel, M.; Belin, C. *Z. Krist.* **1994**, *209*, 542.
(12) Chahine, A.; Tillard-Charbonnel, M.; Belin, C. *Z. Krist.* **1995**, *210*, 80.
(13) Tillard-Charbonnel, M.; Chahine, A.; Belin, C. *Z. Krist.* **1995**, *210*, 162.
(14) Cordier, G.; Müller, V. *Z. Krist.* **1993**, *205*, 133.
(15) Cordier, G.; Müller, V. *Z. Naturforsch. B* **1994**, *49*, 721.
(16) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1993**, *32*, 1612.
(17) Carillo-Cabrera, W.; Caroca-Canales, N.; Peters, N.; Von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1556.
(18) Carillo-Cabrera, W.; Caroca-Canales, N.; Von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 247.
(19) Dong, Z. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6447.
(20) Cordier, G.; Müller, V. *Z. Naturforsch. B* **1994**, *49*, 935.
(21) Cordier, G.; Müller, V. *Z. Naturforsch. B* **1995**, *50*, 23.
(22) Tillard-Charbonnel, M.; Belin, C.; Manteghetti, A.; Flot, D. *Inorg. Chem.* **1996**, *35*, 2583.

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Table 1. Crystallographic Data for $Na_8K_{23}Cd_{12}In_{48}$

compd	$Na_8K_{23}Cd_{12}In_{48}$
formula wt	7943.3
lattice parameters (Å)	$a = b = 17.114(3)$; $c = 10.442(2)$
V (Å^3)	2648.6
Z	1
space group	$P6/mmm$ (no. 191)
μ(MoKα) (cm^{-1})	133.3
transmission factors range	0.2599−0.4510
$F(0,0,0)$	3453
ρ_{calc} (g·cm^{-3})	4.98
$R(F) = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$ (%)	2.74
$Rw(F) = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$ (%)	3.34

Experimental Section

Cadmium (Prolabo 99.999% pure) and indium (Fluka purissimum) were used after surfaces were scraped to remove oxide films. Sodium and potassium from Merck Laboratories were purified using the procedure described elsewhere.[23,24] An alloy of nominal composition $Na_2K_6Cd_3In_{12}$ was prepared by melting together the elements in a niobium reactor which had been weld-sealed in an argon atmosphere.

The mixture was heated up to 750 °C for 36 h, homogenized, and then allowed to cool slowly to room temperature at a rate of 6°/h for crystal growth. The homogeneous product of the reaction, which was air sensitive, was examined under a microscope inside a glovebox filled with purified argon. Crushed small pieces having a metallic luster were inserted in Lindemann glass capillaries to avoid any contact with air and moisture and then checked for singularity by preliminary oscillation and Weissenberg diffraction techniques.

Conventional atomic absorption analyses of single crystals, previously checked by X-ray diffraction, revealed the presence of the elements Na, K, Cd, and In in the ratio 1/2.94(3)/1.46(3)/5.91(9). Oscillation and Weissenberg investigations indicated the crystals displayed hexagonal symmetry, and the best diffracting single crystal of dimensions $0.03 \times 0.16 \times 0.24$ mm^3 was selected and mounted on an Enraf-Nonius CAD-4 automatic four-circle diffractometer. Accurate lattice parameters were determined by least-squares refinement of angular positions of 25 reflections collected and automatically centered on the diffractometer. Crystallographic data are summarized in Table 1.

Integrated diffraction intensities of 4691 reflections were collected at room temperature in the range $4 \leq 2\theta \leq 50°$ using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) within the octants hkl and $h\bar{k}l$ of the hexagonal cell. Profile analysis of a few angle reflections indicated that an $\omega-\theta$ scan method was the most appropriate for data collection. Scan ranges were calculated from the formula Sr $= A + B \tan\theta$ where A depends upon the mosaic spread of the crystal and B allows for increasing peak width due to Kα_1 and Kα_2 splitting; A and B were taken as 1.2 and 0.35, respectively. Maximum scan times of 60 s were programmed. During data collection, the intensities of three standard reflections were checked after every 100 reflections and no significant loss was observed. Data were corrected for background, Lorentz, and polarization effects.

After the accurate composition of the crystal was known, data were also corrected for the absorption effect using the numerical procedure provided by SHELX 76.[25] Intensities of equivalent reflections average well ($R_{int} = 4.8\%$) in the higher hexagonal ($6/mmm$) Laue class.

Structure Solution and Refinement

Since no extinction condition was observed, the possible hexagonal space groups were assumed to be $P622$, $P\bar{6}2m$, $P\bar{6}m2$, $P6mm$, and $P6/mmm$. Although the statistical tests of SHELXS-86[26] indicated the structure to have a strong centrosymmetric character, no solution could be gained by direct methods in space group $P6/mmm$. The heavy atom positions obtained in the noncentrosymmetric group $P\bar{6}m2$ allowed a satisfactory refinement and localization of all atoms in the structure. As soon as a center of symmetry became obvious, the atomic coordinate set was transformed into the one for $P6/mmm$ (no. 191).

Least-squares refinement by full matrix (program SHELX 76) has been carried out using anisotropic temperature factors for all atoms; 55 parameters were refined, using 532 independent reflections with $I > 3\sigma(I)$. Convergence was obtained by minimizing the function $w(|F_o| - |F_c|)^2$ with $w = 1/(\sigma^2(F) + 0.00223F^2)$, and the agreement factors were $R(F) = 2.74\%$ and $Rw(F) = 3.34\%$. Residual electronic densities in the last Fourier difference synthesis ranged between +1.18 and −2.26 e$^-$/Å^3.

When atomic numbers of elements are very close, as is the case for cadmium and indium, they cannot be easily differentiated by X-ray crystallography. Furthermore, structure resolution of intermetallic phases becomes more difficult, as is the case for $Li_{18}Cu_5In_4Ga_{31}$,[12] when near-sized metals happen to occupy same crystallographic sites complementarily.

Structure refinement of $Na_8K_{23}Cd_{12}In_{48}$ with only indium on heavy atom positions provided good reliability factors $R(F) = 2.80\%$ and $Rw(F) = 3.40\%$ and a low residual electron density (in the order of 1 e$^-$/Å^3). Owing to the quality of the single crystal and to fine absorption corrections, cadmium could be distinguished from indium. Refinement of heavy atom positions, each one in his turn, with cadmium gave no better results, except for the 12(n) position (−0.813; 0.0; −0.254) that substantially improved the reliability factors to $R(F) = 2.74\%$ and $Rw(F) = 3.34\%$. The crystallographic formula $Na_8K_{23}Cd_{12}In_{48}$ is very close to the synthesis starting composition ($Na_8K_{24}Cd_{12}In_{48}$) and agrees fairly well with the chemical analysis of single crystals that indicated the presence of 1.46 cadmium atoms per sodium atom. A multiplicity refinement of the alkali metals while the In and Cd atoms were kept fixed, confirmed that, within the 3σ limit, these sites are fully occupied.

Results and Discussion

Final positional and thermal parameters are listed in Table 2, and bond distances are given in Table 3. The three-dimensional structure in the unit cell is built with three indium icosahedra, two indium triangular fragments, and one $Cd_{12}In_6$ tubular cluster; all these units are sheathed by alkali cations (Figures 1 and 2). The icosahedron (4 × In(1), 4 × In(3), and 4 × In(4)) sits on the 3(f) position and displays mmm symmetry, the triangle (3 × In(2)) is located at the 2(d) position with symmetry $\bar{6}m2$, and the $Cd_{12}In_6$ unit (12 × Cd, 6 × In(5)) is at the 1(b) position with $6/mmm$ (D_{6h}) symmetry. Within the empty icosahedron, In−In distances range from 2.968(3) to 3.134(2) Å, and center-to-atom distances that range from 2.805(1) to 3.007(1) Å indicate a noticeable distortion from the regular icosahedral geometry (I_h). The icosahedron is connected to four alike units through In(1)−In(1) bonds of 2.949(3) Å, and is also exo-bonded to four triangles through In(3)−In(2) bonds (3.093(2) Å) and to four $Cd_{12}In_6$ clusters (In(4)−Cd: 3.064(2) Å). The structure can also be viewed (Figure 1) as alternate layers of icosahedra and of $In_3 + Cd_{12}In_6$ units.

Although a few naked clusters have been found for thallium and indium, isolated icosahedra have never been observed in alkali−metal−gallium or indium intermetallic phases; instead, cluster frameworks are formed by exo-bonding of the icosahedral (or other polyhedral) clusters to neighboring clusters, fragments, or even isolated atoms. In this type of connection, each exo-bond reduces by one electron the too high anionic charge the isolated cluster would have. Generally, exo-bonding is achieved for all atoms in the cluster; however, there are intermediate situations where some atoms remain non exo-bonded and bear a lone pair,[27,28] or none[1,29] if some sterical

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[23] Tillard-Charbonnel, M.; Belin, C. *Mater. Res. Bull.* **1992**, *27*, 1277.

[24] Tillard-Charbonnel, M.; Chouaibi, N.; Belin, C. *C. R. Acad. Sci. Paris, Ser. II* **1990**, *69*, 311.

[25] Sheldrick, G. M. *SHELX-76, Program for crystal structure determination*; University of Cambridge: Cambridge, England.

[26] Sheldrick, G. M. *SHELXS-86, Program for crystal structure solution*; Institut für Anorganische Chemie der Universität: Tammannstrasse 4, D 37077 Göttingen, Germany.

[27] Franck-Cordier, U.; Franck-Cordier, G.; Schäfer, H. *Z. Naturforsch. B* **1982**, *37*, 119; **1982**, *37*, 127.

Table 2. Positional and Thermal Parameters for Atoms in $Na_8K_{23}Cd_{12}In_{48}$[a]

atom	position	x	y	z	B_{eq} (Å^2)
In(1)	12(p)	0.49358(9)	0.16062(9)	0	1.05(4)
In(2)	6(m)	0.39369(7)	$2x$	$^1/_2$	1.15(7)
In(3)	12(o)	0.55025(5)	$2x$	0.7498(1)	1.10(5)
In(4)	12(n)	−0.64637(8)	0	−0.1477(1)	1.07(4)
In(5)	6(m)	0.10663(8)	$2x$	1/2	1.72(8)
Cd	12(n)	−0.81300(9)	0	−0.2549(1)	2.04(6)
K(1)	4(h)	$^2/_3$	$^1/_3$	−0.1991(7)	1.6(2)
K(2)	12(o)	0.7912(1)	$2x$	0.3050(4)	1.9(2)
K(3)	6(k)	−0.3692(4)	0	1/2	1.8(2)
K(4)	1(a)	0	0	0	3.1(7)
Na(1)	6(l)	0.8613(3)	$2x$	0	0.7(3)
Na(2)	2(e)	0	0	−0.347(2)	2.1(7)

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
In(1)	0.0147(7)	0.0127(7)	0.0119(6)	0	0	0.0063(7)	0.0133(5)
In(2)	0.0195(8)	0.013(1)	0.0088(9)	0	0	$={}^1/_2U_{22}$	0.0145(9)
In(3)	0.0164(5)	0.0123(7)	0.0117(6)	0.0002(6)	$={}^1/_2U_{23}$	$={}^1/_2U_{22}$	0.0139(6)
In(4)	0.0162(5)	0.0140(7)	0.0096(6)	0	−0.0013(5)	$={}^1/_2U_{22}$	0.0135(6)
In(5)	0.0246(9)	0.030(1)	0.0124(9)	0	0	$={}^1/_2U_{22}$	0.022(1)
Cd	0.0275(7)	0.0265(9)	0.0234(8)	0	−0.0075(6)	$={}^1/_2U_{22}$	0.0259(8)
K(1)	0.021(2)	$=U_{11}$	0.018(4)	0	0	$={}^1/_2U_{11}$	0.020(3)
K(2)	0.028(2)	0.026(4)	0.019(2)	$={}^1/_2U_{13}$	0.003(4)	$={}^1/_2U_{11}$	0.024(3)
K(3)	0.028(3)	0.019(3)	0.017(3)	0	0	$={}^1/_2U_{22}$	0.022(3)
K(4)	0.047(8)	$=U_{11}$	0.025(9)	0	0	$={}^1/_2U_{11}$	0.039(8)
Na(1)	0.011(4)	0.010(5)	0.005(5)	0	0	$={}^1/_2U_{22}$	0.009(4)
Na(2)	0.026(7)	$=U_{11}$	0.03(1)	0	0	$={}^1/_2U_{11}$	0.027(8)

[a] General expression of the thermal parameter is $\exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2\,U_{12}hka^*b^* + 2\,U_{13}hla^*c^* + 2\,U_{23}klb^*c^*]$. $B_{eq} = 8\pi^2U_{eq} = 8\pi^2[\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\cdot\bar{a}_j]/3$.

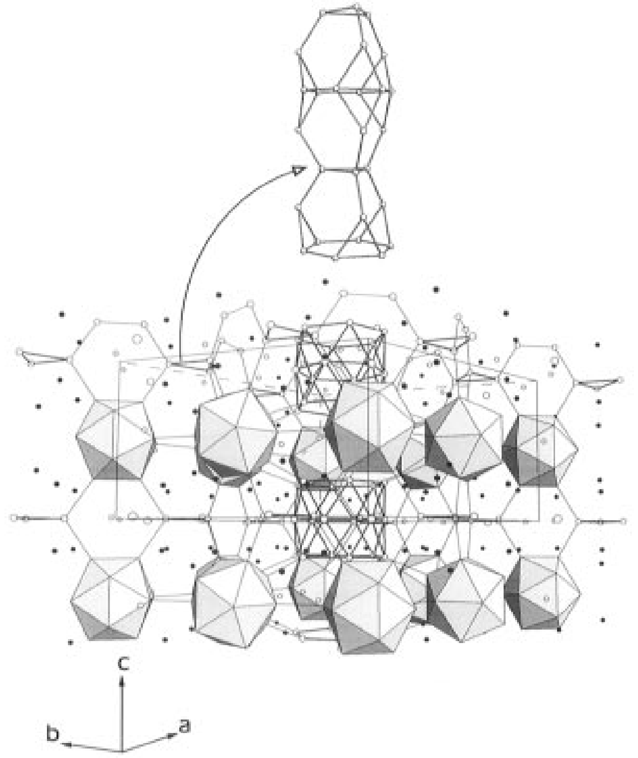

Figure 1. General view, approximately along the [$1\bar{1}0$] axis, of the $Na_8K_{23}Cd_{12}In_{48}$ hexagonal unit cell showing the different clusters and fragment units; for convenience, cell boundaries have been shifted by $^1/_2$ along axes. Indium icosahedra are shaded and $Cd_{12}In_6$ clusters can be viewed in the middle of the figure. For clarity, part of the In_3 units and fused Friauf polyhedra has been extracted. Alkali cations are represented as small isolated circles (Na, open, and K, solid).

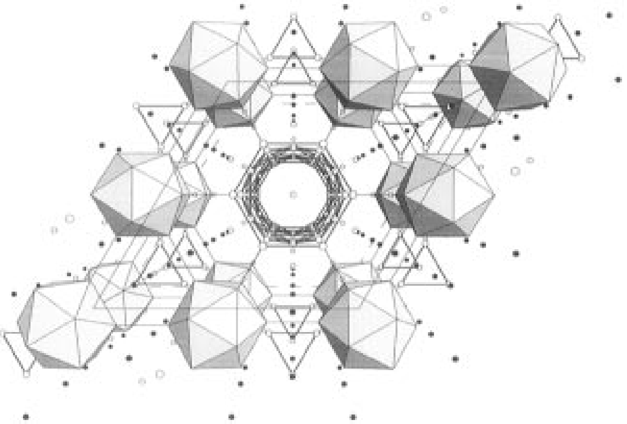

Figure 2. View down the c axis of the hexagonal unit cell of Na_8K_{23}-$Cd_{12}In_{48}$ in order to emphasize the tubular stacking of $Cd_{12}In_6$ clusters. Small isolated circles represent sodium (open) and potassium (solid) cations.

hindrance has pushed the lone pair orbital higher in energy (antibonding region). In gallium cluster frameworks, interpolyhedral 2c−2e bonds are shorter than those within the electron-deficient clusters. For the gallium icosahedron, inter- and intrapolyhedral bond orders calculated with Pauling's formula[30] nicely correlate with the actual bond orders: 1 (exo-bonds) and 0.43 for the 30 bonds within this 26 skeletal electron polyhedron. In thallium and indium compounds, differences between inter- and intrapolyhedral bond lengths are not so evident owing to the increased metallic character of Tl and In; they can reach values as low as 2%, against 10% in Ga phases.

The triangle of tetracoordinated In(2) atoms (In(2)−In(2): 3.099(3) Å) links six icosahedra through In(2)−In(3) exo-bonds (3.093(2) Å). Such a triangular unit has already been found in the indium intermetallic phase $Na_{15}In_{27.4}$, but within a quite different arrangement.[1] In $Na_8K_{23}Cd_{12}In_{48}$, each indium triangle is the shared unit of two Friauf polyhedra (truncated tetrahedra) formed with faces of six triangular-prismatically disposed

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(28) Ling, R. G.; Belin, C. *Acta Crystallogr*. **1982**, *38*, 1101.

(29) Belin, C.; Charbonnel, M. *J. Solid State Chem*. **1986**, *64(1)*, 57.

(30) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542; *Proc. R. Soc. (London)* **1949**, *A196*, 343.

Table 3: Bond Distances Less Than 4.2 Å in $Na_8K_{23}Cd_{12}In_{48}$ (Å)

In(1)	−		In(1)	2.949(3)	K(1)	−	3	In(3)	3.492(2)
	−		In(1)	2.968(3)		−	3	In(2)	3.616(7)
	−	2	In(4)	3.014(1)		−	6	In(1)	3.616(5)
	−	2	In(3)	3.134(2)		−	3	K(2)	3.852(5)
	−		Na(1)	3.526(8)		−		K(1)	4.15(2)
	−	2	K(1)	3.616(5)					
	−	2	K(2)	3.685(4)	K(2)	−	2	In(4)	3.571(3)
						−	2	In(3)	3.622(6)
In(2)	−	2	In(3)	3.093(2)		−		In(5)	3.650(5)
	−	2	In(2)	3.099(3)		−	2	In(1)	3.685(5)
	−	2	K(1)	3.616(7)		−	2	In(2)	3.790(6)
	−	2	K(2)	3.790(3)		−		Na(1)	3.802(7)
	−	2	K(3)	3.865(4)		−	2	Cd	3.810(6)
						−	2	K(3)	3.827(5)
In(3)	−		In(3)	2.979(3)		−	2	K(1)	3.852(5)
	−		In(2)	3.093(2)		−		K(2)	4.073(9)
	−		In(4)	3.104(2)					
	−		In(4)	3.105(1)	K(3)	−	2	In(4)	3.688(1)
	−	2	In(1)	3.134(2)		−	4	In(3)	3.746(4)
	−		K(1)	3.492(2)		−	4	K(2)	3.827(4)
	−	2	K(2)	3.622(6)		−	2	In(2)	3.865(4)
	−	2	K(3)	3.746(4)		−	2	In(5)	3.915(7)
						−	2	Cd	4.034(6)
In(4)	−	2	In(1)	3.014(1)					
	−		Cd	3.064(2)	K(4)	−	2	Na(2)	3.63(2)
	−		In(4)	3.085(2)		−	6	Na(1)	4.11(1)
	−	2	In(3)	3.104(2)		−	12	Cd	4.163(2)
	−	2	K(2)	3.571(3)					
	−	2	Na(1)	3.579(4)	Na(1)	−	2	Cd	3.383(6)
	−		K(3)	3.688(1)		−	2	Cd	3.383(4)
						−	2	In(1)	3.526(8)
In(5)	−	4	Cd	3.043(1)		−	4	In(4)	3.579(4)
	−	2	In(5)	3.161(2)		−	2	K(2)	3.802(7)
	−	2	Na(2)	3.54(1)			2	Na(1)	4.11(1)
	−	2	K(2)	3.650(5)				K(4)	4.11(1)
	−	2	K(3)	3.915(7)					
					Na(2)	−		Na(2)	3.19(4)
Cd	−	2	In(5)	3.043(1)		−	6	Cd	3.342(6)
	−		In(4)	3.064(2)		−	6	In(5)	3.54(1)
	−	2	Cd	3.200(2)		−		K(4)	3.63(2)
	−		Na(2)	3.342(6)					
	−	2	Na(1)	3.383(6)					
	−	2	K(2)	3.810(6)					
	−		K(3)	4.034(6)					
	−		K(4)	4.163(2)					

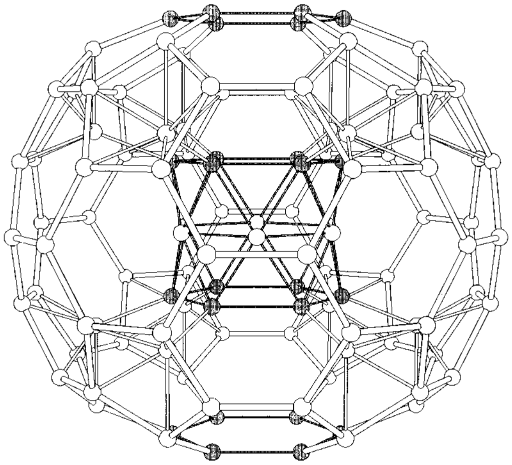

Figure 3. $Cd_{12}In_6$ cluster exo-bonding to neighboring icosahedra in $Na_8K_{23}Cd_{12}In_{48}$. The upper and lower darkened Cd hexagons belong to adjoining $Cd_{12}In_6$ units.

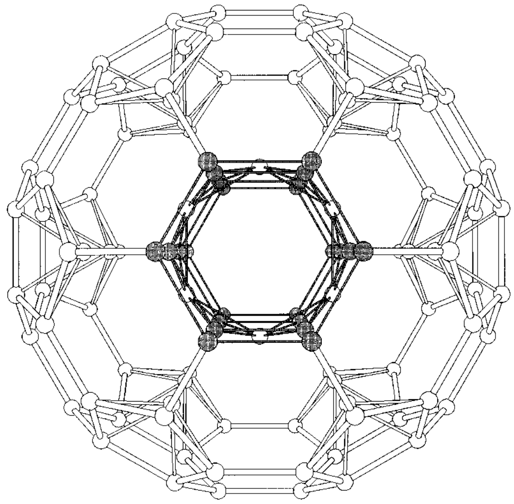

Figure 4. The $Cd_{12}In_6$ cluster viewed down the *c* axis of the Na_8K_{23}-$Cd_{12}In_{48}$ hexagonal cell. Twelve cadmium atoms (dark) are linked to twelve indium atoms that cap, by the inside, the pentagonal faces of the metal fullerane comprising 72 In and 12 Cd atoms.

icosahedra (Figures 1 and 2), and each Friauf polyhedron contains a potassium cation K(1).

The remarkable $Cd_{12}In_6$ cluster results from the superposition of three hexagons, and the waist hexagon is composed of indium atoms (In(5)−In(5): 3.161(2) Å) and is rotated by 30° with respect to the bottom and top, mirror-symmetry related, cadmium hexagons (Cd−Cd: 3.200(2) Å and Cd−In(5): 3.043(1) Å). This open-face polyhedral unit can also be visualized as resulting from the condensation, by hexagon sharing, of two hexagonal antiprisms. A single hexagonal antiprism (drum) of indium has been found in the $A_3Na_{26}In_{48}$ phases (A = K, Rb, Cs).[16,17] The $Cd_{12}In_6$ tubular cluster stuffs a large coordination complex comprising 84 In and 12 Cd atoms (Figures 3 and 4). Similar 96-atom polyhedral complexes with different symmetries have been encountered in $Na_{36}Ag_7Ga_{73}$,[10] $Li_{18}Cu_5In_4Ga_{31}$,[12] and $Na_{35}Cd_{24}Ga_{56}$[23] phases, where they are centered by icosioctahedra (tetra-capped Friauf, 16-atom polyhedra). Recently terms like *carbon-free fullerenes, fullerides, fullercages, and fulleranes* have been applied to some large polyhedral units by Corbett[31] and Nesper[32] owing to structural similarities with the fullerene allotropic forms of carbon. Of course, the carbon fullerenes are individual molecules while group 13 element fulleranes (the suffix *-anes* signifies that there is no double bond) are condensed. They can be seen as generated by cutting the three-dimensional networks through electron-poor polyhedra, and then, they are emphasized by the display of the most electron-rich (2c−2e interpolyhedral bonds) parts of the structures. The outer sphere of the actual fullerane contains 72 In and 12 Cd (84 atoms) forming 12 pentagonal and 32 hexagonal faces. With 126 edges, this large polyhedron satisfies the Euler relation: $V = E - F + 2$ (V = number of vertices, E = number of edges, and F = number of faces). Twelve indium atoms which cap the pentagonal faces by the inside of the fullerane are linked to the Cd atoms of the central $Cd_{12}In_6$ cluster. The metal fullerane contains no less than 34 alkali cations (12 × K(2), 6 × K(3), 2 × K(4), 12 × Na(1), and 2 × Na(2)), and their arrangement around and inside the $Cd_{12}In_6$ cluster is displayed in Figure 5. It is worth noting that the distance between two sodium atoms inside the cluster is relatively short (3.19(4) Å) and close to the sum of Pauling single bond radii.[30] It is only 0.1 to 0.2 Å less than the Na−Na distances observed in other Na^+-containing intermetallic phases[11,15,19] and presumably not significant of some covalent sodium−sodium interactions. On the other hand, we have checked that the site ascribed to Na(2) was not, instead, half-occupied by a potassium atom: first, this would have produced too short K−Cd distances of 3.342(6) Å, and second, this was clearly disproved by the higher value of the agreement

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[31] Sevov, S. C.; Corbett, J. D. *Science* **1993**, *262*, 880.

[32] Nesper, R. *Angew. Chem., Int. Ed.* **1994**, *33(8)*, 843.

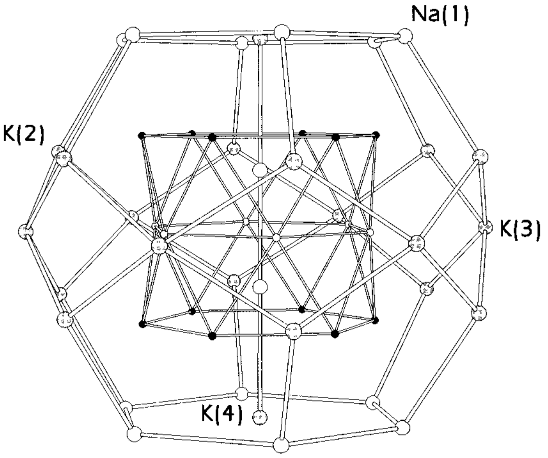

Figure 5. Environment of the $Cd_{12}In_6$ cluster by alkali cations in $Na_8K_{23}Cd_{12}In_{48}$. Small open and solid circles represent indium and cadmium atoms, respectively. Two large open circles inside the tubular cluster indicate Na(2) positions.

factor ($R(F) = 3.5\%$). As reported in Table 3, the smaller alkali cation−Cd or In distances are still within the limits of those found in related compounds.[13,16,17,22,23]

Electronic Structure and Band Calculations

According to the Zintl−Klemm−Busmann concept,[33,34] we can assume that in the $Na_8K_{23}Cd_{12}In_{48}$ compound, the alkali metals donate their electron in order to stabilize the indium/cadmium network. Parallel to electron requirements, alkali cation size and packing limitations probably play an important part in modeling this structure. Wade's rules predict that stabilization of an icosahedron requires a polyhedral electron count (PEC) of 50 of which 26 are skeletal electrons; the remaining 24 electrons, which are nonbonding in a naked icosahedron here, are involved in exo-bonds. Actually, each icosahedron contributes 38 valence electrons to the structure bonding. Tetracoordinated In(2) atoms in the triangular unit may be considered as reduced (In^-). Using formal charges, the compound can then be formulated as follows: 8 Na^+, 23 K^+, 3 In_{12}^{2-}, 2 In_3^{3-}, $Cd_{12}In_6^{19-}$. The $Cd_{12}In_6$ tubular cluster would have a valence electron count (VEC) of 61, including a −19 ionic charge; this high negative charge is not surprising since cadmium is only a two-valence electron element.

Qualitatively, one can estimate the valence electron count of $Cd_{12}In_6$ by using the electron counting approach proposed by Mingos for the condensation of polyhedral clusters.[35,36] The $Cd_{12}In_6$ cluster can be regarded as resulting from the condensation, by hexagonal face sharing, of two hexagonal antiprisms. The M_{12} parent unit is a $n + 3$ skeletal electron pair (30 electrons) arachno cluster with a PEC of 54. The polyhedral electron count for the condensed unit would be equal to the sum of individual parent polyhedral counts minus the count characteristic of the shared unit: a hexagon whose PEC would be that of C_6H_6 (30 electrons). This leads to $(54 \times 2) - 30 = 78$ electrons for the M_{18} polyhedron.

An EHMO calculation for a In_{18} polyhedron built from the condensation of two In_{12} units (atomic coordinates from ref 16 or 17), and where all atoms have been saturated by hydrogen atoms, confirms the polyhedral electron count of 78. The model is quite different for the $Cd_{12}In_6$ cluster where waist In atoms are not outwardly bonded. For this molecular calculation, exobonding of cadmium atoms has been simulated by placing a dummy atom in the position of the outer bonding atoms of the structure with a single (5s) orbital which has been given Slater exponent and energy equivalent to that of the In 5p orbital. The HOMO-LUMO separation is 0.3 eV, the HOMO (e_{1u}) has an overall bonding character, and complete filling would lead to a polyhedral electron count of 80. Since the $Cd_{12}In_6$ cluster is involved in 12 (Cd−In) exo-bonds with neighboring indium icosahedra, its VEC should be $80 - 12 = 68$, seven electrons more than the count given by the ionic formulation $Cd_{12}In_6^{19-}$.

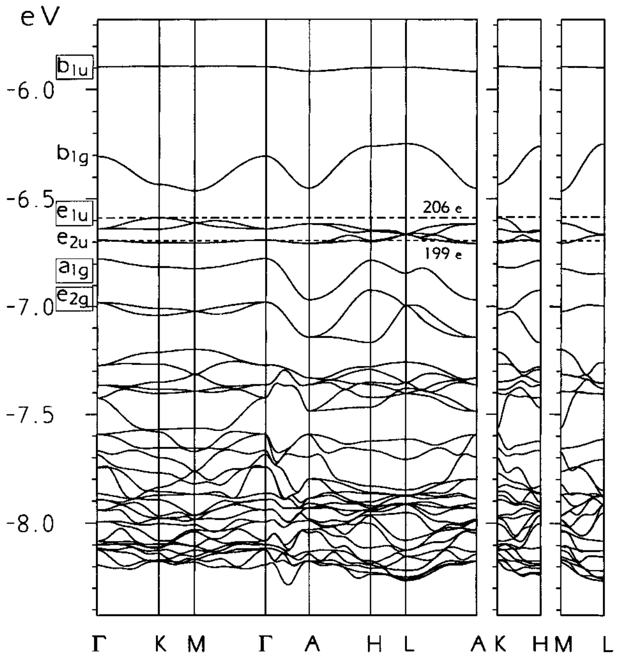

Figure 6. Band structure of the $Na_8K_{23}Cd_{12}In_{48}$ compound. Na and K have been considered as only one-electron donors and neglected in the calculations. The dashed lines mark the Fermi level for 199 and 206 electrons. Also indicated are the symmetries (at point Γ) of the frontier crystal orbitals to which the $Cd_{12}In_6$ cluster contributes almost exclusively. Boxed labels refer to those involving mainly radial-to-hexagon In$p_{x,y}$ orbitals; details are given in Figure 9.

In order to have a more detailed understanding of the problem, we have performed a band structure study of the compound.[37] Our calculations used an effective Hamiltonian of the extended Hückel type[38] with the parameters and exponents given in the Appendix. The diagonal H_{ij} matrix elements were calculated by means of the modified Wolfsberg−Helmholz formula.[39] In our study, sodium and potassium atoms have been considered only as electron donors and have not been taken into account in the calculations. On the other hand, we have shown in recent papers,[22,40,41] that d orbitals of the group 12 elements do not play any important role in the electronic structure of these intermetallic systems, so they were not considered in the present work. Band structure calculations have been carried out in the full energy domain with a repeat unit containing one formula unit. The calculated band structure for the 3-D network of $Na_8K_{23}Cd_{12}In_{48}$ is shown in Figure 6, for clarity, only the energy domain between −8.4 and −5.7 eV has been represented. The

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[33] Klemm, W.; Busmann, E. *Z. Anorg. Allg. Chem.* **1963**, *319*, 297.

[34] Schäfer, H.; Eisenmann, B.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12/9*, 694.

[35] Mingos, D. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1990.

[36] Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1983**, 706.

[37] Whangbo, M. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.

[38] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

[39] Ammeter, J.; Bürgi, H.-B.; Thiebeault, J.; Hoffmann, R. *J. Am. Chem.Soc.* **1978**, *100*, 3686.

[40] Sportouch, S.; Belin, C.; Tillard-Charbonnel, M.; Rovira, M. C.; Canadell, E. *Nouv. J.* Chim. **1995**, *19*, 243.

[41] Chahine, A.; Tillard-Charbonnel, M.; Belin, C.; Canadell, E. To be submitted for publication.

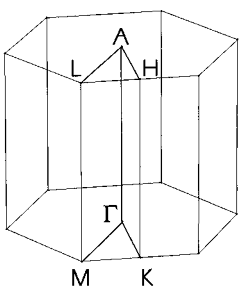

Figure 7. The three-dimensional Brillouin zone of the hexagonal cell (*P*6/*mmm*) delimited by the special k-points Γ(0,0,0), *A*(0,0,$^1/_2$), M($^1/_3$,$^1/_3$,0), L($^1/_3$,$^1/_3$,$^1/_2$), K($^1/_2$,0,0), and H($^1/_2$,0,$^1/_2$).

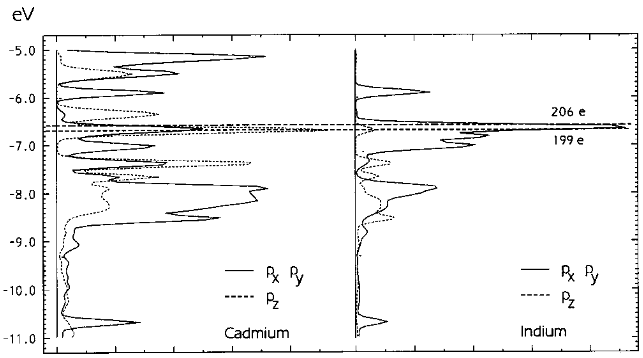

Figure 8. Relative In and Cd$p_{x,y}$ and p_z contributions within the tubular cluster. Fermi levels for 199 and 206 electrons are indicated by dashed lines.

different wave vector labels are those usual for the hexagonal Brillouin zone and are schematically represented in Figure 7. Below the Fermi level which is indicated for 199 electrons (−6.69 eV), there is a group of three relatively dispersed bands. Very close to the Fermi level, a group of four almost flat bands is separated from one more dispersive band (above the Fermi level) by a substantial gap. Crystal orbital analysis at point Γ shows that between −7 and −6 eV practically only the $Cd_{12}In_6$ fragment orbitals contribute to the bands. A more detailed analysis (see partial DOS in Figure 8) shows that indium atoms of the $Cd_{12}In_6$ fragment contribute mainly by their p_x, p_y orbitals. In fact, there are six radial (to hexagon) indium $p_{x,y}$ orbitals of which combinations (a_{1g}, e_{2g}, e_{1u}, and b_{1u} in symmetry D_{6h}) are able, in the actual flattened conformation of $Cd_{12}In_6$, to overlap, in bonding or antibonding combinations, with the Cd $p_{x,y}$ orbitals. As can be seen in Figure 9, the e_{2g} orbital (−6.98 eV at point Γ) results from In−In and Cd−Cd π antibonding and Cd−In π bonding interactions. The a_{1g} orbital (−6.78 eV) is π bonding at the waist In atoms and slightly Cd−In π antibonding, and the degenerate e_{1u} which lie at −6.63 eV, just above the Fermi level, is globally π bonding at In−In, but unoccupied for 199 electrons. The b_{1u} combination is found higher in energy (−5.89 eV), owing to a stronger π antibonding character at the waist In atoms, though some σ bonding occurs at the Cd atoms. There is one degenerate and mainly nonbonding crystal orbital (e_{2u}, −6.68 eV, nonboxed label in Figure 6) cut by the Fermi level which essentially results from combinations of the Cd $p_{x,y,z}$ orbitals, but with a very small participation of the In p_z orbitals. The relatively dispersed b_{1g} orbital (−6.31 eV, nonboxed label in Figure 6) has no contribution from In atoms and only results from Cd p_z orbital π antibonding overlapping.

The electrical resistivity of a single crystal has been measured using a two-probe method (direct current: 10−100 mA) in the range 213−333 K. The room temperature resistivity is on the order of 5 × 10^{-4} Ω cm with a positive temperature coefficient of 0.23 × 10^{-2} K^{-1}. This poor metal-like resistivity is consistent with the (open shell) electronic structure.

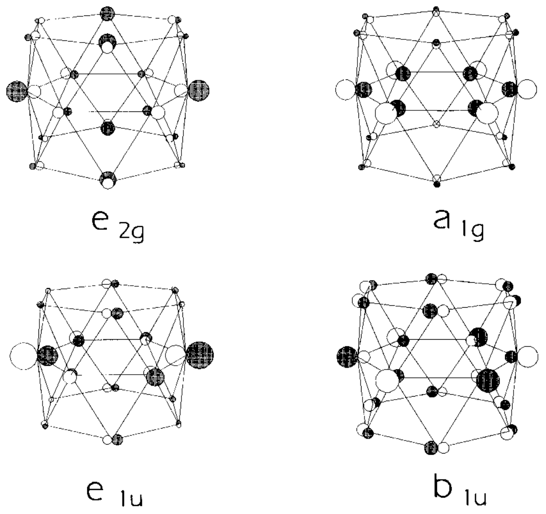

Figure 9. Schematic representation of the $Cd_{12}In_6$ radial In$p_{x,y}$ orbital contributions to the frontier crystal orbitals of $Na_8K_{23}Cd_{12}In_{48}$.

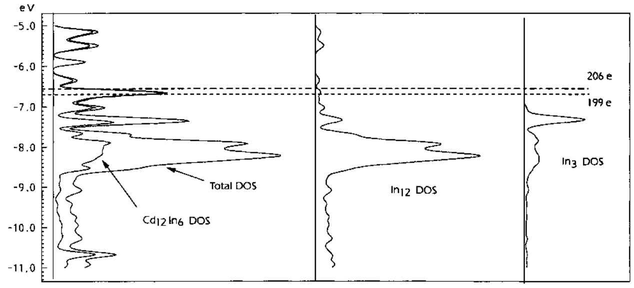

Figure 10. Total density of states for $Na_8K_{23}Cd_{12}In_{48}$ and partial DOS for the $Cd_{12}In_6$, In_{12}, and In_3 fragments. Fermi levels for 199 and 206 electrons are indicated by dashed lines.

Another informative description of the electronic structure of the compound is given by the analysis of the densities of states (DOS)[42] which can be interpreted like an energy level diagram for a molecular system. These densities of states have been calculated with a set of 90 k-points in the irreducible wedge of the Brillouin zone, but only the *p*-dominated energy domain between −11 and −5 eV is represented in Figure 10, with Fermi level indicated for 199 and 206 electrons. The metallic character of the compound is also supported by the practically half-filled band in the total DOS for the actual count of 199 electrons. The icosahedral and triangular clusters are energetically more stabilized than the tubular $Cd_{12}In_6$ cluster, In_3 has no contribution in the DOS near Fermi level (see partial DOS in Figure 10), while In_{12} has a small contribution which is sufficient to avoid any trapping of the “conducting” electrons in the $Cd_{12}In_6$ states. Furthermore, there also can be some polarization by the cations around and inside the cluster affording enough electron delocalization for conductivity to occur. On the other hand, analysis of the crystal orbital overlap populations (COOP)[43] for the different types of bonds in the structure shows that strong icosahedron−icosahedron and icosahedron−triangle interpolyhedral In−In bonds have reached an optimal overlap population at nearly 0.5 eV below the actual Fermi level (−6.69 eV, 199 electrons). However, the overlap population for the Cd−In bond between icosahedron and $Cd_{12}In_6$ increases slightly up to −6.25 eV (208 electrons). This different behavior might partly result from some misfit of the H_{ii} terms of Cd versus In orbitals, which

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(42) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 846.
(43) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 1150.

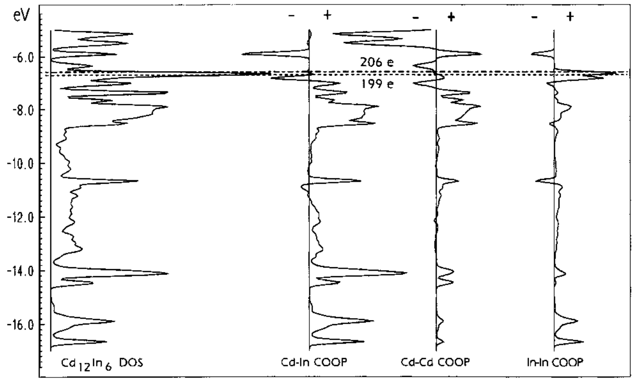

Figure 11. Partial DOS for the $Cd_{12}In_6$ cluster and crystal orbital overlap population (COOP) for each skeletal bond type. Fermi levels for 199 and 206 electrons are indicated by dashed lines.

Table 4. Calculated Overlap Populations for Different Types of Bonds within the $Cd_{12}In_6$ Tubular Cluster as a Function of the Electron Count in $Na_8K_{23}Cd_{12}In_{48}$

no. of electrons	overlap population		
	In−In	Cd−In	Cd−Cd
192	0.3106	0.3284	0.2544
196	0.3002	0.3402	0.2362
198	0.3711	0.3264	0.2417
199	0.3700	0.3273	0.2427
200	0.3690	0.3282	0.2437
206	0.4552	0.3280	0.2413

originate from two different sources (see Appendix). We will now focus on the COOP curves related to In−In, Cd−In, and Cd−Cd skeletal bonds within the tubular cluster $Cd_{12}In_6$ (Figure 11), which clearly indicate bonding contributions for all bond types up to −7.20 eV (192 electrons). As can be seen in Table 4, the Cd−Cd overlap population is maximum at 192 e, Cd−In at 196 e, and In−In at 206 electrons. Although the Cd−In and Cd−Cd interactions are antibonding in the domain between −7.2 and −6.69 eV, they are largely compensated in the same energy range by the In−In bonding interactions. A look at the low energy levels indicates that s orbitals of In and Cd atoms are involved in In−In and Cd−In bonding within the tubular cluster. As shown by the dispersion curves and total DOS (Figure 6 and 10), it is obvious that the whole structure could accept up to 206 electrons (closed shell) without destabilization, then with an anionic charge of −26, the $Cd_{12}In_6$ cluster would have a PEC of 80 (VEC = 68) in agreement with the EHT result for the isolated cluster.

Concluding Remarks

This work illustrates, once again, how size factors and electron requirements on clusters are tightly responsible for the modeling of these intermetallic phases. Structural novelty, every time, arises from the ability of these intermetallic systems to incorporate a large variety of clusters; this is clearly demonstrated for $K_6(NaCd)_2Tl_{12}Cd$ $[K_6Na_2Cd_3Tl_{12}]$ and $Na_8K_{23}Cd_{12}In_{48}$ $[K_{5.75}Na_2Cd_3In_{12}]$ compounds which, with practically the same number of valence electrons per [formula], 50 and 49.75, display different structures and properties (respectively, semiconducting and metallic). The former contains only nearly isolated icosahedral $Tl_{12}Cd^{12-}$ clusters but $Na_8K_{23}Cd_{12}In_{48}$ is richer in clusters moieties including empty indium icosahedra, triangular indium fragments, and the tubular $Cd_{12}In_6$ cluster, linked to each other within a 3-D framework. The $Cd_{12}In_6$ cluster is quite unusual and lies at the center of a 84-atom polyhedron built with surrounding icosahedra. Such large polyhedral units have already been encountered in intermetallic phases containing Ag_4Ga_{12} and Ga_4Cd_{12} icosioctahedra having high anionic charges (−12 and −16, respectively),[10,23] which are properly compensated since these icosioctahedra are centered by an alkali cation can be surrounded by as many alkali cations as they have deltahedral faces. The Zintl−Klemm−Busmann concept holds for the $Na_8K_{23}Cd_{12}In_{48}$ compound with electrons counts that can still be rationalized. With 199 valence electrons, $Na_8K_{23}Cd_{12}In_{48}$ is an open-shell compound with a relatively poor metal-like resistivity, and the electron conduction is due to slight overlapping of the highest lying and partially filled bands of the $Cd_{12}In_6$ cluster with neighboring icosahedral cluster states and also presumably to some overlapping with some cation states. The electron deficiency of the compound is almost restricted to the partially filled orbitals of the waist In atoms in $Cd_{12}In_6$, and it is evident that the structure would accept up to 206 electrons (closed shell) without noticeable destabilization because the extra electrons would fill levels that are still bonding. The cation packing limitation is probably the main reason for the shortage of electrons in the structure. The possibility of doping this structure to 206 electrons by replacing the alkali metal counterions of the $Cd_{12}In_6{}^{19-}$ anion by the appropriate number of alkaline-earth cations (this would increase to −26 the anionic charge of $Cd_{12}In_6$) might depend upon the ability of surrounding icosahedra to resist the strong increase of the Coulombic field. On the other hand, a closed shell structure could also be gained by replacing seven cadmium atoms by some group 13 elements; these studies are in progress.

Acknowledgment. We thank Martin Köckerling for having kindly provided to us a PC adaptation of the EHT band calculation program.

Appendix

Exponents and parameters used in the calculations

atom	orbital	H_{ii}, eV	λ
In	5s	−12.60	1.90
	5p	−6.19	1.68
Cd	5s	−12.50	2.30
	5p	−6.60	2.10

The values for In are from ref 44 and those for Cd are from ref 45.

Supporting Information Available: Tables of anisotropic displacement parameters for the atoms in $Na_8K_{23}Cd_{12}In_{48}$ and listing of structure factors (4 pages). Ordering information is given on any current masthead page.

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(44) Janiak, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924.
(45) Mercier, H.; Mathey, Y.; Canadell, E. *Inorg. Chem.* **1987**, *26*, 963.